Extractability of Zinc Granulated with Macronutrient Fertilizers in Relation to Its Agronomic Effectiveness

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Zinc sulfate or ZnO was granulated with various macronutrient fertilizers and the agronomic effectiveness of Zn in these fertilizers was determined in greenhouse pot studies. These fertilizers were also extracted by various reagents and the percentage recovery of the total Zn by each extractant was correlated with the agronomic effectiveness of Zn in these fertilizers. The percentage recovery of Zn from these fertilizers by deionized H_2O, 0.01 and 0.001*N* HCl, an acidic K_2SO_4 solution, and solutions containing chelating agents in each case was highly correlated with agronomic effectiveness. However, the correlation was highest for H_2O. The solution pH of orthophosphate fertilizers was inversely related to the agronomic effectiveness of Zn in these fertilizers. There was no relationship between the total Zn in a fertilizer and its immediate availability to plants.

Various zinc sources are granulated with macronutrient fertilizers for application to Zn-deficient soils. This provides a more uniform application to soils than a separate application of small amounts of a Zn source. However, chemical reactions between the Zn source and the macronutrient fertilizer during manufacturing and storage, or after soil application, may result in decreased effectiveness of the applied Zn. Nikitin and Rainey (1952) found that the H_2O solubility of $ZnSO_4$ was reduced when it was incorporated with nonacid-forming mixed fertilizers. Jackson *et al.*, (1962) reported that the level of H_2O-soluble Zn decreased with increased pH of the fertilizer system when $ZnSO_4$ or a mixture of ZnO and $ZnSO_4$ was added to mixed fertilizers.

Various greenhouse pot tests have been conducted by the authors to determine the agronomic effectiveness of several Zn sources when granulated with various macronutrient fertilizers. Results of these tests show that early crop response to applied Zn is significantly affected by the macronutrient carrier (Mortvedt and Giordano, 1969). Terman *et al.* (1966) also reported that crop response to Zn in greenhouse pots was greater when $ZnSO_4$ was granulated with NH_4NO_3 or $(NH_4)_2SO_4$ than with several P sources.

Even though some Zn sources are not immediately available to plants when applied with certain macronutrient fertilizers, the applied Zn may have residual value. Results of a previous study showed that an ammoniated phosphate fertilizer containing either $ZnSO_4$ or ZnO was ineffective for the first corn crop (Mortvedt, 1968). However, when the soil in each greenhouse pot was mixed well before recropping, the resulting second crop yields and Zn uptake were higher. This would imply that although some macronutrient carriers of Zn are ineffective in supplying Zn to the immediate crop on Zn-deficient soils, they might help to maintain available Zn levels in other soils.

Prediction by a chemical test of the effectiveness of Zn for crops when Zn sources are granulated with macronutrient fertilizers would be important. The level of H_2O-soluble Zn in some macronutrient fertilizers containing $ZnSO_4$, ZnO, or ZnEDTA (ethylenediamine tetraacetic acid) has been related to crop response to Zn in both field and greenhouse studies (Ellis *et al.*, 1965, Giordano and Mortvedt, 1969, and Mortvedt, 1968). This study compares the efficiency of several chemical extractants in predicting the immediate effectiveness of Zn for corn when $ZnSO_4$ or ZnO was granulated with various macronutrient fertilizers.

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MATERIALS AND METHODS

The macronutrient fertilizers containing $ZnSO_4$ or ZnO which were selected for this study (Table I) had been evaluated previously in greenhouse pot experiments by the authors. Results of these experiments were reported in the following papers: Giordano and Mortvedt, 1966, 1969; Mortvedt, 1968; and Mortvedt and Giordano, 1967a, 1969. Urea, NH_4NO_3, $NH_4H_2PO_4$, and $(NH_4)_2HPO_4$ were reagent grade materials. Ammonium polyphosphate (APP) is a plant product obtained by ammoniation of superphosphoric acid, and triammonium pyrophosphate (TPP) is the main polyphosphate constituent of APP. Concentrated superphosphate (CSP) and its ammoniated counterpart (ACSP) were plant products. Ammonium phosphate nitrate (APN) is a granular fertilizer produced by ammoniating a mixture of HNO_3 and H_3PO_4. Nitric phosphate (NP) is produced by reaction of a mixture of HNO_3 and H_3PO_4 with rock phosphate, followed by ammoniation and granulation. Urea ammonium phosphate (UAP) is a granulated mixture of urea and $(NH_4)_2HPO_4$. The NPK fertilizers containing Zn were produced by ammoniating a mixture of $(NH_4)_2SO_4$, ordinary superphosphate, CSP, KCl, and $ZnSO_4$ in a laboratory batch-type ammoniator granulator using a formulation for a 5–8.8–16.6 (5–20–20) grade fertilizer. The numbers after each NPK fertilizer indicate ammoniation of the superphosphates in the fertilizer as a percentage of the maximum.

