

## Acidic Ammonium Polyphosphate Fertilizer as Carriers for Manganese

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A number of acidic ammonium polyphosphate fertilizers which varied in pH (2.20-4.20) and non-orthophosphate content were evaluated as potential carriers of manganese (Mn). Fertilizer residues recovered after reacting ammonium polyphosphate-MnSO<sub>4</sub>·H<sub>2</sub>O blends with soil contained from 6 to 82% of the applied Mn. Reaction and precipitation of the Mn with the fertilizer phosphate increased with increasing fertilizer pH. X-Ray analysis of the residues identified

only one reaction product, Mn<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O within the pH range studied. Manganese uptake by oats in the growth chamber from a point application of the fertilizer blends was dependent upon the fertilizer pH and distance of Mn diffusion from the point of application. The data indicate that under-ammoniated polyphosphates with a saturated pH less than 2.65 would be most effective as Mn carriers.

Chemical reactions between fertilizer materials and micronutrients can determine the effectiveness of the micronutrient when applied to the soil. Fertilizer pH plays an important role in the movement and availability of Mn when applied to the soil with phosphate carriers (Hossner and Richards, 1968; Mederski and Hoff, 1958; Mederski *et al.*, 1960; Steckel *et al.*, 1948). Fertilizers that are acid-forming generally increase solubility and promote the movement of applied Mn in soil (Fiskell, 1965). Hossner and Richards (1968) reported that an ammonium polyphosphate was a suitable carrier of Mn when compared to monoammonium phosphate and superior to diammonium and calcium phosphate. Mortvedt and Giordano (1970) reported that an ammonium polyphosphate and triammonium pyrophosphate were inferior carriers of Mn compared to all other materials tested. The differences noted are in all likelihood due to the pH (degree of ammoniation) of the ammonium polyphosphate.

Hossner and Blanchar (1970) pointed out the importance of fertilizer pH and polyphosphate content on the reactions of Mn with ortho- and pyrophosphate carriers. At fertilizer pH values less than 5.0, residues which form would be expected to contain manganese ammonium pyrophosphate species rather than manganese ammonium orthophosphate when a system containing Mn, orthophosphate, and pyrophosphate is involved. Manganese orthophosphates do not precipitate at a pH less than 4.0 but a large portion of the Mn may precipitate as the pyrophosphate. Pyrophosphate species expected to precipitate in this pH range would be Mn<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O and Mn(NH<sub>4</sub>)<sub>2</sub>H<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O (Hossner and Blanchar, 1970).

Due to the high reactivity of Mn with pyrophosphate compared to orthophosphate at low pH, this experiment was designed to test the effectiveness of Mn when applied with a series of acidic polyphosphate carriers.

### MATERIALS AND METHODS

**Fertilizer Preparation.** Ammonium polyphosphate fertilizers were prepared by ammoniating and heating reagent grade or wet process phosphoric acid in a laboratory reactor equipped with a mechanical foam breaker. The materials were removed from the reactor, ground to less than 80 mesh, and dried at 25°. Fertilizer pellets were prepared with a laboratory press. Each pellet consisted of an ammonium polyphosphate fertilizer (0.8 g of P) blended with MnSO<sub>4</sub>·H<sub>2</sub>O (0.2 g of Mn). The Mn concentration varied from 5.0 to 5.8% due to differences in P con-

centration of the ammonium polyphosphates. The pellets were reacted with soil (Hossner and Blanchar, 1968) and the amount of Mn which remained in the fertilizer residue was determined.

**Growth Chamber Experiment.** Ammonium polyphosphate blended with MnSO<sub>4</sub>·H<sub>2</sub>O was tested on a Selma silt loam soil (pH 7.0; easily reducible Mn, 9.9 ppm). One-hundred grams of acid-washed quartz sand was placed in the bottom of a plastic pot. A section of Tygon tubing which extended into the quartz sand bed was taped to the inside of the pot. Fifteen-hundred grams of soil was fertilized with adequate N and K and premoistened to field capacity. Half of the premoistened soil was placed on top of the quartz sand bed in the pot. The soil was tamped gently, and then a small core (1.5-cm diameter, 1.5-cm deep) was removed from the center of the pot. The fertilizer treatment of ammonium polyphosphate (0.8 g of P) and MnSO<sub>4</sub>·H<sub>2</sub>O (0.2 g of Mn) was placed in the hole and the remainder of the soil added. Oats (*Avena sativa*, Brave) were planted as a test crop. Each treatment was replicated four times.

Pots were watered twice daily with half the required water added through the Tygon tube and half to the soil surface. The purpose of the split application of water was to minimize leaching of the fertilizer zone.

