Crop Response to Applied Zinc in Ammoniated Phosphate Fertilizers

John J. Mortvedt

Various granular ammoniated phosphate fertilizers were compared as carriers containing 2% zinc as zinc oxide, zinc sulfate, or Zn-EDTA for corn grown in greenhouse pots. Forage yields and zinc uptake were very low when the inorganic sources were incorporated with ammoniated fertilizers but were satisfactory when Zn-EDTA was the source of zinc. Crop response to zinc in these fertilizers increased with a decrease in zinc concentration in the granule or when finely ground, both of which resulted in better distribution of applied zinc in the soil. The agronomic effectiveness of zinc sulfate incorporated with an NPK fertilizer during the manufacturing process decreased with increasing degree of ammoniation and was related to the level of water-soluble zinc in these fertilizers. These results suggest that the agronomic effectiveness of inorganic zinc sources is low when incorporated with ammoniated phosphate fertilizers.

Deficiencies of zinc have been more frequently noted as cropping has become more intensive. Moreover, less zinc is being added as a contaminant in today's higher-analysis fertilizers. It is essential that zinc sources be uniformly applied to soil because the zinc application rate is generally low. In addition, the percentage recovery of applied zinc by the immediate crop is less than 10% (Giordano and Mortvedt, 1966). Incorporation of micronutrients into macronutrient fertilizers has been recognized as a practical means of applying these elements to the soil (Nikitin, 1954). However, chemical reactions may occur during the manufacturing process, in storage, or after soil application, which may decrease effectiveness of the added micronutrient. Nikitin and Rainey (1952) found reduced solubility of zinc sulfate incorporated with nonacid-forming fertilizers. Jackson *et al.* (1962) reported decreased levels of water-soluble zinc with increased pH of the fertilizer system when zinc sulfate or basic zinc sulfate was added to mixed fertilizers.

The addition of zinc sulfate monohydrate can cause caking in certain fertilizers (Caro *et al.*, 1960). Excessive caking resulted when this zinc source was incorporated with mixed fertilizers which normally exhibited a tendency to cake. This tendency to cake was overcome by including ammoniated superphosphate in the mixture, suggesting that reactions occurred during ammoniation which reduced the caking ability of the zinc salt.

More than half of the fertilizer phosphorus currently used in the United States is applied in the form of mixed fertilizers (Harre, 1967). Moreover, most mixed fertilizers are manufactured by processes which involve the ammoniation of superphosphate (Hignett and Brabson, 1961). Reactions occurring during ammoniation of superphosphate may reduce levels of water-soluble phosphorus. Reversion of available phosphorus forms to less available apatites also may occur as a result of over ammoniation (Jacob and Ross, 1931). If zinc salts are incorporated with superphosphates and subsequently ammoniated, reactions during the ammoniation process may form products which are unavailable to plants.

Various chelated zinc sources also are applied to the soil in combination with commercial fertilizers. However, care must be taken when these zinc sources are incorporated with fertilizers because the organic chelates may be decomposed during the manufacturing process. Ellis *et al.* (1965) reported that Zn-EDTA was ineffective in supplying zinc to pea beans when incorporated with an ammoniated NPK fertilizer during the manufacturing process, but it was a satisfactory zinc source when coated on this fertilizer. The level of water-soluble zinc was 10% when this zinc source was incorporated, 100% when coated on ammoniated NPK fertilizer. Subsequent chemical analyses of the fertilizer revealed that the EDTA was decomposed during the manufacturing process, presumably by the acid reaction of the ordinary superphosphate before ammoniation. When the method of incorporation was changed to minimize decomposition of the EDTA, this zinc source was equally effective for plants when incorporated with the ammoniated fertilizer during the manufacturing process and coated on or mixed with the fertilizer just before application in the field (Brinkerhoff *et al.*, 1966).