Fine powders of either $ZnSO_4$ or ZnO were mixed with each macronutrient fertilizer to contain about 2% of Zn by weight. These mixtures were pressed into tablets, crushed, and -8 $+10$ mesh granules weighing about 20 mg. each were selected for use. Therefore, the number of granules applied at each Zn rate was held constant as crop response to Zn has been found to be related to the number of granule sites in the soil (Giordano and Mortvedt, 1966). The pH values of the fertilizer solutions are those resulting after equilibration of 1 gram of each mixture with 7 ml. of deionized H_2O for 1 hour (Table I).

The granular macronutrient carriers were mixed with the soil to supply Zn at rates of 3, 6, and 12 mg. per 3 kg. of soil in each greenhouse pot. A standard treatment of either fine $ZnSO_4$ or fine ZnO mixed alone with the soil was included in each experiment. Crop response to both Zn sources was

Table I. Solution pH, Level of Water-Soluble Zinc, and Agronomic Effectiveness of Zinc When Zinc Sulfate or Zinc Oxide Was Granulated with Various Macronutrient Fertilizers

Macronutrient Fertilizer	Solution pH		Water-Soluble Zn, % of Total		Agronomic Effectiveness, %[a]			
					Forage Yield		Zn Uptake	
	$ZnSO_4$	ZnO	$ZnSO_4$	ZnO	$ZnSO_4$	ZnO	$ZnSO_4$	ZnO
Urea	6.3	7.6	80	2	40	12	64	15
NH_4NO_3	4.8	6.9	100	6	59	8	58	4
Ammonium polyphosphate	5.5	5.7	90	96	78	70	49	55
Triammonium pyrophosphate	6.1	6.4	100	100	90	70	93	60
$NH_4H_2PO_4$	3.6	4.1	70	6	75	24	63	28
$(NH_4)_2HPO_4$	7.5	8.2	9	0.1	20	15	25	32
Concentrated superphosphate	2.8	2.8	90	100	93	91	72	54
Ammoniated superphosphate	5.4	5.9	1	1	17	13	12	10
Ammonium phosphate nitrate	5.0	5.6	7	2	19	12	9	4
Nitric phosphate	5.2	6.7	0.1	0.1	11	7	16	4
Urea ammonium phosphate	7.3	7.9	2	1	8	8	9	11
NPK-0	3.5	...	100	...	48	...	23	...
NPK-10	3.6	...	59	...	49	...	27	...
NPK-30	3.6	...	50	...	40	...	18	...
NPK-40	3.7	...	29	...	18	...	9	...
NPK-50	4.0	...	15	...	6	...	4	...
NPK-100	5.3	...	1	...	2	...	1	...

[a] A value of 100% indicates that the Zn source granulated with macronutrient fertilizer was equal to fine $ZnSO_4$ or ZnO in supplying Zn to corn.

comparable when they were applied to the soil in this manner (Giordano and Mortvedt, 1966). The soil used in all of these studies was Nolichucky sandy clay loam (pH 7.3), a noncalcareous, Zn-deficient surface soil derived from sandstone and shale. Other characteristics of this soil were: organic matter, 2.7%; cation exchange capacity, 6.7 *me.*/100 grams; total Zn, 51 ppm; and 0.1*N* HCl extractable Zn, 2.7 ppm. Corn (*Zea mays* L., var. Funks G-76, 5 plants per pot) was the test crop in all experiments. The plants were harvested after a growth period of 6 to 8 weeks and dry forage yields were determined. The plant tissue was analyzed for Zn by atomic absorption spectroscopy and Zn uptake was calculated. Results of a previous greenhouse experiment (Mortvedt and Giordano, 1967b) showed that Zn uptake by corn grown on the same soil increased with dry matter production throughout a six-week growth period.

The slope of each linear response curve for forage yield and Zn uptake was determined by the least squares method. The agronomic effectiveness of each fertilizer as a carrier of Zn was then determined by division of the slope of each response curve by that of the standard treatment. A value of 100% indicates that the slope of a fertilizer response curve was equal to that of the standard treatment. Hereafter in the text the term, agronomic effectiveness, refers to this comparison; and it is generalized to mean the relative availability to crops of Zn applied with fertilizers.

