Crop Response to Zinc Oxide Applied in Liquid and Granular Fertilizers

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Various liquid and granular fertilizers were compared as carriers containing 2% zinc as zinc oxide for corn grown in greenhouse pots. When mixed with the soil, all liquid, *L*, fertilizers were similar in effectiveness but were superior to the granular, *G*, carriers. The superiority of liquid carriers was attributed to the better distribution of applied zinc throughout the soil. Forage yields and zinc uptake were lower with localized than with mixed placement. When band applied, the agronomic effectiveness of zinc carriers was: Urea-ammonium nitrate (*L*) = ammonia–ammonium nitrate, (*L*) > 11–37–0 (*L*) = triammonium pyrophosphate (*G*) = ammonium polyphosphate, (*G*) > 7–21–7 fertilizer (*L*, containing polyphosphate) > monoammonium phosphate (*G*) > ammonium nitrate (*G*) > 6–18–6 fertilizer (*L*, containing only orthophosphate). Spot-placed anhydrous ammonia was not effective as a zinc carrier, while 11–37–0 solution and clay suspension fertilizers were equally effective.

Uniform application of sources of zinc or other micronutrients in the field is difficult because of the low rates used. Application with macronutrient fertilizers may be the most economical and effective means to supply micronutrients to crops. Greenhouse studies (*3*, *7*) and field experiments (*2*, *5*) show that some granular macronutrient fertilizers are agronomically effective as zinc carriers. However, zinc in these carriers generally is not as effective as finely ground zinc sulfate or zinc oxide mixed with the soil without a carrier.

The use of nitrogen solutions and anhydrous ammonia for direct application has increased from 8% of the total nitrogen applied in 1947 to 64% in 1964 (*7*, *8*, *10*). The application of all liquid fertilizers accounted for 22% of the total tonnage of fertilizers produced in 1964, as compared to less than 3% in 1954. However, there is little information concerning the agronomic effectiveness of micronutrients applied with these fertilizers.

One disadvantage of using certain liquid mixed fertilizers as micronutrient carriers is the limited amount of micronutrient which can be dissolved (*9*, *12*). This prohibits the use of certain macronutrient carriers because it is not possible to dissolve sufficient amounts of micronutrients in the carrier. When polyphosphates are included in the base solution, the dissolution of copper, iron, manganese, and zinc sources is increased greatly. For example, the solubility of zinc oxide in 11–37–0 (polyphosphate) solution is 2.0% zinc and that in 8–24–0 (orthophosphate) solution is 0.05% zinc (*11*). The concentration of micronutrients can also be increased in liquid fertilizers by adding a suspending agent such as Attapulgite clay. When clay is added at the rate of 1 to 3%, this material gels in an aqueous system and gives a relatively stable suspension (*11*). The nutrient levels then are restricted mainly by the viscosity of the product (*9*). It is not known if the presence of the clay in suspension or slurry fertilizers will affect the plant availability of added zinc.

This paper presents the results of two greenhouse pot experiments conducted to compare various liquid, suspension, and granular fertilizers as carriers of zinc oxide for corn.

Methods and Materials

Analyses and Preparation of Fertilizers. Partial chemical analyses of the experimental fertilizers are shown in Table I. Solid ammonium nitrate (AN) and monoammonium phosphate (MAP) were reagent grade materials. The ammonium polyphosphate (APP) was made by ammoniation of superphosphoric acid, followed by granulation. Triammonium pyrophosphate (TPP), one of the main constituents in APP, was prepared in the laboratory. Each of these materials and zinc oxide as fine powders were mixed to give fertilizers containing 2% zinc. Each fertilizer was then pressed into tablets, crushed, and $-8 + 10$ mesh granules screened for use.

The liquid fertilizers containing 2% zinc (by weight) were prepared as outlined below. For simplicity, all materials containing significant quantities of nonorthophosphates will subsequently be termed polyphosphates, even though the chief form was pyrophosphate in the various fertilizers.

Urea-Ammonium Nitrate (UAN). Zinc oxide was dissolved in an aqueous solution of urea and AN. Anhydrous ammonia was added until the pH of the solution was 7.0 to 7.5.

Ammonia-Ammonium Nitrate, (AAN). Anhydrous ammonia was added to an aqueous solution of AN until the solution pH was 10. Zinc oxide was then dissolved in this solution.