This paper presents the results of three greenhouse pot experiments conducted to determine the response of corn to zinc added as zinc sulfate, zinc oxide, or Zn-EDTA [(ethylenedinitrilo)tetraacetic acid] to ammoniated concentrated superphosphate (ACSP). Effects relating to the degree of ammoniation, stage of manufacturing process during which the zinc source was added, granule size, and concentration of zinc in the granule on the availability of zinc were also studied.

PROCEDURE AND RESULTS

General Greenhouse Procedure. Nolichucky sandy clay loam (pH 7.3), a noncalcareous, zinc-deficient eroded surface soil derived from sandstone and shale, was the test soil. The following nutrients were mixed with 3 kg.

National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Ala. 35660

of soil per pot: Nitrogen was equalized to 600 mg. with ammonium nitrate (AN), phosphorus to 500 mg. with concentrated superphosphate (CSP), and potassium to 200 mg. with potassium sulfate. Adequate amounts of the other micronutrients and magnesium were also mixed with the soil. In a separate series of pots in each experiment, fine zinc sulfate was mixed with the soil to supply the same rates of zinc as that applied in the fertilizer treatments. This served as the standard treatment with which results of all three experiments could be compared. Five corn plants (*Zea mays L;* var. Funks G-76) per pot were grown for about 6 weeks during which the soil moisture was maintained at approximately 0.3 atm. with deionized water. Dry forage yields from three replications of each treatment were determined at harvest, and the plant tissue was analyzed for zinc by atomic absorption spectroscopy.

Experiment 1. Partial chemical compositions of the zinc carriers used in this experiment are shown in Table I. Zinc oxide or zinc sulfate monohydrate was incorporated with CSP, ACSP, or a mixture of AN and CSP to provide the same nitrogen-phosphorus ratio as that in ACSP. Incorporation of these zinc sources with ACSP was accomplished by mixing powders of each with CSP and ammoniating the mixture by means of a batch-type ammoniator-granulator. The fertilizer was moistened slightly during the process to promote retention of ammonia. Each zinc source was also "incorporated" after ammoniation by mixing the appropriate amount of the zinc source with zinc-free ACSP. The pH of a saturated aqueous solution of each product was determined with a combination glass electrode. The level of water-soluble phosphorus was lower in ACSP than in CSP, which agrees with the results of others (Hignett and Brabson, 1961; Wright *et al.*, 1963). All products were pressed into tablets, crushed, and screened to give −8+10 mesh granules containing about 2% zinc.

These products were mixed with the soil to furnish 3, 6, or 12 mg. of zinc per pot (2, 4, and 8 pounds of zinc per acre, respectively). Corn was planted March 23 and harvested May 2, 1966.

Dry forage yields and zinc uptake were much higher when fine zinc sulfate was mixed with the soil than when either zinc oxide or zinc sulfate was applied with ACSP (Figure 1). Based on forage yields and zinc uptake, the relative effectiveness of zinc in ACSP compared with that of fine zinc sulfate was less than 17%, as determined by the least squares method (Table II). Crop response to zinc was not improved when either zinc source was incorporated after, rather than before, ammoniation. These data are not shown. Apparently the reaction products were similar whether these zinc sources were added before or after ammoniation of the CSP and subsequently applied to the soil.

When AN and CSP were mixed to give the same nitrogen-phosphorus ratio as that in ACSP, yields and zinc uptake were much higher than those with ACSP for both zinc sources. However, crop response was even higher when these zinc sources were applied with CSP. Forage yields were similar with both zinc sources when incorporated with CSP, but Zn uptake was higher with zinc sulfate.

