

MAKING
BETTER
DECISIONS

TB 97-4
Zinc Fertilizers



Department of Soil and Crop Science
Agricultural Experiment Station

Colorado
State
University

Agricultural
Experiment
Station

Department
of Soil and
Crop Sciences

September 1997

Zinc Plant Availability as Influenced by Zinc Fertilizer Sources and Zinc Water-solubility

Mohamed Amrani
Dwayne G. Westfall
Gary A. Petersen

Zinc plant availability as influenced by zinc fertilizer sources and zinc water-solubility

M. Amrani¹, D. G. Westfall², and G.A. Peterson²

ABSTRACT

Zinc (Zn) fertilizer application has increased during the past three decades. This increase has created the need for more information regarding the availability and agronomic effectiveness of Zn containing fertilizers because some fertilizer metals are not effective. Plant availability of eight commercialized Zn fertilizer materials having different water solubilities was measured in a greenhouse experiment. Corn (*Zea mays L.*) plants were grown for 40 days in a soil amended with lime to two pH's: 6.3 and 7.4. To evaluate the effect of pH, some Zn fertilizers were used at both soil pH levels. All Zn fertilizers were used in the pH 7.4 soil for Zn fertilizers comparison purposes. The experimental design was a factorial combination of pH, Zn fertilizers, and Zn rates (equivalent to 0, 5, 10, 20 lb Zn/A). Visual symptoms, dry matter production, and elemental (Zn, Cd, Pb) concentrations and uptakes were determined. Dry matter production and Zn uptake increased significantly when the soil pH decreased from 7.4 to 6.3. The highest dry matter production was obtained with ZnSO₄ (ZnSO₄·H₂O, 99.9% total water soluble Zn), Zn20 (Zn oxysulfate, 98.3% total water soluble Zn), and Zn27 (Zn oxysulfate, 66.4% total water soluble Zn) (27.9, 27.7, and 26.5 g/pot, respectively). While ZnFe (Zn iron ferrite, 0.3% total water soluble Zn), ZnK (Zn oxide, KO61, 1% total water soluble Zn), and ZnOS (Zn oxysulfate, 0.7% total water soluble Zn) were less effective followed by Zn40 (Zn oxysulfate, 26.5% total water soluble Zn) and ZnOxS (Zn oxysulfate, 11% total water soluble Zn). The same trend was observed for Zn concentration and uptake. Regression correlations showed that the higher the water solubility, the more effective the Zn fertilizer in increasing dry matter yields. Assuming that 5 to 10 lb

Zn/A are the rates commonly recommended, more than a 50% water solubility is needed to adequately supply the crop's needs. Less fertilizer is needed as the solubility increases. The Cd and Pb concentrations and uptakes in corn forage were not significant for any of the sources and rates.

INTRODUCTION

Availability of nutrients from soils and/or fertilizers is a function of complex chemical, physical, and biological interactions. Zinc is among the micronutrients required for normal growth and plant development. A Zn deficiency can severely impair crop growth and decrease yield. Some crops are more sensitive to lower soil Zn levels than others. Among the Zn sensitive crops are corn, sorghum, flax, and grapes. Zinc deficiency is very common in soils with pH greater than 8. Zinc deficiency is generally corrected by applying Zn fertilizers. However, only those Zn sources which are soluble or may be solubilized at the plant root are suitable as a source of Zn. Zinc sulfate-containing fertilizers are the most common Zn fertilizers used to correct Zn deficiency. Among other sources of Zn also being marketed are, Zn-Fe compounds which are the least soluble, and their contribution to Zn in soil solution is expected to be minimal. The form of Zn in these fertilizer materials controls their availability to plants. Zinc fertilizer solubility is reported to be affected by soil pH and soil organic matter (Lindsay, 1979; Harter, 1983; Barrow, 1986; Taylor, 1995).

The degree of solubility is related to the process used in fertilizer manufacturing, and the primary product used as a Zn source. Therefore, to maximize profit for both farmers and manufacturing companies, optimum solubility of Zn material for

1. Visiting Scientist, Researcher INRA, PO. Box 589, Settat, Morocco.

2. Professors, Department of Soil and Crop Sciences, Colorado State University, Fort Collins CO. 80521.

F. 10/22/92
C. Jones

MATERIALS AND METHODS

optimum agronomic effectiveness should be maintained. Mortvedt and Gilkes (1993) suggested bulk blending Zn sources with granular NPK fertilizers to assure homogeneous incorporation of Zn.

Zinc fertilizers commonly have been manufactured from industrial by-products such as ZnO. To prepare granular Zn fertilizer from ZnO, H₂SO₄ is added to improve granulation. The greater the addition of H₂SO₄ to ZnO, which forms ZnSO₄, the greater the water solubility of Zn in the final fertilizer material (Mortvedt, 1992). These Zn fertilizer materials are called Zn oxysulfates. By-products also may contain some heavy metals (Cd, Pb, and Ni), but, Mortvedt and Gilkes (1993) postulated that it is unlikely that these heavy metals would cause significant environmental concern because of the low application rates of Zn fertilizers. Only 1.1 10⁻³ lb/A of Cd would be associated with a Zn application rate of 4.5 lb/A from a fertilizer containing 40% total Zn and 100 mg Cd/kg (Mortvedt and Gilkes, 1993). Kuo and Baker (1980) found that Cd is more likely to cause problems in acid soils. Increasing soil pH leads to increasing sorption of heavy metals by the soil and minimizes plant uptake.

The objective of our study was to evaluate the effectiveness of some commercial Zn granular fertilizer materials to correct Zn deficiencies in soils testing low in Zn. We also evaluated plant uptake of Cd and Pb from these Zn fertilizer materials.