Anhydrous Ammonia. Zinc oxide and AN–necessary for dissolution of the zinc oxide—were placed in a stainless steel reaction chamber in a ratio of 2 moles of AN per mole of zinc oxide. Sufficient liquid anhydrous ammonia was introduced under pressure so that the final zinc concentration was 2%.

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Table I. Partial Chemical Analysis of Liquid and Granular Fertilizers Containing Zinc Oxide

Fertilizer and Grade	Total N, %	Total P, %	% of Total P		Total K, %	Total Zn, %
			Ortho	Poly		
		Liquid Fertilizers				
UAN (28–0–0)	28.0	...	...	...	...	2.1
AAN (36–0–0)	36.2	...	...	...	...	2.0
NH_3 (77–0–0)	76.7	...	...	...	...	2.0
11–37–0 (solution)	10.3	15.5	32	68	...	1.9
11–37–0 (suspension)	11.7	16.8	32	68	...	2.0
Poly A (8–25–0)	8.4	11.0	100	0	...	2.0
Poly B (9–29–0)	9.3	12.8	76	24	...	2.0
Poly C (10–34–0)	10.4	15.0	53	47	...	2.0
Poly D (11–37–0)	11.3	16.4	25	75	...	2.0
6–18–6 (Ortho)	5.9	7.8	100	0	5.0	2.0
7–21–7 (Poly)	7.0	9.2	28	72	5.7	2.0
		Granular Fertilizers				
AN (34–0–0)	34.1	...	...	...	...	2.0
MAP (12–60–0)	11.9	26.4	100	0	...	2.0
APP (15–61–0)	14.8	26.8	45	55	...	2.0
TPP (16–56–0)	16.4	24.4	0	100	...	2.0

11–37–0 (Solution and Suspension). TVA 11–37–0 is a nearly neutral solution containing nitrogen in the ammoniacal form. About half of the phosphorus is in the orthophosphate form and the remainder in the polyphosphate form. Zinc oxide was wetted with water and then dissolved in 11–37–0. The 11–37–0 suspension fertilizer was prepared by adding 3% by weight of Attapulgite clay to the 11–37–0 solution and then adding zinc oxide.

"Poly" Solutions. Solutions *A*, *C*, and *D* were prepared by simultaneous addition of anhydrous ammonia and water to phosphoric acids containing 54, 76, and 79% P_2O_5, respectively. The resulting polyphosphate contents were 0, 50, and 75% of the total phosphorus contents. Solution *B* was made by blending equal amounts of solutions *A* and *C*. Zinc oxide was wetted and added to each solution. The zinc oxide did not dissolve in solution *A* (0% polyphosphate); so it was shaken vigorously to form a suspension before application to the soil.

6–18–6. Potassium chloride was dissolved in 8–24–0 base solution to give the desired fertilizer grade. Zinc oxide was added but very little was dissolved in this ammonium orthophosphate solution. This material was shaken to form a suspension before application to the soil.

7–21–7. KCl was dissolved in 11–37–0 to give the desired fertilizer grade. All of the added zinc oxide dissolved in this ammonium polyphosphate solution.

Greenhouse Procedure

The soil used in these studies was Nolichucky sandy clay loam (pH 7.3), a noncalcareous, zinc-deficient, surface soil derived from sandstone and shale. Two experiments were conducted using corn (*Zea mays* var. Funk's G-76) as the test crop. The following nutrients were mixed with 3 kg. of soil per pot: Nitrogen was equalized to 600 mg. with AN, phosphorus to 500 mg. as concentrated superphosphate, and potassium to 200 mg. as potassium sulfate. Adequate amounts of the other micronutrients and magnesium were also mixed with the soil. Five corn plants per pot were grown for 7 weeks during which the soil moisture was maintained at approximately 0.3 atm. with deionized water. Dry forage yields from triplicates of each treatment were determined at harvest, and the plant tissue was analyzed for zinc by atomic absorption spectroscopy.