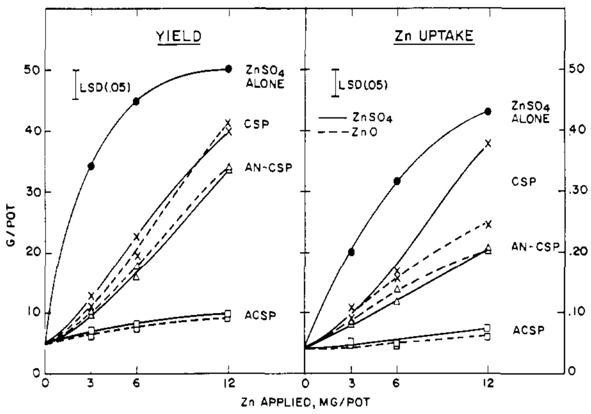

Figure 1. Forage yields and zinc uptake by corn, as affected by application of zinc sulfate or zinc oxide with various macronutrient fertilizers—experiment 1

Table II. Relative Effectiveness of Various Fertilizers as Carriers of Zinc Oxide and Zinc Sulfate for Corn—Experiment 1

Zinc Source	Zinc Carrier	Relative Effectiveness, % Forage yield	Zinc uptake
ZnO	ACSP	13	10
ZnO	AN-CSP	72	42
ZnO	CSP	91	54
$ZnSO_4$	ACSP	17	12
$ZnSO_4$	AN-CSP	70	46
$ZnSO_4$	CSP	85	92
$ZnSO_4$[a]	...	100	100

[a] Fine $ZnSO_4$ mixed with soil.

Table I. Partial Chemical Composition of Zinc Carriers—Experiments 1 and 2

Zinc Source	Zinc Carrier	pH	N Total, %	P Total, %	P w-s P, % of total	Zn Total, %	Zn w-s Zn, % of total
ZnO	ACSP	5.9	5.8	18.9	46	1.8	1
ZnO	AN-CSP	3.5	5.2	17.1	80	2.0	60
ZnO	CSP	3.3	...	20.2	81	2.0	71
$ZnSO_4$	ACSP	5.7	6.2	17.8	48	1.8	1
$ZnSO_4$	AN-CSP	3.4	5.1	16.6	80	2.0	84
$ZnSO_4$	CSP	3.2	...	19.6	81	2.0	90

Experiment 2. ACSP containing zinc oxide or zinc sulfate was finely ground and diluted with zinc-free ACSP to provide zinc concentrations of 0.45% in ACSP. These products, as well as ACSP containing 1.8% zinc, were each pressed into tablets, crushed, and screened to provide granules of −8+9, −12+14, and −35+50 mesh sizes. The first two granule sizes are in the size range presently used in the fertilizer industry, and the third was included to give the wider range in granule size. All materials were mixed with the soil to provide the same zinc application rates as in experiment 1. Corn was planted June 22 and harvested August 3, 1966.

Yields and zinc uptake in the first crop increased with decrease in granule size when zinc sulfate was incorporated in ACSP (Figure 2). However, there was very little difference in crop response between the medium and coarse size granules; neither was very effective in supplying zinc

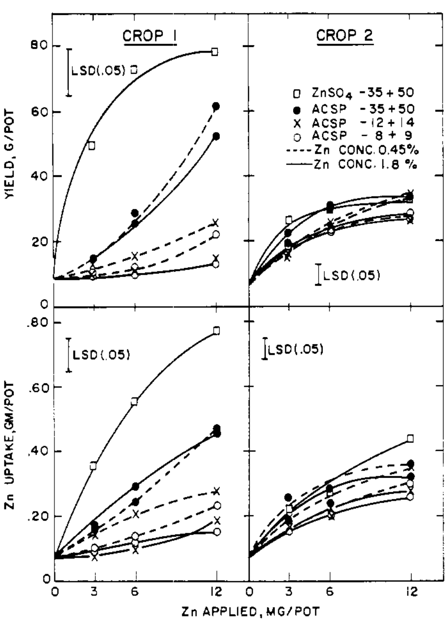

Figure 2. Forage yields and zinc uptake from two successive crops of corn, as affected by granule size and zinc concentration in ACSP—experiment 2

to the corn crop. Forage yields and zinc uptake were similar, regardless of zinc concentration in the −35+50 mesh granules; but crop response to zinc in the medium and coarse size granules increased with a decrease in zinc concentration from 1.8 to 0.45%. Response to zinc supplied as zinc oxide was similar to that with zinc sulfate in this fertilizer, and the results with zinc oxide are not shown. As in experiment 1, crop response to fine zinc sulfate mixed with the soil was much higher than with either zinc source in ACSP.