Soil from the A horizon of a loamy sand soil classified as loamy, mixed, mesic arenic Ustollic Haplargid was used in this study. Selected chemical and physical characteristics of this soil are presented in Table 1. The soil was chosen because it was low in Zn availability (DTPA-Zn = 0.48 mg kg⁻¹).

The soil initially had a pH of 5.1 and was limed to pH levels, either 6.3 or 7.4 by adding 0.1 and 1.5% by weight of CaCO₃, respectively. The granular commercial Zn fertilizer materials used in this investigation were given different symbols, and their characteristics are provided in Table 2. Zinc fertilizer granules were added to each pot at rates equivalent to 0, 5, 10, and 20 lb Zn/A (0, 2.1, 4.2, and 8.4 mg Zn kg⁻¹ of soil). The granule mesh size was typical for each Zn fertilizer source and therefore, Zn fertilizer materials were not ground or altered. Alteration of the physical granule characteristics of the materials (grinding) will artificially increase agronomic performance. In order to evaluate these materials under conditions similar to those in commercial agriculture, we used the fertilizer sources in the physical condition as found in fertilizer bags.

Corn seeds (cv P3732) were planted in 8.8 lbs of soil placed in plastic pots and thinned after 9 days to 5 plants/pot. Supplemental plant nutrients were added as reagent grade materials at planting as follows: 226 mg N/pot and 500 mg P/pot (monoammonium phosphate), 500 mg K/pot (K₂SO₄), and 10 mg Fe/pot (FeEDDHA).

→ WE'RE USING 25% MORE SOIL

Table 1. Selected physical and chemical characteristics of the soil, before liming, used in study.

| Paste | | | AB-DTPA | | | | | | |
|--------|-----|-------|---------------------|--------------------|-----|------|------|------|-----|
| pH | EC | OM | P | NO ₃ -N | K | Zn | Fe | Mn | Cu |
| | | --%-- | mg kg ⁻¹ | | | | | | |
| Soil * | 0.7 | 0.5 | 15 | 22 | 245 | 0.48 | 21.6 | 31.1 | 1.5 |

* original soil pH was 5.6. Soil was limed to pH 6.3 or 7.4 before the experiment was initiated.

Three additional N applications of 105 mg N/pot each as NH_4NO_3 were added at 13, 22, and 32 days after planting. Pots were watered regularly with deionized water to bring the soil to approximately 90% of field capacity.

The experiment including all eight Zn sources was conducted on the soil amended to 7.4 (Table 2). Only four Zn sources (Zn20 (98.3%), Zn27 (66.4%), Zn40 (26.5%), and ZnOS (0.7%)) were evaluated at both soil pH 6.3 and 7.4. The experiment was a factorial treatment arranged in a randomized complete block design with four replications.

Forty days after planting, we harvested above ground corn forage. All samples were dried at 60°C for 4 days. After weighing and grinding samples to pass 0.5-mm mesh, a 0.5-g portion was digested for multi-element analysis by inductively-coupled plasma (ICP) using a modified method by Huang and Schulte (1985). The procedure consisted of adding 5 ml of concentrated HNO_3 to a plant sample of 0.5 g, and pre-digesting overnight. The temperature was then increased to 60°C for 30 minutes, followed by adding 3 ml H_2O_2 and digested at 120°C for about 90 minutes. The ICP analyses were performed on the digestate for Zn, Cd, and Pb.

Four Zn fertilizer materials (ZnSO_4 (99.9%), Zn20 (98.3%), Zn27 (66.4%), and Zn40 (26.5%))

were analyzed for total Zn, Cd, and Pb contents using $\text{HNO}_3\text{-HClO}_4$ acid digest (Self and Rodriguez, 1997). The other four Zn fertilizer materials (ZnOS (0.7%), ZnOxS (11%), ZnK (1%), and ZnFe (0.3%)) were analyzed using $\text{HNO}_3\text{-HClO}_4\text{-HF}$ techniques (Self and Rodriguez, 1997). Also, water soluble Zn, Cd, and Pb were determined by using AOAC official method 965.09 (AOAC, 1995).

Two levels of statistical analysis were performed on the data collected in this experiment: (i) effect of all eight Zn fertilizers on growth and uptake for all soils at pH 7.4 and (ii) effect of four Zn fertilizers on growth and uptake at pH 6.3 and 7.4 (Table 2).

Differences in dry matter production, nutrient levels, and total plant uptake for individual treatments were analyzed statistically using a SAS (1985) program and considered significant at $P < 0.05$.

Description of Zn materials used:

ZnSO_4 (99.9%):

Zinc sulfate monohydrate: Sulfuric acid is added to dissolve either Zn metal or ZnO (Zn oxide) followed by dehydration to form $\text{ZnSO}_4\cdot\text{H}_2\text{O}$. This product is usually about 100% water-soluble.

Table 2. Total Zn, Cd, and Pb content and Zn water solubility of Zn materials used in study.

| Zn Source | Zn Fertilizer Symbol | Total Zn | Water Soluble Zn | Total Cd | Total Pb | Water soluble Cd | Water soluble Pb | Soil pH Evaluated | |
|--|-------------------------|--------------|------------------|--------------------------------|----------|------------------|------------------|-------------------|---|
| | | ----- %----- | | -----mg kg ⁻¹ ----- | | 6.3 | 7.4 | | |
| $\text{ZnSO}_4\cdot\text{H}_2\text{O}$ | ZnSO_4 (99.9%) | 35.5 | 99.9 | 61 | 90 | 57 | 48 | | x |
| Zn oxy-sulfate | Zn20 (98.3%) | 20.4 | 98.3 | 75 | 158 | 34 | 30 | x | x |
| " | Zn27 (66.4%) | 27.3 | 66.4 | 43 | 178 | 31 | 25 | x | x |
| " | Zn40 (26.5%) | 39.9 | 26.5 | 28 | 293 | 18 | 7 | x | x |
| " | ZnOxS (11%) | 37.7 | 11.0 | 43 | 1,866 | 19 | 148 | | x |
| " | ZnOS (0.7%) | 17.5 | 0.7 | 435 | 23,070 | 125 | 199 | x | x |
| Zinc iron ferrite | ZnFe (0.3%) | 20.1 | 0.3 | 22 | 97 | 66 | 54 | | x |
| KO61 | ZnK (1%) | 15.0 | 1.0 | 359 | 19,170 | <0.1 | <0.1 | | x |