Experiment 1. The liquid fertilizers listed in Table II were applied to Nolichucky soil to furnish 6 mg. of zinc per pot (4 pounds of zinc per acre). In one series, all of the fertilizer solutions except anhydrous ammonia were applied by diluting the required volume to 50 ml., atomizing on the soil, and mixing. In a second series, the liquid fertilizers were spot-placed in the center of the pot by injecting the required amount of undiluted solution directly into the soil with a hypodermic syringe at a depth of 4 inches. Liquid anhydrous ammonia was spot-placed in the moist soil with the injector apparatus described by Papendick and Parr (*6*). Half of the pots in each series were incubated on greenhouse benches 4 weeks prior to planting, with the soil moisture maintained at about 0.3 atm. Half were planted immediately after application of the zinc fertilizers. Corn was planted in all pots on July 16 and harvested September 2, 1965.

Experiment 2. All of the liquid and solid fertilizers listed in Table I were applied to the soil at a rate of 6 mg. of zinc per pot. The soil materials were mixed throughout the soil as $-8+10$ mesh granules. All liquid fertilizers except anhydrous ammonia were diluted to 50 ml. and poured on the dry soil surface. Anhydrous ammonia was injected into moist soil as

Table II. Dry Forage Yields and Uptake of Zinc by Corn, as Affected by Time and Method of Application of Liquid Fertilizers Containing Zinc Oxide (Experiment 1)

Zinc Carrier	Yield, G./Pot		Zn Uptake, Mg./Pot	
	Mixed	Spot-placed	Mixed	Spot-placed
Applied at Planting				
UAN	56.2	16.7	0.55	0.15
AAN	60.8	7.5	0.55	0.08
11–37–0 (solution)	54.8	29.8	0.39	0.22
11–7–0 (suspension)	54.5	33.9	0.44	0.22
NH_3	. . .	7.4	. . .	0.08
No Zn	5.2		0.04	
Applied Four Weeks Prior to Planting				
UAN	50.2	6.6	0.41	0.06
AAN	57.2	12.5	0.38	0.10
11–37–0 (solution)	53.9	22.6	0.41	0.23
11–37–0 (suspension)	54.4	25.2	0.38	0.18
NH_3	. . .	9.3	. . .	0.07
No Zn	4.7		0.03	
Incubation	N.s.		N.s.	
Carrier	N.s.		[a]	
Placement	[b]		[b]	
Carrier × placement	[b]		[b]	

[a] Significant at 5% level. [b] Significant at 1% level.

described above. The soil in each of these pots was removed after 24 hours, mixed, and replaced.

Band placement of these fertilizers was simulated by filling each pot half full of soil, applying the fertilizer to this surface, and then filling the pot with soil. A wooden template with a 3-inch diameter circle was pressed into the soil surface of the half-filled pot to leave an impression on the soil. The appropriate number of zinc-containing fertilizer granules was uniformly distributed on the soil around the ring. For band application of the liquids, the required volume of all liquid fertilizers except the anhydrous ammonia solution was diluted with deionized water so that 2 ml. of the diluted liquid would supply 6 mg. of zinc. This was applied dropwise with a pipet to the soil around the ring. The anhydrous ammonia solution was spot-placed in the same manner as described for experiment 1. Corn was planted on January 3 in a circle 2 inches above and 1 inch outside of the fertilizer band and harvested February 28, 1966.

Results

Experiment 1. Forage yields were not significantly different when UAN, AAN, or the 11–37–0 fertilizers were mixed with the soil (Table II). There was also no significant change in yield when these zinc carriers were mixed with the soil 4 weeks prior to planting.

