ZINC DEFICIENCY CORRECTION IN CORN AS AFFECTED BY CERTAIN PROPERTIES OF FOUR VIRGINIA SOILS, AND THE APPLICATION OF ZINC SULFATE, ZINC CHELATES, AND COAL ASH

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INTRODUCTION

During the recent years, zinc (Zn) deficiency has been observed in corn (*Zea mays* L.) with increasing frequency in Virginia and the Southeastern states. The deficiency has occurred most often on light-textured Atlantic Coastal Plain soils derived from marine sediments and on upland soils derived from various grades of limestone and shale. Laboratory analyses have shown that Zn deficient soils have pH levels of 6.3 or greater and high concentrations of available P. It is not known if Zn deficiency is actually occurring more frequently or if scientists and farmers are more aware of the problem now than they have been in the past. Increased fertility levels may lead to greater occurrences of Zn deficiency.

As farmers attempt to produce greater amounts of food materials, the problem of Zn deficiency must be solved to facilitate maximum production. This investigation was initiated to assess the value of several Zn bearing materials and methods of their application for the correction of Zn deficiency. Several synthetic Zn chelates, $ZnSO_4$, and coal ash, a by-product of the coal burning electric power companies, were used in greenhouse and field studies in an attempt to increase corn yields on soils where Zn nutritional problems have occurred. Specific objectives of the investigation were as follows:

1. To determine the concentrations of Zn contained in coal ash and to evaluate its availability to plants in greenhouse studies; also, to determine what levels of coal ash, if any, might be toxic to plants.

2. To determine the effect of soluble silica in soil solution, as altered by coal ash application, on Zn availability.

3. To evaluate rate and placement of $ZnSO_4$, Zn-ethylenediamene tetraacetate (Zn-EDTA), and Zn-diethylenetriamine pentaacetate (Zn-DTPA) for correction of Zn deficiency of corn in the field.

4. To determine the residual effects of $ZnSO_4$ and Zn-EDTA applications on corn grain production.

REVIEW OF LITERATURE

Zinc deficiency of corn is commonly known as "white bud". The typical symptoms are interveinal chlorosis, necrosis of the lower leaves, and shortened internodes. The emerging leaves usually appear extremely chlorotic and are almost white in color (81). The author has observed that the lower leaves of many Zn deficient corn plants also develop a red color.

Factors Affecting Zinc Availability

Total Zn in soils has been found to vary from 10 to 300 ppm, but this rarely is an adequate index of Zn availability to plants (77). A high level of total Zn in the soil is not necessarily indicative of high Zn availability due to numerous factors which can alter the availability of Zn. These factors include soil reaction, organic matter, nutrient interactions, temperature, moisture, cultural practices, varieties, and soil mineralogy. Although each of the above factors will be discussed separately, it is recognized that interrelationships exist between these factors with respect to Zn availability.

Soil reaction: Investigation has shown that Zn availability varies inversely with soil pH (50, 63, 69, 74, 83, 89). Brown and Jurinak (18) found that applied $CaCO_3$ had a greater effect on Zn availability when added to fine textured than to coarse textured soils. Navrot and Ravikovitch (59), working with calcareous soils, reported that Zn availability was inversely related to the native $CaCO_3$ levels present. They further found that the decrease in Zn availability was greatest when the $CaCO_3$ was associated with the clay fraction of the soil, indicating some type of adsorption mechanism.

Research has indicated that decreases in available Zn at higher pH levels are not due to high soil Ca activities. Wear (89) found that Zn availability could be decreased when either $CaCO_3$ or Na_2CO_3 was used to increase soil pH. He also reported that high levels of Ca applied as $CaSO_4$ had no effect on Zn availability. Several investigators (14, 33, 76, 82) have shown that decreasing soil pH by the addition of N and P fertilizers can increase Zn availability to plants.