Zn20 (98.3%), Zn27 (66.4%), Zn40 (26.5%), ZnOS (0.7%), and ZnOxS (11%):

Zinc oxy-sulfate: these products are formed by adding H_2SO_4 to Zn feedstocks, commonly ZnO. The solubility of these fertilizer materials is related to the amount of H_2SO_4 added during the manufacturing process. Some Zn oxysulfate products contain high Fe, which results in lower solubility. The water solubility and plant availability of Zn in Zn oxysulfate fertilizers range widely (If Zn oxysulfate materials contain high levels of Fe, this usually indicates that the feedstock may have contained KO61).

ZnFe (0.3%):

Zinc iron ferrite: Reagent grade zinc-iron oxide ($ZnFe_2O_4$). This product was manufactured specifically for evaluation in this study since $ZnFe_2O_4$ is the major component of KO61.

ZnK (1%):

The $ZnFe_2O_4$ described above is the major component of KO61 (ZnK (1%)). Zinc-rich feedstock (usually flue dust) is partially acidified by H_2SO_4 which forms Zn compounds of low water solubility. KO61 is the EPA designation of this material and it is classified as a hazardous waste until brought under the beneficial use regulations and used as a fertilizer material.

RESULTS AND DISCUSSION

Visual Symptoms

No nutrient deficiency symptoms other than those for Zn were observed. Within 5 days after emergence, corn grown with no Zn fertilization (0 Zn) and those receiving ZnFe (0.3%), ZnK (1%), ZnOxS (11%), and ZnOS (0.7%) showed distinct Zn-deficiency symptoms (Photo 1). Pronounced bands of chlorosis occurred on the leaves, starting

near the leaf whorl. As growth continued, these chlorotic bands turned white. Plant growth was stunted and shortened internodes were obvious on the control, ZnFe (0.3%), and ZnK (1%) treatments. By the end of growing period, 1- to 3-fold variations in plant height were observed. The ZnFe (0.3%) and ZnK (1%) treatments had the smallest growth and exhibited severe Zn deficiency symptoms (Photos 2 and 3). The growth response to $ZnSO_4$ (99.9%) at the four rates of Zn application are shown in Photo 4. Five lbs Zn/A from $ZnSO_4$ (99.9%) satisfied the Zn requirement of the plant. This observation was substantiated by the dry matter production data.

Dry matter production

Dry matter production data in the soil pH 7.4 study are plotted in Fig. 1 as a function of Zn rate for each Zn fertilizer.

The yield data for all sources and rates at this pH are given in Table 3 and the statistical analysis is

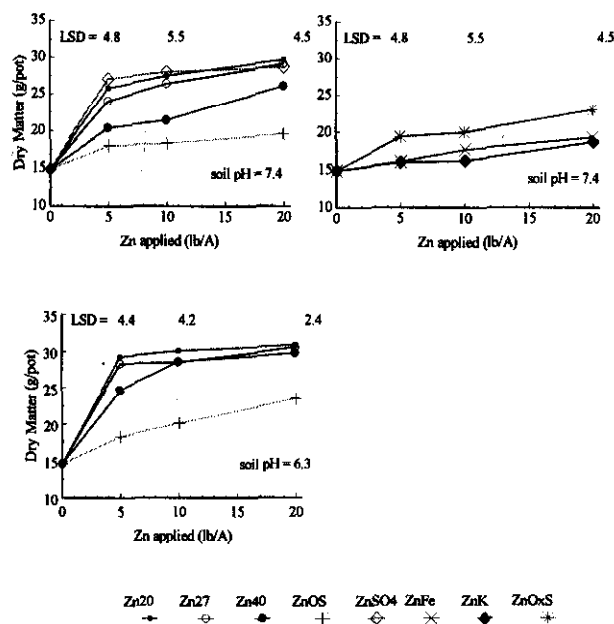
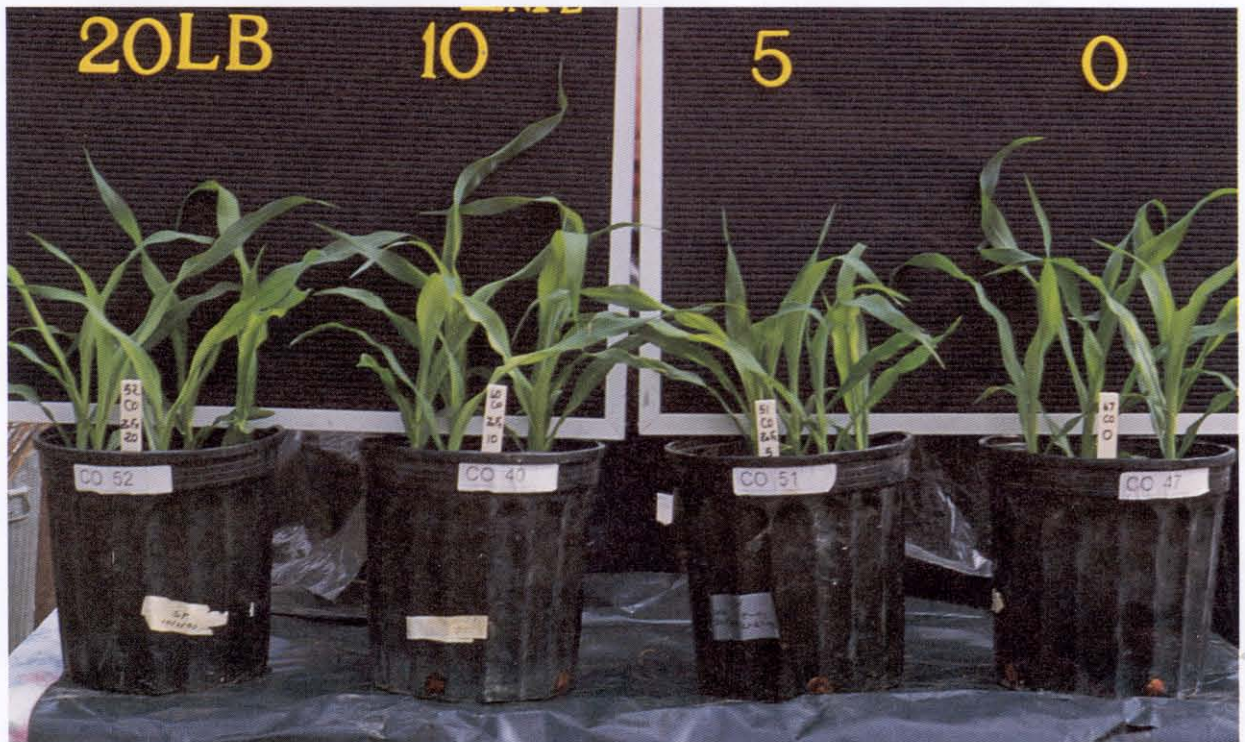