The extractants which were used in this study were deionized H_2O and other aqueous solutions. Two normalities of HCl and an acidic K_2SO_4 solution were included to provide relatively rigorous extraction of Zn from the fertilizers. Ammonium citrate, the extractant used for determination of available P in fertilizers, and neutral *N* $NH_4C_2H_3O_2$ were also included. The chelating agents were EDTA and its Na salt, Na_2H_2EDDHA [Na salt of ethylenediamine di(*o*-hydroxyphenyl-acetic acid)], and DTPA (diethylene triamine pentaacetic acid) and its Na salt. Another extracting solution, 0.005*M* DTPA + 0.01*M* $CaCl_2$ buffered at pH 7.3 with $N(CH_2C_2OH)_3$, was included. The latter solution was developed as an extractant for determining available Fe and Zn in soils (Lindsay and Norvell, 1967). In addition, 6*N* HCl was used as an extractant for total Zn. Preliminary studies showed that this extractant dissolved as much Zn from the fertilizers as that dissolved by concentrated HCl in the official procedure for determination of total Zn (Association of Official Agricultural Chemists, 1965).

The extraction procedure was as follows: Grind a representative sample of each fertilizer to −35 mesh and weigh 0.50 gram of fertilizer into a 50-ml. Erlenmeyer flask; add 5 ml. of extractant, shake vigorously for 1 hour, and filter through Whatman 42 paper; and dilute the filtrate immediately to the appropriate volume with deionized H_2O and analyze for Zn. Preliminary studies showed that recovery of Zn by deionized H_2O remained constant after 15 minutes extraction and with extracting solution–fertilizer ratios ranging betwen 10 and 50.

The percentage recovery by each extractant of the total Zn in each fertilizer was then correlated with the agronomic effectiveness of each fertilizer in terms of forage yield and Zn uptake.

RESULTS AND DISCUSSION

The most effective macronutrient carrier of either $ZnSO_4$ or ZnO was CSP, followed by TPP, APP, and $NH_4H_2PO_4$ (Table I). The agronomic effectiveness of these macronutrient carriers relative to fine $ZnSO_4$ or fine ZnO mixed alone with the soil ranged from 70 to 93% with forage yields and from 49 to 93% with Zn uptake. Urea, NH_4NO_3 and $NH_4H_2PO_4$ were effective carriers of $ZnSO_4$ only. The agronomic effectiveness of the NPK fertilizers as a carrier of $ZnSO_4$ decreased with increasing degree of ammoniation of the superphosphates in the fertilizer. Other ammoniated phosphate fertilizers, APN, NP, ACSP, UAP, and $(NH_4)_2HPO_4$, were ineffective carriers of either Zn source. The poor performance of these ammoniated phosphate fertilizers may have been due to the formation of $ZnNH_4PO_4$, a compound with a very low level of H_2O-soluble Zn (Frazier *et al.*, 1966).

The level of H_2O-soluble Zn in these fertilizers is shown in Table I. Zinc sulfate remained almost completely H_2O-soluble when it was incorporated with NH_4NO_3, urea, APP, TPP, CSP, and NPK-O. When $ZnSO_4$ was incorporated with NPK fertilizers, the level of H_2O-soluble Zn decreased with increasing degree of ammoniation. The level of H_2O-

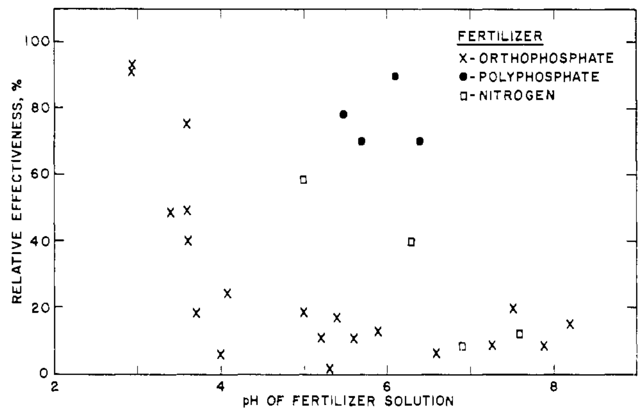

Figure 1. Relationship between fertilizer solution pH and agronomic effectiveness of zinc as zinc sulfate or zinc oxide granulated with various macronutrient fertilizers

Table II. Correlation Coefficients Relating Extractable Zinc as Percentage of Total Zinc Content to Agronomic Effectiveness of Zinc as Zinc Sulfate or Zinc Oxide Granulated with Various Macronutrient Fertilizers

Extractant	pH of Extracting Solution	Correlation Coefficient, r^a Forage yield	Zn uptake
H_2O	5.8	0.92	0.84
0.001*N* HCl	3.5	0.90	0.85
0.01*N* HCl	2.6	0.90	0.83
0.04*N* $KHSO_4$ + K_2SO_4	2.8	0.84	0.76
N $NH_4C_2H_3O_2$	7.0	0.48	0.62
NH_4 citrate[b]	7.0	0.67	0.57
0.001*M* EDTA	3.1	0.83	0.67
0.001*M* Na_2H_2EDTA	4.8	0.91	0.83
0.001*M* Na_2H_2EDDHA	9.5	0.84	0.70
0.001*M* DTPA	3.1	0.83	0.67
0.001*M* Na_3DTPA	10.8	0.87	0.71
0.005*M* DTPA + 0.01 *M* $CaCl_2$ + $N(CH_2CH_2OH)_3$	7.3	0.91	0.87
6*N* HCl		0.28	−0.16