Organic matter: Many of the effects of soil organic matter on Zn availability are associated with the complexing of Zn by certain functional groups (35, 40, 42, 43, 44, 51, 61, 71). Himes and Barber (40) reported that both humic and fulvic acid fractions of soil organic matter are capable of adsorbing Zn. Schnitzer (71), working with fulvic acid, found that Zn is complexed by both phenolic hydroxyl and acidic carboxyl groups. Greering and Hodgson (35) have shown that water soluble organic materials such as acetic acid, amino acids, and some peptides complex Zn. The complexing of Zn by these naturally occurring compounds increases the effective activity of Zn in soil solution. Diffusion is considered to be the main process by which Zn is transported to the plant root (61). It has been reasoned that a greater amount of Zn in solution can lead to an increased amount of Zn diffusing to the plant roots (43, 44). In practice, this has been achieved to the greatest extent by the application of synthetic Zn chelates such as EDTA to soils (13, 86).

Nutrient interactions: There appear to be several nutrient interactions that affect the availability of Zn to plants. The most thoroughly studied relationship is that between Zn and P. Numerous investigations have reported a decrease in availability of both indigenous and applied Zn due to added P on a wide variety of crops (10, 20, 29, 52, 55, 56, 63, 69, 74). High amounts of available soil P appear to decrease Zn utilization by a P-Zn interaction within the plant (7, 9, 11, 21, 22, 64, 72, 73, 75, 83). Boawn and Legget (11) have postulated that this interaction occurs in the aerial parts of the plant, while others have suggested that it occurs in the root (7, 64). Viets, Boawn, and Crawford (83) have reported a high concentration of P in Zn deficient plants, while several other investigations have shown that Zn levels in plants decrease more in the tops than in the roots with high P fertilization (11, 22, 64, 72, 73, 75). These effects may be the result of inorganic P inhibiting the movement of Zn across cell membranes as reported by Bowen (15).

According to Stukenholtz et al. (75) and Ward et al. (88), high amounts of K present in the soil tend to alleviate the effects of excess P. Feuhring and Soofi (31) reported that high Mn increased the Zn requirement of corn plants. Nitrogen levels were found to increase the Zn requirement of subterranean clover by Ozanne (62). He suggested the formation of a protein-Zn complex in the plant roots. Other investigators, however, have found that the addition of N fertilizers will usually increase Zn utilization by plants due to a lowering of the soil pH (14, 30, 82).

Temperature and soil moisture: Zinc deficiency seems to be most prevalent during cool wet weather. The availability of soil Zn has been shown to decrease at lower temperatures, especially where high soil P levels were present (6, 29, 32, 55, 64, 72, 87). Ganiron et al. (32) found constant Zn levels in the root and shoot of corn plants under various temperature regimes, indicating that Zn uptake rather than translocation is influenced by lower temperatures. However, Sharma et al.(72), in working with rice, demonstrated that at depressed temperatures Zn tended to accumulate in the roots, leading to the conclusion that translocation might be affected. Evidence has also been presented showing that Zn uptake by corn is increased at lower moisture levels (88). It is difficult to separate the effects of low temperatures and high soil moisture levels, since both conditions usually prevail during spring seasons when Zn deficiency is most prevalent.

Cultural practices: Several cultural practices have led to increased Zn deficiency. Land leveling for gravity irrigation purposes has resulted in severe Zn deficiency in the western United States (12, 23). The process of leveling exposes the subsoil which may be more calcareous and usually contains less indigenous Zn than the surface soil. Hibbard (39) observed that Zn is accumulated in the soil surface where trees have been growing for long periods of time. It has been shown that Zn availability is lowered by rotational cropping with sugar beets, especially where the sugar beet tops were left on the soil (8, 14). The mechanism responsible for decreased Zn availability to crops following sugar beets is not known, but it has been reported that sugar beets remove as much as 1.5 times as much Zn as sorghum or potatoes (14).

Varieties: The susceptibility of different varieties of corn and navy beans to Zn deficiency has been shown to vary (1, 37). Susceptible varieties of corn appeared to have less extensive root systems than resistant varieties (37). The susceptible corn plants were also found to have decayed root systems. In navy beans, susceptible varieties contained higher levels of both P and Fe than resistant varieties (1). It is not known whether these differences found between susceptible and non-susceptible varieties were the cause or the result of Zn deficiency.