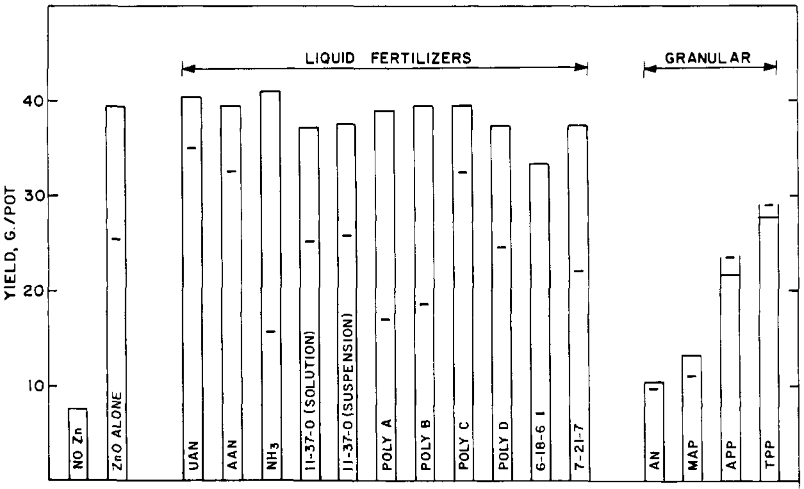
Yields were much lower when these fertilizers were spot-placed in the soil. However, yields were higher with both 11–37–0 materials than with UAN, AAN, and anhydrous ammonia with this placement method. This may have been related to the high soil pH associated with applications of ammonia-containing liquids. Results reported in a previous paper (*4*) indicated that the response of corn to zinc sulfate applied with several nitrogen sources, including anhydrous ammonia, was related to their effect on the soil pH. A decrease in uptake of both native and applied zinc was associated with an increase in soil pH.

Spot-placing the 11–37–0 solutions 4 weeks prior to planting resulted in slightly lower yields than where these materials were spot-placed just before planting. Since growth was poor with spot-placed UAN, AAN, and anhydrous ammonia, yield differences associated with the different times of application of these carriers are probably not meaningful.

Zinc concentrations in the forage ranged from 7 to 11 p.p.m.; therefore, zinc uptake was highly correlated with yield. Zinc uptake was much greater with UAN and AAN than with 11–37–0, despite the small yield differences when these carriers were mixed with the soil just prior to planting. However, there was no difference in zinc uptake when these fertilizers were applied 4 weeks prior to planting.

Experiment 2. Forage yields and zinc uptake were higher with the liquid than with the granular macronutrient carriers mixed with the soil (Figures 1 and 2). With this placement method there was very little difference in agronomic effectiveness among the liquid fertilizers as zinc carriers; they were similar to finely ground zinc oxide mixed with the soil.

The agronomic effectiveness of the granular fertilizers as carriers of zinc oxide when mixed with the soil was: TPP = APP > MAP = AN. Other tests (*3*, *13*)

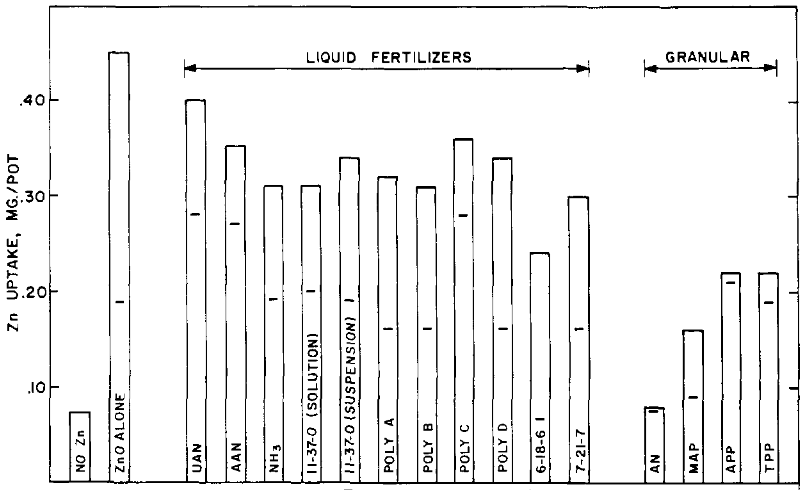


TEST FOR SIGNIFICANCE*

	NO Zn	ZnO ALONE	UAN	AAN	NH_3	11-37-0 (SOLUTION)	11-37-0 (SUSPENSION)	POLY A	POLY B	POLY C	POLY D	6-18-6 I	7-21-7	AN	MAP	APP	TPP
MIXED		a	a	a	a	a	a	a	a	a	a	b	a	e	e	d	c
BANDED		b	a	a	c d	b	b	c	b c	a	b c	e	b c	e	d e	b c	a

*BARS WITH THE SAME LETTERS BELOW ARE NOT SIGNIFICANTLY DIFFERENT AT THE 5% LEVEL

Figure 1. Yield of dry corn forage, as affected by mixing (entire bar) and banding (lower bar) liquid and granular fertilizers containing zinc oxide (experiment 2)