After the first crop harvest, the corn roots were removed and the soil was thoroughly mixed and replaced in each pot. A second corn crop was planted August 12 and harvested September 22, 1966. Additional nitrogen and potassium were applied to the soil surface as solutions of AN, calcium nitrate, magnesium nitrate, and potassium sulfate after planting.

In the second crop, neither yield nor zinc uptake was affected by zinc concentration in the granule, granule size, or zinc source in ACSP (Figure 2). Crop response to zinc in ACSP was equal to that applied as fine zinc sulfate, although maximum yields were much lower in the second crop.

Experiment 3. Partial chemical compositions of the experimental fertilizers used in this experiment are shown in Table III. Zn-EDTA was incorporated with CSP and the mixture was ammoniated as described previously. This zinc source was granulated with zinc-free ACSP and also with CSP for comparison with similar products containing zinc oxide or zinc sulfate, which were tested in experiment 1.

Zinc sulfate was incorporated with an NPK fertilizer which was ammoniated to varying degrees. Reagent-grade zinc sulfate heptahydrate, commercial-grade ordinary superphosphate, CSP, and potassium chloride were mixed in a laboratory batch-type ammoniator-granulator to produce a 5–8.8–16.6 (5–20–20) fertilizer. The amount of sulfuric acid ordinarily used in this fertilizer formulation was then added, along with sufficient ammonia to neutralize the acid. A sample was removed for analysis and enough ammonia added to ammoniate 10% of the superphosphate in the fertilizer. This procedure was repeated until the superphosphate was fully ammoniated.

Table III. Partial Chemical Composition of Zinc Carriers—Experiment 3[a]

Zinc Source	Lb. NH_3 per Unit P_2O_5	N Total, %	P		K Total, %	Zn	
			Total, %	w-s P, % of total		Total, %	w-s Zn, % of total
Zn-EDTA	...	...	20.6	83	...	0.2	100
Zn-EDTA	3.8	6.2	19.5	53	...	0.2	100
Zn-EDTA	3.8	5.0	16.9	51	...	1.8	94
Zn-EDTA	0.6	3.6	7.5	84	14.4	1.9	100
$ZnSO_4$	0.6	4.1	8.1	83	15.4	2.5	84
ZnO	0.6	4.6	8.2	70	16.1	2.0	60
$ZnSO_4$	0.0	2.0	9.1	84	17.5	2.4	100
$ZnSO_4$	0.4	2.4	9.1	77	16.9	2.3	59
$ZnSO_4$	1.2	2.4	8.8	59	17.4	2.2	43
$ZnSO_4$	1.6	3.2	8.9	47	17.1	2.3	29
$ZnSO_4$	2.1	4.0	8.5	40	16.6	2.3	15
$ZnSO_4$	4.1	5.3	8.1	29	15.3	2.1	1

[a] All products made from a 5–8.8–16.6 fertilizer formulation except the first three products, where CSP was the base material.

Additional products were made to compare all three zinc sources incorporated with the NPK fertilizer. Zinc sulfate, zinc oxide, and Zn-EDTA were each incorporated with the materials described in the preceding paragraph and the formulation (including some ammonium sulfate) was ammoniated to 15% of full ammoniation.

All products were pressed into tablets, crushed, and screened to −8+10 mesh granules containing from 1.9 to 2.4% zinc. These were mixed with the soil to provide 6, 12, and 24 mg. of zinc per pot. Corn was planted April 15 and harvested May 25, 1967.