Figure 1. Corn dry matter production in a greenhouse as affected by all eight Zn fertilizer sources and rates at soil pH 7.4 and four Zn fertilizers at soil pH 6.3 and 7.4.



Photo 1. Zinc deficiency symptom on corn 22 days after emergence.

Photo 2. Effect of ZnFe (0.3% total water soluble Zn) on growth of corn 17 days after emergence.



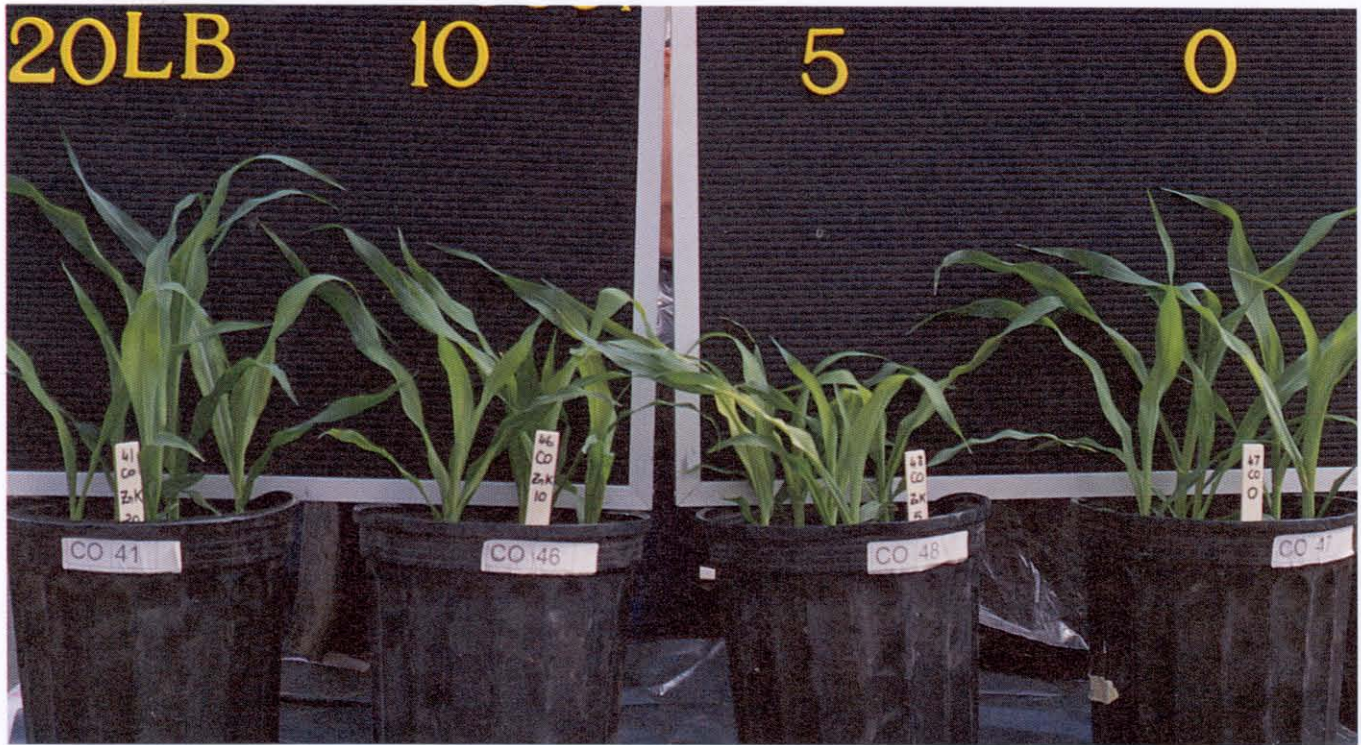


Photo 3. Effect of ZnK (1% total water soluble Zn) on growth of corn 17 days after emergence.



Photo 4. Effect of $ZnSO_4$ (99.9% total water soluble Zn) on growth of corn 22 days after emergence.



Photo 5. Effect of Zn20 (98.3% total water soluble Zn) on growth of corn 22 days after emergence.