Soil mineralogy: Soil mineralogy appears to have an effect on Zn availability. Tiller and Hodgson (79) found that Zn was adsorbed to a greater extent by vermiculite than by montmorillonite or kaolinite. Elgabaly, Jenny, and Overstreet (28) reported that more Zn was taken up by barley roots from bentonite than from kaolinite. Elgabaly and Jenny (27) postulated that Zn added to a montmorillonite system may enter the octahedral layer and become non-exchangeable.

It has been indicated that the Zn in soil solution is in equilibrium with solid phase $ZnSiO_3$ and amorphous SiO_2 (54, 78). Tiller (78) found that adding silica to a montmorillonite system increased the adsorption of Zn and that adsorption also increased at higher Zn levels. In contrast, Peaslee and Frink (65) reported that Zn uptake by tomatoes was not decreased by adding H_2SiO_3 to a soil. The soils used in the study had pH levels in a range of 4.5 to 5.2, and Zn availability is normally quite high under these conditions.

Functions of Zinc in the Plant

Zinc appears to function in plants mainly as a constituent of metalloenzymes. Winder and O'Hara (93, 94) found that Zn deficiency decreased the activities of glycerol dehydrogenase and lactate dehydrogenase from *Mycobacterium smegmatis*. They also reported that Zn deficiency resulted in higher levels of phospholipids and inorganic polyphosphates, suggesting an inhibition of P utilization reactions. Grimm and Allen (36) found that Zn was required for the formation of cytochromes a, b, and c and cytochrome oxidase. Also, the RNA and protein contents of several plants appeared to be lower where Zn was deficient (49, 70, 85, 92). It is not known if Zn is required for synthesis of RNA or if Zn deficiency causes the accelerated degradation of RNA. Kessler and Monselise (49) found that ribonuclease activity was increased in Zn deficient citrus leaves.

Plant Response to Zinc Bearing Materials

Numerous Zn bearing materials have been used in attempts to correct Zn deficiency in corn. Some of the materials were inorganic such as $ZnSO_4$, $ZnCO_3$, ZnO, or Zn residue clinker, and organic such as the Zn-EDTA, Zn-DTPA, and Zn polyflavonid (4, 5, 13, 17, 19, 24, 29, 66, 74, 83, 84, 95). This literature review emphasizes coal ash and $ZnSO_4$ which were used in greenhouse studies and $ZnSO_4$, Zn-EDTA, and Zn-DTPA which were used in field studies.

Coal ash: Several studies (26, 27, 67) have shown that coal ash consists of mostly Si and Al oxides or hydroxides; varying contents of B, V, Mn, Fe, Si, Ca, Mg, Zn, and Mo; and low amounts of N. Rees and Sidrak (67) reported that a coal ash contained 750 ppm total Zn, whereas 2.5% acetic acid extracts of a coal ash and a soil contained 212.8 and 168.0 ppm Zn respectively. In contrast, Cope (26), using the same extractant, reported a lower concentration of Zn in a coal ash-soil mixture than in a soil alone. He also has shown a lower Zn content of barley when grown on coal ash-soil mixtures when compared to soil alone. The decreased Zn availability after the addition of coal ash may have been due to an increase in soil pH. Difficulties associated with the reclamation of coal ash disposal areas by revegetation have been attributed to high concentrations of soluble salts, Al and B, high pH, and P deficiency (26, 41, 45, 46).

Zinc sulfate and synthetic Zn chelates: Field investigations have been conducted to evaluate the effect of rate and placement of $ZnSO_4$ on corn yield. Rates of $ZnSO_4$ application ranging from 2.2 to 11.2 kg Zn/ha have corrected Zn deficiency of corn on numerous soils (4, 5, 29, 66, 83, 95). Higher corn yields were obtained where $ZnSO_4$ was broadcast and plowed down than where an equal rate of $ZnSO_4$ was either banded or sidedressed (66). Under conditions of adequate N, application of NH_4NO_3 with banded $ZnSO_4$ resulted in higher corn yield than an equal rate of $ZnSO_4$ banded alone (66). This increase in availability of indigenous and applied Zn resulted from a decrease in soil pH due to NH_4NO_3 application (33, 66, 82).