Forage yields and zinc uptake by corn from these fertilizers are shown in Table IV. The effectiveness of each fertilizer relative to fine zinc sulfate mixed with the soil was determined for each zinc rate. The average of these values is presented in Table V. The relative effectiveness of Zn-EDTA incorporated with ACSP in terms of forage yields was 84%. The increased availability of zinc in Zn-EDTA is shown by the zinc uptake data. Zn-EDTA was 151% as effective as zinc sulfate mixed with the soil. When Zn-EDTA was granulated with zinc-free CSP or ACSP, the concentration of zinc in the products was inadvertently made at 0.2% instead of 2.0%. This error was not found until after the experiment was begun, so zinc was applied at only one tenth of the desired rate. Nevertheless, the forage yields with both products applied at the highest rate (2.4 mg. of zinc per pot) were 80% of the forage yields where Zn-EDTA was incorporated with ACSP during the manufacturing process to contain 2.0% zinc. However, zinc uptake was much lower where the two former products were applied.

When each zinc source was incorporated with fully ammoniated ACSP, the relative effectiveness of Zn-EDTA (Table V) was at least five times that of zinc sulfate or zinc oxide (Table II). When all three sources were each incorporated with the NPK fertilizer (15% of full ammoniation), zinc sulfate was less than half as effective as Zn-EDTA in terms of forage production but was less effective in terms of zinc uptake (Table V). Zinc oxide was even less effective in this fertilizer.

The relative effectiveness of zinc sulfate applied with the NPK fertilizer decreased with increasing degree of ammoniation (Table V). In terms of corn forage yields, zinc sulfate in nonammoniated NPK fertilizer was 48% as effective as fine zinc sulfate mixed with the soil, decreasing to 2% with full ammoniation. The corresponding values for zinc uptake were 26 and 1%, respectively.

DISCUSSION

Results of these studies indicate that the availability of zinc to plants is low when zinc oxide or zinc sulfate is incorporated with ammoniated phosphate fertilizers. Reactions between inorganic zinc sources and components of the fertilizer apparently result in products of low solubil-

Table V. Relative Effectiveness of Various Ammoniated Fertilizers as Carriers of Zinc for Corn—Experiment 3

Zinc Source	Zinc Carrier	Ammoniation, %	Relative Effectiveness, % Forage yield	Zinc uptake
Zn-EDTA	ACSP	100	84	151
Zn-EDTA	ACSP[a]	100	36	18
Zn-EDTA	CSP	0	34	18
Zn-EDTA	NPK	15	82	168
$ZnSO_4$	NPK	15	37	27
ZnO	NPK	15	27	17
$ZnSO_4$	NPK	0	48	26
$ZnSO_4$	NPK	10	49	27
$ZnSO_4$	NPK	30	40	18
$ZnSO_4$	NPK	40	18	9
$ZnSO_4$	NPK	50	6	4
$ZnSO_4$	NPK	100	2	1
$ZnSO_4$[b]	...	...	100	100

[a] Zn-EDTA granulated with zinc-free ACSP after ammoniation.
[b] Fine $ZnSO_4$ mixed with soil.

Table IV. Forage Yields and Zinc Uptake by Corn, as Affected by Incorporation of Various Zinc Sources in Macronutrien Fertilizers—Experiment 3