The oat plants were grown for 30 days in a phytotron with a 16-hr day (24°) and an 8-hr night (18°). Light intensity in the chamber was about 3000 ft-candles. At the end of the experiment, the entire above-ground portion of the plant was harvested for analysis. The plant tissue was washed, dried, and weighed prior to wet digestion.

Manganese movement from the site of fertilizer application was determined in each pot (Hossner, 1968). The volume of soil containing fertilizer Mn was calculated assuming a spherical distribution from the site of application. Fertilizer residues remaining at the site of placement were carefully exposed, removed, and subjected to chemical and X-ray analysis.

**Chemical Methods.** Plant samples were digested in HNO<sub>3</sub> and HClO<sub>4</sub> and analyzed for P and Mn. Fertilizer residues were digested in HClO<sub>4</sub> prior to analysis for Mn and P. Manganese was determined by atomic absorption. Phosphorus was determined colorimetrically by the vanadomolybdophosphoric acid method. Nitrogen was determined on a separate sample by the Kjeldahl method.

Powdered samples of fertilizer residues were examined by X-ray diffraction with a Norelco high-angle goniometer and CuK<sub>2</sub> radiation.

The saturated pH of the fertilizer was determined on the liquid phase obtained by shaking a 1:3 fertilizer-to-water mixture periodically for 24 hr. Additional dry fertilizer was added, periodic shaking was resumed for 24 hr, and the pH again was determined. This procedure was repeated until the pH of the solution phase was constant.

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**Table I. The Effect of Ammonium Polyphosphate Fertilizer Properties on the Amount of Mn Found in Fertilizer Residues<sup>a</sup>**

pH <sup>b</sup>	Fertilizer		Residue Mn, mg	Mn <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> ·(P <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> ·2H <sub>2</sub> O
	Nonorthophosphate content %	N %		
2.20	40.4	9.3	13	—
2.20	36.0	9.4	21	—
2.35	46.9	10.0	12	—
2.65	50.1	10.8	42	+
2.70	56.4	10.6	29	+
2.71	50.4	10.6	71	+
3.10	45.2	11.4	110	+
3.30	46.2	11.5	119	+
3.30	49.3	11.5	129	+
3.40	51.3	11.7	111	+
3.55	42.0	11.9	100	+
3.65	56.0	11.9	134	+
3.80	44.1	12.9	141	+
3.85	58.6	12.4	150	+
4.20	48.0	13.7	157	+

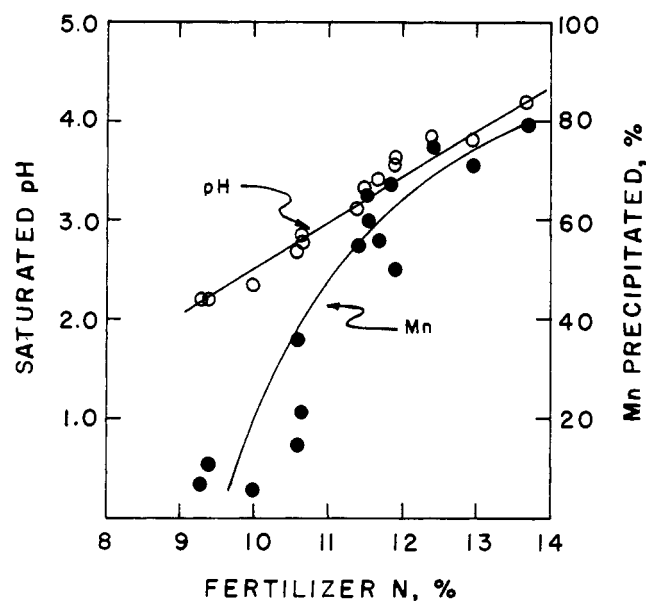
<sup>a</sup> Fertilizer initially consisted of 800 mg of P and 200 mg of Mn.  
<sup>b</sup> pH of saturated fertilizer solution.