Photo 6. Effect of Zn27 (66.4% total water soluble Zn) on growth of corn 22 days after emergence.



Photo 7. Comparison of check (0 lb Zn/A) ZnFe (0.3%), ZnSO₄ (99.9%), and ZnOS (0.7%) (left to right) on growth of corn 30 days after emergence.



Photo 8. Comparison of the effect of ZnSO₄ (99.9%) at 5 lb Zn/A and ZnOS (0.7%) at 20 lb Zn/A on the growth of corn 30 days after emergence.

shown in Table 4. Differences in dry matter productions among Zn sources were highly significant, indicating large differences in the performance of the fertilizer materials tested. At a Zn rate of 5 lb/A, the increase in dry matter production ranged from 7 to 82 % with ZnK (1%) and ZnSO₄ (99.9%), respectively, as compared to the check (0 lb Zn/A). Large visual differences in corn growth were observed (compare Photos 3 and 4). When Zn rate was increased to 20 lb/A, Zn20 (98.3%) increased dry matter production by 100% compared to 26% by ZnK (1%) (compare Photos 5 and 3). The increase reached 112% at pH 6.3 with Zn20 (98.3%) (Fig. 1).

Based on the growth response of corn, three groups of granular Zn fertilizer materials can be identified: (i) ZnFe (0.3%), ZnK (1%), and ZnOS (0.7%) caused no significant response

to Zn application, (ii) Zn40 (26.5%) and ZnOxS (11%) moderately increased corn dry matter production as Zn rate increased, particularly in the more acid soil (Fig. 1), and (iii) ZnSO₄ (99.9%), Zn20 (98.3%), and Zn27 (66.4%) (Photo 6) all increased dry matter production significantly over the control. A visual comparison of some of the Zn fertilizer sources are shown in Photo 7, at 5 lb Zn/A. The very low agronomic effectiveness of ZnFe (0.3%), ZnK (1%), ZnOS (0.7%), and ZnOxS (11%) is mainly related to their lower water solubility and subsequent low Zn availability (Table 2). The application of high rates of Zn from a fertilizer containing low water solubility Zn did not satisfy plant need (Photo 8). These findings substantiate those reported by Mortvedt (1992) who concluded that 35 to 50% of the total Zn should be in a water-soluble form

Table 3. Corn dry matter production, Zn concentration, and Zn uptake as influenced by granular Zn fertilizer materials and rate at soil pH 7.4.

| Zn Fertilizer | Dry matter | | | Zn concentration | | | Zn uptake | | |
|--------------------------------------|-----------------|------|------|--------------------------------|------|------|------------------|-------|-------|
| | Zn rate (Lb/A) | | | | | | | | |
| | 5 | 10 | 20 | 5 | 10 | 20 | 5 | 10 | 20 |
| | -----g/pot----- | | | -----mg kg ⁻¹ ----- | | | -----mg/pot----- | | |
| ZnSO ₄ (99.9%) | 27.1 | 28.7 | 28.0 | 14.8 | 11.1 | 19.9 | 0.399 | 0.315 | 0.558 |
| Zn20 (98.3%) | 25.8 | 27.5 | 29.7 | 10.3 | 10.3 | 17.3 | 0.267 | 0.285 | 0.515 |
| Zn27 (66.4) | 24.0 | 26.4 | 29.1 | 13.8 | 10.2 | 14.3 | 0.330 | 0.270 | 0.416 |
| Zn40 (26.5%) | 20.4 | 21.4 | 26.1 | 11.7 | 9.2 | 14.0 | 0.237 | 0.197 | 0.367 |
| ZnOxS (11%) | 20.0 | 19.4 | 23.0 | 7.6 | 9.9 | 14.1 | 0.153 | 0.196 | 0.318 |
| ZnOS (0.7%) | 18.3 | 18.0 | 19.6 | 10.5 | 14.7 | 15.6 | 0.199 | 0.259 | 0.313 |
| ZnK (1%) | 16.2 | 16.0 | 18.7 | 7.4 | 11.1 | 9.1 | 0.121 | 0.180 | 0.158 |
| ZnFe (0.3%) | 16.1 | 17.7 | 19.3 | 9.2 | 9.8 | 9.7 | 0.151 | 0.178 | 0.186 |
| LSD _{0.05} (within sources) | 4.8 | 5.5 | 4.5 | 4.1 | 5.2 | 4.5 | 0.109 | 0.140 | 0.126 |
| Check (0 lbZn/A) | 14.9 | | | 8.8 | | | 0.133 | | |

in order for a granular Zn fertilizer material to be an effective Zn source.

A Zn application rate of 5 lb/A was sufficient to maximize dry matter production when Zn was applied as Zn20 (98.3%), Zn27 (66.4%), and ZnSO₄ (99.9%) (Table 3). In fact, no significant differences were observed between 5 as compared to 10 and 20 lb/A. In contrast, Zn40 (26.5%) required 10 lb/A to obtain optimum dry matter production (Fig. 1). This result clearly shows that water solubility of granular Zn fertilizer was related to subsequent availability. The Zn20 (98.3%) and ZnSO₄ (99.9%) contain 20.4% and 35.5% total Zn, respectively, and their rates of increase in dry matter production were greater than with Zn40 (26.5%) and ZnOxS (11%) containing 40% and 36% total Zn, respectively (Fig. 1). Water solubility is the key. This is substantiated by the fact that the increase in dry matter production was highly correlated with water-soluble Zn ($r=0.92^{**}$). Maximum dry matter production (DM, g/pot) was related to percentage water solubility of the Zn fertilizer (PWS) by the following equation:

$$DM = 20.5 + 0.10*(PWS) \quad R^2 = 0.84^{**}$$

An increase of 10% of the percentage water solubility of the Zn fertilizer would increase dry matter production by 1 g dry matter/pot (5%). The increase in dry matter production for all Zn application rates as a function of percentage water-soluble Zn was fitted to the Mitscherlich equation (Fig. 2). The higher the content of water-soluble Zn in the fertilizer material, the lower the Zn application rate that are required to obtain maximum production.