TEST FOR SIGNIFICANCE*

	NO Zn	ZnO ALONE	UAN	AAN	NH_3	11-37-0 (SOLUTION)	11-37-0 (SUSPENSION)	POLY A	POLY B	POLY C	POLY D	6-18-6 I	7-21-7	AN	MAP	APP	TPP
MIXED		a	a	a b	b c	b c	b	b c	b c	a b	b	c d	b c	e	d e	c d	c d
BANDED		b	a	a	b	b	b	b	b	a	b	c	b	c	c	b	b

*BARS WITH THE SAME LETTERS BELOW ARE NOT SIGNIFICANTLY DIFFERENT AT THE 5% LEVEL

Figure 2. Zinc uptake by corn, as affected by mixing (entire bar) and banding (lower bar) liquid and granular fertilizers containing zinc oxide (experiment 2)

have shown that APP was equal to AN and slightly better than MAP as a carrier of zinc sulfate. The reaction products formed from these macronutrient carriers with the added zinc oxide may differ from those with zinc sulfate, causing a difference in plant availability of zinc. Probably, water-insoluble zinc oxide applied with macronutrient fertilizers must be solubilized before the applied zinc will diffuse into the surrounding soil and be more accessible to plant roots. The agronomic effectiveness of the above granular fertilizers would thus be related to their solubilizing effect on zinc oxide.

With band application the liquids were not consistently superior to the granular materials (lower bars in Figures 1 and 2). Yield and zinc uptake were highest from UAN, AAN, and the Poly C solution. Granular TPP and APP as well as the 11–37–0 solution and suspension were slightly less effective. Anhydrous ammonia, the 7–21–7 fertilizer, and the Poly *A*, *B*, and *D* solutions were less effective as zinc oxide carriers with this placement method. MAP, AN, and the 6–18–6 liquid fertilizer were the poorest zinc oxide carriers. Localized placement resulted in decreased forage yields and zinc uptake with liquid fertilizers but had little effect on the results with the granular materials.

Discussion

With little exception, crop response was greater with mixed than with band or spot placement. This probably was due to the better distribution of zinc throughout the soil. Results of a previous study (*3*) indicated that movement of applied zinc into the surrounding soil was rather limited and crop response was related to the volume of zinc-affected soil. Possibly, the carriers may have exerted a greater influence on the applied zinc oxide when band applied. Since most of the fertilizers used in this study were neutral or basic in reaction, this would tend to reduce the solubility of the applied zinc. The importance of good distribution of applied zinc in the soil was especially evident with the anhydrous ammonia fertilizer. This fertilizer was as effective as any zinc carrier when the soil was mixed thoroughly after the solution had been spot-placed in the soil. However, it was ineffective in both experiments when spot-placed in the soil without subsequent mixing.

The superiority of the liquid fertilizers over the granular fertilizers as zinc carriers in experiment 2 appears to be due to the more complete distribution of zinc throughout the soil. This resulted largely from the method used for applying the liquids. The results of these experiments agree with those of Brown and Krantz (*1*) who reported higher corn yields and zinc uptake when zinc sulfate was applied to the soil as a solution rather than as granules. They also noted that mixing both liquid and granular zinc sulfate with the soil resulted in greater yields and zinc uptake than did spot placement.

Agronomic effectiveness of various ortho- and polyphosphate fertilizers as zinc carriers was compared in experiment 2. When mixed with the soil, the liquid orthophosphate fertilizers (6–18–6 fertilizer and Poly A solution) were as effective as the polyphosphate solutions. However, the 6–18–6 material was much less effective when band applied. The solubility of zinc oxide in the orthophosphate solutions was very low. These materials were shaken so the zinc oxide was in suspension before application, but this method probably would not be practical under field conditions. There was little difference between the Poly A, B, and D solutions, but the Poly C solution (containing 50% polyphosphate) was superior when these materials were band applied. Granular TPP was superior to MAP as a carrier of zinc oxide with either placement method. As would be predicted from its constituents, the agronomic effectiveness of APP as a zinc carrier was between that of TPP and MAP.

There was very little difference in forage yields and zinc uptake when zinc oxide was applied in the solution or in the suspension fertilizer of 11–37–0 in either experiment. This suggests that any sorption of the applied zinc on the clay suspending agent in the 11–37–0 suspension did not affect plant availability of zinc.

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