Zinc Source	Zinc Carrier	Ammoniation, %	Forage Yield, G./Pot 6 Mg. Zn/Pot	12	24	Zn Uptake, Mg./Pot 6 Mg. Zn/Pot	12	24
Zn-EDTA	ACSP	100	42.9	43.7	43.2	0.34	0.65	1.14
Zn-EDTA	ACSP[a]	100	15.1	22.2	35.7	0.08	0.11	0.21
Zn-EDTA	CSP	0	15.9	19.0	34.4	0.09	0.12	0.16
Zn-EDTA	NPK	15	43.5	43.9	40.4	0.40	0.74	1.12
$ZnSO_4$	NPK	15	16.6	22.9	33.4	0.11	0.15	0.22
ZnO	NPK	15	16.6	16.7	25.3	0.11	0.09	0.15
$ZnSO_4$	NPK	0	13.0	22.2	44.0	0.09	0.14	0.28
$ZnSO_4$	NPK	10	16.6	27.3	37.2	0.09	0.19	0.22
$ZnSO_4$	NPK	30	15.0	21.2	34.2	0.08	0.14	0.17
$ZnSO_4$	NPK	40	10.6	12.6	21.7	0.07	0.08	0.11
$ZnSO_4$	NPK	50	9.6	8.9	11.9	0.06	0.05	0.09
$ZnSO_4$	NPK	100	9.0	8.0	9.3	0.05	0.05	0.06
$ZnSO_4$[b]	...	...	43.0	45.8	48.6	0.25	0.44	0.76
None	...	...	7.9			0.05		

[a] Zn-EDTA granulated with zinc-free ACSP after ammoniation.
[b] Fine $ZnSO_4$ mixed with soil.

ity. The most probable reaction product is zinc ammonium phosphate, a compound with a very low level of water-soluble zinc (Frazier *et al.*, 1966). Results obtained in experiment 3 show that Zn-EDTA is more effective in supplying zinc to plants than is zinc oxide or zinc sulfate when incorporated with ammoniated fertilizers. Apparently the chelated zinc does not react with the phosphorus fertilizer to form unavailable reaction products during ammoniation or after application to the soil.

The decrease in agronomic effectiveness of zinc sulfate incorporated with the NPK fertilizer was related to the level of water-soluble zinc in this fertilizer (Figure 3). The decrease in relative effectiveness was greatest when the per cent ammoniation increased from 30 to 50%. This was accompanied by a decrease in level of water-soluble zinc from 43 to 15% of the total zinc in the fertilizer. This suggests that the level of water-soluble zinc in the fertilizer must be greater than 40% for satisfactory crop response to zinc. Further evidence for the relationship between the level of water-soluble zinc in a fertilizer and its agronomic effectiveness is shown by the results obtained in experiment 1. Crop response to zinc was much better when applied in CSP and AN-CSP than in ACSP. The level of water-soluble zinc in the first two products was greater than 60% as compared with less than 1% of the total zinc in ACSP. The pH of the saturated solution of ACSP was higher then that of AN-CSP or CSP (Table I). Therefore, the level of water-soluble zinc was related to the pH of these fertilizer systems, as shown by Jackson *et al.* (1962).

Results of experiment 3 indicated that the availability of zinc in ACSP was higher when the granule size was decreased to $-35+50$ mesh, although this is not in the size range usually found in commericial fertilizers. Crop response to zinc in the granular fertilizers also increased with a decrease in zinc concentration in the granule, which agrees with the results of a previous study (Giordano and Mortvedt, 1966). In the second crop, mixing the soil after crop 1 resulted in higher crop yields and zinc uptake with coarse and medium ACSP granules. This suggests that zinc incorporated as zinc sulfate or zinc oxide with ACSP may have some residual value after soil tillage, even though immediate availability of zinc in granular ACSP is very low.

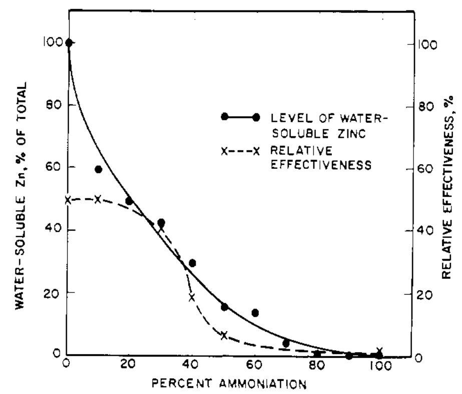

Figure 3. Effect of degree of ammoniation of CSP on the level of water-soluble zinc in a NPK fertilizer and its effectiveness relative to fine zinc sulfate—experiment 3

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