Multiple regression was performed to relate dry matter production (DM, g/pot) to both rate of applied Zn (Zn, lb/A) and percentage of water-soluble Zn in the fertilizer materials (PWS):

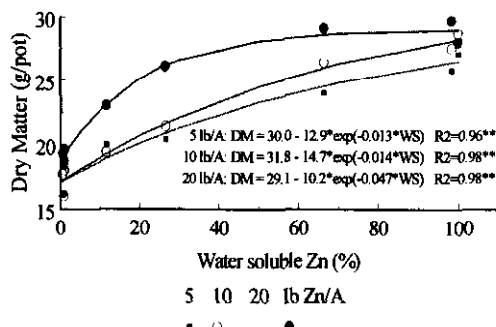


Figure 2. Effect of percentage water-soluble Zn in the fertilizer materials on dry matter production at the three Zn application rates used in study.

$$DM = 13.3 + 0.9*Zn + 0.1*PWS - 0.03*Zn^2 + 0.004*Zn*PWS - 0.0008*PWS^2$$

$$R^2 = 0.88^{**}$$

All parameters of this equation were significant at $P = 0.05$. This means that increasing the percentage of water-soluble Zn in the fertilizer will decrease the Zn rate required for maximum crop growth.

These results show that when Zn fertilizer is applied at a rate of 5 lb Zn/A, the fertilizer should contain at least 50% of water-soluble Zn to obtain maximum corn dry matter production and growth. As the Zn solubility decreases, an increasing Zn rate is needed to obtain maximum crop growth.

Dry matter was affected by soil pH, as well as Zn sources and rates (Table 4). However, the interactions, pH x Zn fertilizer and pH x Zn rate were not significant indicating that the four Zn fertilizers evaluated in this part had the same effect on growth at both soil pH levels. Dry matter production was lower at pH 7.4 (23.8 g/pot) as compared to pH 6.3 (26.9 g/pot) (Table 5).

Table 4. Analysis of variance evaluating the interactions of soil pH (6.3 and 7.4), Zn fertilizer sources (Zn20 (98.3%), Zn27 (66.4%), Zn40 (26.5%), and ZnOS (0.7%), and rates.

| Source | Dry matter | Zn conc. | Cd conc. | Pb conc. | Zn uptake | Cd uptake | Pb uptake |
|---------------------------|------------|----------|----------|----------|-----------|-----------|-----------|
| ----- Probability * ----- | | | | | | | |
| pH | 0.001 | 0.609 | 0.368 | 0.603 | 0.027 | 0.573 | 0.409 |
| Zn Fert. | 0.001 | 0.001 | 0.142 | 0.457 | 0.001 | 0.677 | 0.545 |
| pH x Zn Fert. | 0.072 | 0.001 | 0.503 | 0.376 | 0.001 | 0.525 | 0.285 |
| Rate | 0.001 | 0.001 | 0.125 | 0.066 | 0.001 | 0.296 | 0.066 |
| pH x rate | 0.494 | 0.531 | 0.581 | 0.392 | 0.282 | 0.619 | 0.401 |
| Zn Fert x rate | 0.501 | 0.003 | 0.535 | 0.515 | 0.001 | 0.705 | 0.539 |
| pH x rate x Zn Fert | 0.188 | 0.127 | 0.437 | 0.163 | 0.478 | 0.304 | 0.163 |

* a probability of < 0.05 is considered statistically significant.

Table 5. Effect of soil pH on dry matter, Zn concentration, and total Zn uptake by corn.

| Soil pH | Dry Matter | Zn conc. | Zn uptake |
|---|------------|----------|-----------|
| -- g/pot-- -- mg kg ⁻¹ -- --mg/pot-- | | | |
| 6.3 | 26.9 | 12.7 | 0.341 |
| 7.4 | 23.8 | 12.3 | 0.304 |
| LSD _{0.05} | * | NS | * |
| Check | 14.7 | 8.9 | 0.131 |

* significant at p=0.05.

Zinc Concentration and Uptake

Zinc Concentration

Zinc concentrations in the corn tissue at harvest were significantly affected by Zn rate and Zn fertilizer source (Tables 3 and 6). At a Zn application rate of 5 lb/A, plant concentrations varied from 7.4 to 14.8 mg Zn kg⁻¹ plant tissue with ZnK (1%) and ZnSO₄ (99.9%), respectively. These values increased to 9.1 and 19.9 mg Zn kg⁻¹, respectively, with the same fertilizers when Zn

application rate was increased to 20 lb/A (Table 3). Fertilizers with low water solubility of Zn did not supply enough Zn to meet the crop's needs.

A comparison among Zn fertilizers showed that large increases in plant Zn concentrations were obtained with ZnSO₄ (99.9%), Zn20 (98.3%), and Zn27 (66.4%) (Table 3) at various rates as compared to the check (0Zn) treatment. Zinc concentrations with ZnSO₄ (99.9%) and Zn20 (98.3%) maximized at 19.9 and 17.3 mg Zn kg⁻¹ at the Zn application rate of 20 lb/A, a two-fold increase as compared to the control (8.8 mg kg⁻¹). Zinc fertilizers such as Zn40 (26.5%), ZnOS (0.7%), and ZnOxS (11%) were marginally effective in supplying Zn to the plant if applied at high Zn rates, usually 20 lb/A. The effectiveness of ZnFe (0.3%) and ZnK (1%) was very low. The application of 20 lb/A of Zn as ZnFe (0.3%) and ZnK (1%) did not increase Zn concentration significantly above the control (0Zn), 9.1 and 9.7 mg kg⁻¹, respectively, suggesting that their low water solubilities were the main reason for their poor performances. The Zn concentrations were 1.5- to 3-fold higher when using ZnSO₄ (99.9%) or Zn20 (98.3%) compared to ZnFe (0.3%) or ZnK (1%).