## RESULTS

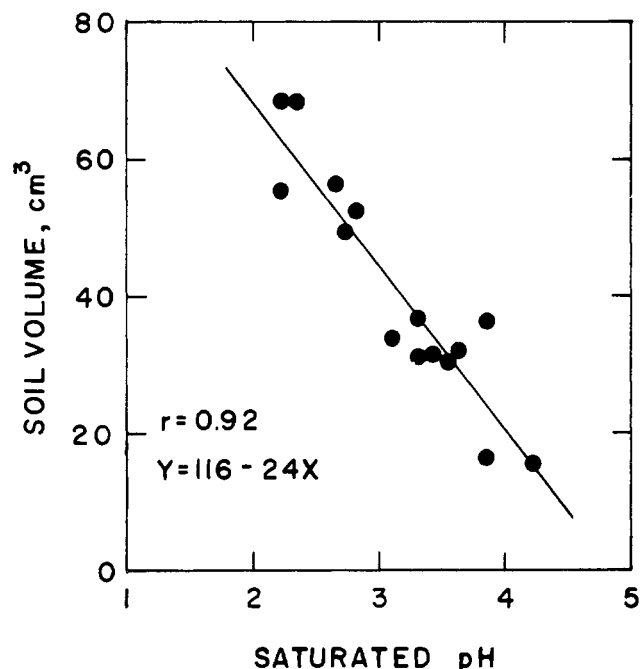
Data presented in Table I summarize the fertilizer pH, nonorthophosphate, and percent N in the original fertilizer. Also included in Table I is the amount of Mn in the residue and the presence or absence of Mn<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>·(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·H<sub>2</sub>O in the fertilizer residue. There were no Mn compounds detected by X-ray diffraction in fertilizer residues formed from fertilizers with a pH of 2.35 or less. A small residue sample was collected, however, and 5 to 10% of the applied Mn was recovered in it. Manganese ammonium pyrophosphate, Mn<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>·2H<sub>2</sub>O, was identified in all residue samples from fertilizers with a pH of 2.65 or greater. This was the only Mn compound identified and was present when the amount of applied Mn in the residue was greater than 10%. The identification of a compound was based upon detection of the three strongest diffraction peaks. There was no evidence in this study that the Mn was precipitating at the pellet site as orthophosphate. Also, there was no apparent correlation between the nonorthophosphate content of these fertilizers and the precipitation of Mn. Polyphosphate content ranged between 36 and 56% of the total P.

The relationship between the percent of N in the original fertilizer and the saturated pH is shown in Figure 1. The relationship is linear between pH 2.2 and 4.2, with a high degree of correlation. Also illustrated in Figure 1 is the relationship between fertilizer N and the percent of applied Mn precipitated at the site of fertilizer placement. For these materials less than 10% of the applied Mn precipitated in place when the fertilizer contained less than 10% N. Quite a lot of variation in the amount of Mn precipitated did occur, however, even at an equivalent fertilizer N percentage. This is particularly true in the mid-region of the curve.

The distribution of applied Mn in growth chamber pot experiments was highly correlated with the pH of the ammonium polyphosphate fertilizer (Figure 2). Greater movement of Mn into the soil surrounding the site of fertilizer placement occurred as the fertilizer pH decreased. The increase in Mn-affected soil as influenced by fertilizer pH was linear and highly significant. A decrease of fertilizer pH by 1 unit resulted in an increase of 24 cm<sup>3</sup> of soil which contained fertilizer Mn. A fertilizer with a pH of 2.2 resulted in 5.8% of the total soil volume being affected by fertilizer Mn.



**Figure 1.** Influence of percent fertilizer N in some ammonium polyphosphate fertilizers on the saturated pH of the fertilizer and the percent of applied Mn which precipitates with the fertilizer when applied at a rate of 5.0-5.8% Mn.



**Figure 2.** Relationship between saturated fertilizer pH and volume of soil containing fertilizer Mn.

Increased movement of the Mn into the surrounding soil was reflected in a higher concentration of Mn in the plants growing in this soil (Figure 3). A significant increase in dry matter production due to Mn application was not obtained so these data are not presented. The concentration of Mn in oats plants increased from 28 to 60 ppm with decreasing fertilizer pH. The Mn concentration of plants in soil not treated with Mn was 25 ppm. As would be expected from previous observations, there was also an increase in plant Mn concentration with increasing volume of soil affected by fertilizer Mn. This relationship is presented in Figure 4.

## DISCUSSION

To be effective when applied with phosphate fertilizers, Mn should be incorporated into or blended with acidic

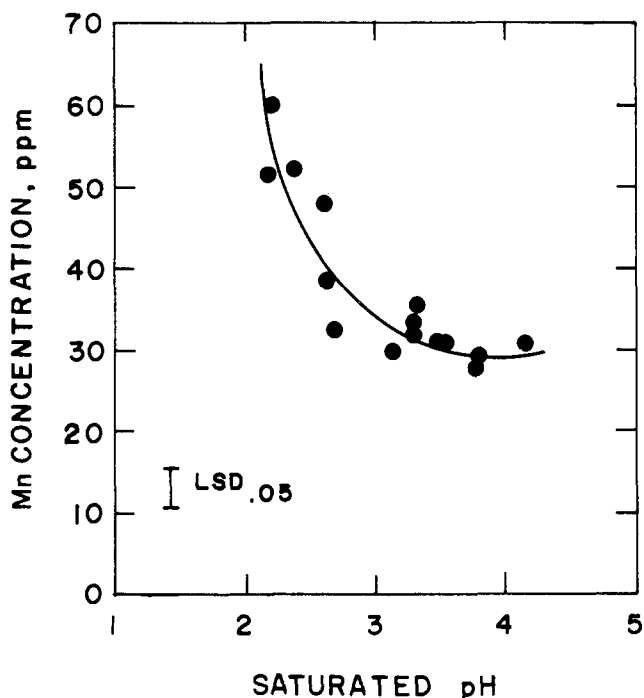


Figure 3. The effect of saturated fertilizer pH on the concentration of Mn in oat tissue.