[a] *r* values required for significance at 95 and 99% probability levels were 0.38 and 0.48, respectively.
[b] Extractant used in A.O.A.C. procedure for determination of available P in fertilizers.

soluble Zn was almost 100% when ZnO was incorporated with TPP, APP, and CSP. Dissolution of ZnO in aqueous solutions of these fertilizers was probably due to the sequestering action of the polyphosphates and to the acidic solution of CSP. Less than 10% of the total Zn was H_2O-soluble when either $ZnSO_4$ or ZnO was incorporated with the ammoniated phosphate fertilizers.

The level of H_2O-soluble Zn in these fertilizers was highly correlated with the agronomic effectiveness of their Zn. The correlation coefficients (*r*) were highest when deionized H_2O was the extractant, although significant correlation resulted with most other extractants (Table II). The weak acid extractants and the acidic K_2SO_4 solution dissolved more ZnO from certain carriers than did deionized H_2O, but the r values were not appreciably different. The r values for ammonium citrate and $NH_4C_2H_3O_2$ were much lower than for H_2O, so these extractants would not be as useful in predicting the agronomic effectiveness of Zn in fertilizers. Extracting solutions containing chelating agents dissolved more Zn than was H_2O-soluble from some of the fertilizers which were not very effective as Zn carriers. Therefore, the r values for these extractants were slightly lower than those for H_2O. There was very little difference in the amount of Zn dissolved from these fertilizers by the acid and the Na-salt solutions of either EDTA or DTPA. However, the acid chelate solutions dissolved more Zn from each of the NPK fertilizers, which may account for their slightly lower r values.

A significant inverse relationship was found between the pH of the fertilizer solutions and the agronomic effectiveness of Zn in these fertilizers (Figure 1). There was considerable point scatter when all of the fertilizers were included, so this represents only a general relationship. The solution pH of CSP containing either Zn source was 2.8 and its agronomic effectiveness was the highest of the fertilizers studied. In contrast, $(NH_4)_2HPO_4$ had a solution pH of 7.5 and 8.2 with $ZnSO_4$ and ZnO, respectively, and it was not an effective carrier of either Zn source. The two polyphosphate fertilizers were almost as effective carriers as CSP even though their solution pH values ranged from 5.5 to 6.4. The *r* value for the plot of forage yield *vs.* fertilizer solution pH shown in Figure 1 increased from −0.45 with all fertilizers to −0.68 when only the orthophosphate fertilizers were included in the correlation. Corresponding *r* values for Zn uptake were −0.20 and −0.45, respectively. Therefore, knowledge of the fertilizer solution pH may be of some value in predicting the agronomic effectiveness of Zn in these orthophosphate fertilizers. Orthophosphate fertilizers having solution pH values greater than 4 probably are not agronomically effective carriers of either $ZnSO_4$ or ZnO.

In this study, the percentage of the total Zn in a fertilizer that is H_2O-soluble was best related to the agronomic effectiveness of Zn when $ZnSO_4$ or ZnO were granulated with macronutrient fertilizers. It is likely that this chemical test would also be valid for other Zn sources. Ellis *et al.* (1965) noted that crop response to ZnEDTA was higher when it was coated onto, rather than incorporated with, a granular mixed fertilizer. The level of H_2O-soluble Zn also decreased from 100% to 10% of the total Zn with the coating and incorporation methods, respectively. Therefore, the portion of the total Zn which is H_2O-soluble should be considered as immediately available to plants when Zn sources are granulated with macronutrient fertilizers.

The applied Zn must be H_2O soluble to diffuse from the granule into the soil. The greater the diffusion gradient, the more soil would be affected by applied Zn. However, carrier-Zn reactions might reduce the amount of Zn which is free to diffuse, so the concentration gradients near the granule site would not be as high and it would result in decreased movement of applied Zn in the soil (Mortvedt and Giordano, 1967c). Crop response to applied Zn also was related to the volume of Zn-affected soil (Giordano and Mortvedt, 1966). Therefore, the immediate plant availability of applied Zn should be better related to the H_2O soluble portion than to the total Zn in fertilizers.

There was no relationship between the total Zn in each fertilizer and its agronomic effectiveness (Table II). Yet, the only value that is listed on a fertilizer label is the percentage of total Zn in the fertilizer. This implies that the total amount of Zn is immediately available to plants. The data presented in this and previous papers by the authors show that the agronomic effectiveness of Zn varies greatly when Zn sources are granulated with various fertilizers; thus, the percentage of Zn which is listed on a fertilizer label may not give the true agronomic value of Zn in the fertilizer.

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