Table 6. Analysis of variance evaluating the interactions of eight Zn fertilizer sources and rates.

| Source | Dry matter | Zn conc. | Cd conc. | Pb conc. | Zn uptake | Cd uptake | Pb uptake |
|---------------------------|------------|----------|----------|----------|-----------|-----------|-----------|
| ----- Probability * ----- | | | | | | | |
| Zn Fert. | 0.001 | 0.001 | 0.081 | 0.142 | 0.001 | 0.115 | 0.166 |
| Rate | 0.001 | 0.001 | 0.223 | 0.661 | 0.001 | 0.382 | 0.615 |
| Zn Fert x rate | 0.817 | 0.084 | 0.500 | 0.218 | 0.123 | 0.514 | 0.220 |

* a probability of < 0.05 is considered statistically significant.

The linear relationship between Zn concentration (Znconc, mg kg⁻¹) in plant tissue and percentage water soluble Zn (PWS) was significant:

$$\text{Znconc} = 12.3 + 0.06 \cdot \text{PWS} \quad R^2 = 0.62^*$$

An increase of 10% water-soluble Zn would result in an increased Zn concentration of 0.6 mg kg⁻¹ (5%).

Soil pH had a non significant effect on Zn concentrations in corn plant tissue (Table 4). Earlier studies showed that Zn concentration and uptake can be decreased significantly with increasing soil pH level (Handreck, 1994; Singh et al., 1995).

Zinc Uptake

Zinc uptake was plotted as a function of Zn fertilizer sources and rates (Fig. 3). At a Zn application rate of 5 lb/A, Zn uptake was 3 fold higher with ZnSO₄ (99.9%) than with ZnK (1%) (Table 3). The ranking of the Zn fertilizers in relation to their ability to supply Zn to the plant was: ZnSO₄ (99.9%) > Zn20 (98.3%) > Zn27 (66.4%) > Zn40 (26.5%) > ZnOxS (11%) > ZnOS (0.7%) > ZnFe (0.3%) > ZnK (1%). This order exactly matches the order of decreasing water-solubilities of Zn fertilizers (Table 2).

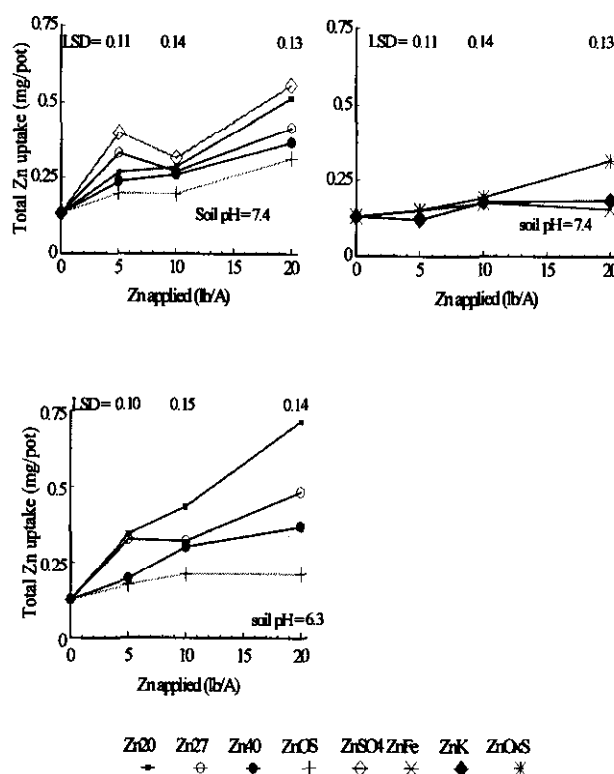


Figure 3. Total Zn uptake by corn in a greenhouse as affected by all Zn fertilizer sources and rates at soil pH 7.4 and four Zn fertilizers at soil pH 6.3 and 7.4.

Table 7. Effect of Zn application rate on heavy metal uptake by corn (averaged across Zn fertilizer materials).

| Zn rate | Cd conc. | Pb conc. | Cd uptake | Pb uptake |
|--|----------|----------|-----------|-----------|
| --- lb/A----- mg kg ⁻¹ -----mg/pot----- | | | | |
| 0 | 0.813 | 1.450 | 0.012 | 0.020 |
| 5 | 0.675 | 0.338 | 0.014 | 0.007 |
| 10 | 0.463 | 0.644 | 0.008 | 0.026 |
| 20 | 0.359 | 1.038 | 0.012 | 0.017 |
| LSD _{0.05} | NS | NS | NS | NS |

Table 8. Comparison of Cd and Pb concentrations and uptake by corn from fertilizer materials used in study (averaged across Zn rates).

| Zn Fertilizer | Cd conc. | Pb conc. | Cd uptake | Pb uptake |
|--|----------|----------|-----------|-----------|
| ----- mg kg ⁻¹ -----mg/pot----- | | | | |
| ZnSO ₄ (99.9%) | 0.092 | <0.001 | 0.003 | <0.001 |
| Zn20 (98.3%) | 0.383 | 0.258 | 0.010 | 0.006 |
| Zn27 (66.4%) | 0.408 | 0.908 | 0.010 | 0.024 |
| Zn40 (26.5%) | 0.783 | 0.600 | 0.019 | 0.013 |
| ZnOxS (11%) | 0.175 | <0.001 | 0.003 | <0.001 |
| ZnOS (0.7%) | 0.650 | 0.675 | 0.011 | 0.015 |
| ZnK (1%) | 0.367 | 0.050 | 0.005 | 0.001 |
| ZnFe (0.3%) | 0.242 | 0.050 | 0.004 | 0.001 |
| LSD _{0.05} | NS | NS | NS | NS |
| Check | 0.500 | 0.575 | 0.007 | 0.008 |