materials. Based on the data in this report, when the carrier is a polyphosphate-based material, the pH should be less than 2.65. For the present range of ammoniated materials, this would mean a product with less than 10% total N. Polyphosphate-based materials present a problem in that they contain pyrophosphate molecules which react to form insoluble  $Mn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$  at pH values as low as 2.65 and perhaps lower. Although not detected in this study,  $Mn(NH_4)_2H_4(P_2O_7)_2 \cdot 2H_2O$  also has been reported to form below a pH of 4.0 when the pyrophosphate content is greater than 40% of the total P (Hossner and Blanchar, 1970). Precipitation of these insoluble compounds results in a decreased efficiency of the applied Mn. Increasing fertilizer pH results in increasing Mn precipitation with essentially all of the Mn precipitating at the site of placement at pH 6.0. Any Mn which precipitates at the site of placement is greatly reduced in its effectiveness. A concentrated zone of fertilizer solution surrounds the insoluble residue, effectively limiting plant root penetration (Blanchar and Caldwell, 1966). Even if the roots are able to grow to the precipitated Mn, the compounds present are of low solubility and may not provide adequate Mn nutrition for rapidly growing plants.

In addition to reducing Mn availability, precipitation may also limit the initial utilization of the fertilizer phosphate. Giordano and Mortvedt (1969) showed decreased movement of P in soil when Mn was combined with  $(NH_4)_3HP_2O_7$ . Greater movement of P was observed when the Mn was combined with the orthophosphate material  $NH_4H_2PO_4$ . An ammonium polyphosphate fertilizer containing 5% Mn could result in the precipitation of 19% of the total applied P as  $Mn_3(NH_4)_2(P_2O_7)_2 \cdot 2H_2O$  if an adequate pyrophosphate concentration were present. If the Mn precipitated entirely as  $Mn(NH_4)_2H_4(P_2O_7)_2 \cdot 2H_2O$ , the amount of phosphate precipitated could be high as 45%. For ammonium polyphosphate fertilizers with saturated pH values greater than 5.0, the reaction product would likely be  $Mn(NH_4)_2P_2O_7 \cdot H_2O$  (Frazier *et al.*, 1966; Lehr *et al.*, 1967). At these pH values essentially

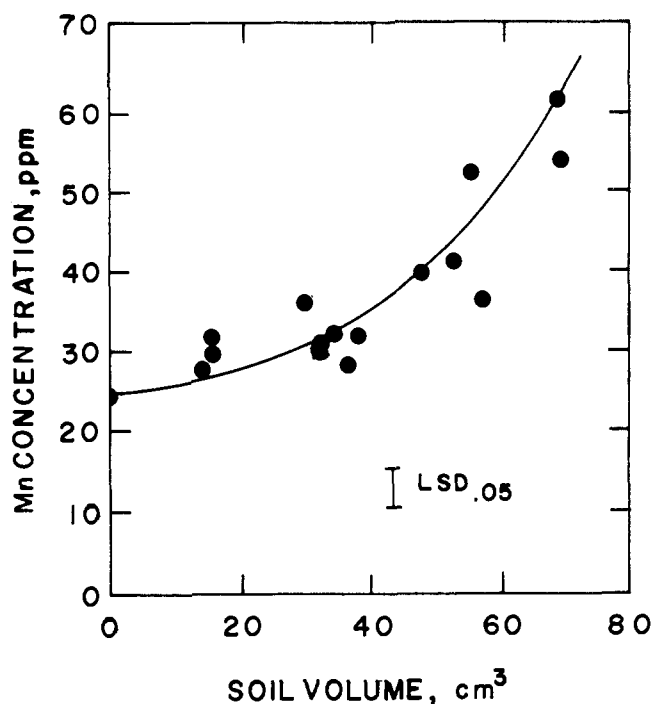


Figure 4. Manganese concentration of oat tissue as influenced by the volume of soil containing fertilizer manganese.

100% of the Mn would precipitate with about 28% of the phosphate.

Although initial availability and movement of P is reduced, the residual availability of the phosphate should not be impaired. In fact, the rate of P reversion may be reduced in that an additional reaction product is inserted into the reversion sequence. Reaction of pyrophosphate with the soil cations such as Mn, Fe, Ca, and Mg to form relatively insoluble but unstable pyrophosphate products in the soil may actually increase the availability of P over an entire growing season and partially account for the increased effectiveness sometimes attributed to polyphosphate compared to orthophosphate carriers (Terman and Engelstad, 1966).

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