The correlation between Zn uptake (Zn_{up}, mg/pot) and percentage water-soluble Zn in the fertilizers (PWS) was highly significant. The regression between these two parameters is as follows:

$$\text{Zn}_{up} = 0.24 + 0.003 * \text{PWS} \quad R^2 = 0.87^{**}$$

An increase in water soluble Zn in a fertilizer by 10% would result in 12.5% increase in Zn plant uptake.

The Zn uptake increased significantly as the soil pH become more acid (Table 5). Increasing pH from 6.3 to 7.4 significantly

decreased the total Zn uptake from 0.341 to 0.304 mg Zn/pot (Table 5). These results confirmed the finding by Boswell et al. (1988) who reported that applied Zn increased Zn shoot uptake by 4 mg kg⁻¹ at pH 5.3 and only by 0.3 mg kg⁻¹ at pH 6.6.

Cd and Pb concentrations and uptake

Fertilizer analysis showed that water-soluble Cd ranged from trace amounts (ZnFe (0.3%)) to 125 mg Cd kg⁻¹ (ZnOS (0.7%)), while Pb concentration ranged from trace amounts to 199 mg Pb kg⁻¹ for the same fertilizers, respectively (Table 2). The Cd and Pb

concentrations and uptakes by corn plants, as affected by rate and source are shown in Table 7 and 8. No significant impact was found as a result of Zn fertilizer rate or source. No treatment significantly affected Cd and Pb concentrations or plant uptake (Table 4).

CONCLUSIONS

Corn growth, Zn concentration, and Zn uptake were increased by increasing Zn application rates of fertilizers that are water-soluble. The agronomic effectiveness of the eight granular Zn fertilizers studied was as follows: ZnSO₄ (99.9%) > Zn20 (98.3%) > Zn27 (66.4%) > Zn40 (26.5%) > ZnOxS (11%) > ZnOS (0.7%) > ZnFe (0.3%) > ZnK (1%). High correlations were found between water solubility of Zn in the fertilizer material and measured plant parameters. We suggest that granular Zn

fertilizers should have water-soluble Zn levels of at least 50% to be effective in supplying adequate Zn levels for the current crop. Our results confirmed the earlier findings of Mortvedt (1992) who concluded that 40% Zn water solubility was required to supply the crop's Zn needs.

Total Zn in a fertilizer is not enough to successfully determine Zn requirement for a crop. Farmers should receive information about the degree of Zn water solubility of granular Zn fertilizers.

ACKNOWLEDGMENTS

This research was supported by the Colorado State University Agricultural Experiment Station, CoZinCO Sales, and Agrium U.S. Inc. Appreciation is expressed to all sponsors of this research project.

REFERENCES

- AOAC Official Method 965.09. 1995. Nutrients (Minor) in fertilizers. Atomic Absorption Spectrophotometric Method. 15th Edition.
- Barrow, N.J. 1986. Testing a mechanistic model. 2. The effect of time and temperature on retention of zinc with soils. *J. Soil Sci.* 37:277-287.
- Boswell, F.C., M.B. Parker, and T.P. Gaines. 1988. Soil zinc and pH effects on zinc concentrations of corn plants. *Commun. Soil Sci. Plant Anal.* 20:1575-1600.
- Handreck, K.A. 1994. Effect of pH on the uptake of cadmium, copper, and zinc from soilless media containing sewage sludge. *Commun. Soil Sci. Plant Anal.* 25:1913-1927.
- Harter, R.D. 1983. Effect of soil pH on adsorption of lead, copper, zinc, and nickel. *Soil Sci. Soc. Amer. J.* 47:47-51.
- Huang, C-Y L. and E.E. Schulte. 1985. Digestion of plant tissue for analysis by ICP emission spectroscopy. *Commun. Soil Sci. Plant Anal.* 16:943-958.
- Kuo, S. and A.S. Baker. 1980. Sorption of copper, zinc, and cadmium by some acid soils. *Soil Sci. Soc. A. J.* 44:969-974.
- Lindsay, W.L. 1979. Zinc in soils and plant nutrition. *Adv. Agron.* 24:147-181.
- Mortvedt, J.J. 1992. Crop response to level of water-soluble zinc in granular zinc fertilizers. *Fert. Res.* 33:249-255.
- Mortvedt J.J and R.J. Gilkes. 1993. Zinc fertilizers. pp 33-44. *In Zinc in soils and plants.* Robson, A.D. ed. Kluwer Academic Publishers, Dordrecht.
- SAS Institute Inc. 1985. SAS User's guide: Statistics. Version 5 edition. SAS Institute Inc., Box 8000, Cary, NC 27511-8000.
- Self, J.R. and J.B. Rodriguez. 1997. Laboratory manual for soil and plant analysis. Soil, Water, and Plant Testing Lab. Colorado State University. Fourth ed.
- Singh, B. R., R.P. Narwal, A.S. Jeng, and A. Almas. 1995. Crop uptake and extractability of cadmium in soils naturally high in metals at different pH levels. *Commun. Soil Sci. Plant Anal.* 26:2123-2142.
- Taylor, R.W., K. Hassan, A.A. Mehadi, and J.W. Shuford. 1995. Zinc sorption by some Alabama soils. *Commun. Soil Sci. Plant Anal.* 26:993-1008.