Greenhouse research has shown that Zn deficiency of corn plants can be corrected by a lower rate of Zn application as Zn-EDTA than as $ZnSO_4$ (13, 19, 24, 74). The greater Zn supplying power of Zn-EDTA has been attributed to its ability to support higher amounts of Zn in solution (13) which leads to a greater Zn mobility in the soil (19). In several field experiments, 0.67 to 1.0 kg Zn/ha of banded Zn-EDTA was as effective in increasing pea bean yield as 3.4 to 4.5 kg Zn/ha of banded $ZnSO_4$ (47, 84). In other field investigations where similar rates of the two sources were banded, only $ZnSO_4$ increased corn yield (29).

Although Zn chelates are able to support greater amounts of Zn in solution at higher pH levels than $ZnSO_4$, they usually have a maximum pH at which they are most effective in complexing Zn. Zinc-EDTA is most stable from pH 6.5 to 7.0. Below this range, Fe^{3+} and H^+ become competitive with the Zn, whereas above pH 7.0, Ca^{2+} becomes competitive (60). In contrast to this, Zn-DTPA has been found to be stable at pH 7.3. It has been shown that in soil systems with high pH levels, Zn-DTPA supports greater levels of Zn in solution than Zn-EDTA (60).

Associated with the problem of initially correcting Zn deficiency is that of preventing it from recurring in future years. The lack of published research has made it difficult to determine whether to add Zn in a single large application or small yearly applications. Equivalent corn yields have been obtained by applying either 6.3 kg Zn/ha as banded $ZnSO_4$ in two or three annual applications or 52.5 kg Zn/ha as broadcast $ZnSO_4$ in one application (17, 84). On one Michigan soil, the yields of pea beans were increased more by a single large application of $ZnSO_4$ than by small annual additions (17, 84).

COAL ASH AS A SOIL AMENDMENT FOR THE CORRECTION OF ZINC DEFICIENCY IN CORN: I. BOTTOM ASH AND HIGHLY ALKALINE FLY ASH

A major source of coal ash is derived from the burning of pulverized coal by electric power industry. Because of the increased emphasis on environmental pollution control, this industry is faced with the problem of coal ash disposal. Fly ash is a type of coal ash that is collected by electrostatic and mechanical precipitation in contrast to the material retained in the lower part of the furnace known as bottom ash. The uses of coal ash have been primarily restricted to road bed stabilization and substitution for cement. However, in 1968 only 17.5% of almost 30 million tons of fly ash, bottom ash, and boiler slag produced was used commercially (3). The remainder was disposed of at a considerable expense to the coal burning electric power industry.

Due to the high amounts of Zn contained in coal ash, it might be feasible to use coal ash as a soil amendment for the correction of Zn deficiency. The objectives of this study were to determine the total Zn contained in coal ash and to evaluate its availability to plants in greenhouse experiments. A second aspect of this research was to determine what levels of coal ash, if any, might be toxic to plants.

Experimental Methods

Seventeen samples of fly ash and one sample of bottom ash were collected from various electric power companies throughout the United States. The coal ashes were prepared for total Zn analyses by fusing the samples with Na_2CO_3 and dissolving the fused mass in 0.5N HCl as described by Kanehiro and Sherman (48). Acid extractable Zn was obtained by shaking 7.5g ash with 75 ml of 1.0N HCl for 2 hours. The samples were centrifuged and a 50 ml aliquot of the clear extract was dried on a hot plate. The dried residue was dissolved in 50 ml of 0.5N HCl. Zinc in solution from total and extractable Zn analyses was determined by atomic adsorption spectrophotometry.

A Frederick silt loam, Typic Paleudult (clayey, kaolinitic, mesic), known to be deficient in Zn for the growth of corn under greenhouse and field conditions, was used for this experiment. The soil had an organic matter content of 1.5%, pH of 6.5, and a 0.1N HCl extractable Zn content of 1.0 ppm. The soil was air dried and passed through a stainless steel screen having 1-cm openings in preparation for a greenhouse investigation.

Amendments to 2100g soil consisted of 0, 6.3, and 12.6 mg Zn as $ZnSO_4$ in factorial combination with 0, 4.2, and 8.4 g $CaCO_3$. Other treatments included were coal ash from three sources applied in amounts equivalent to 6.3 mg Zn as 1.0N HCl extracts or 6.3, 12.6, 25.2, 50.4, and 100.8 mg Zn as unaltered coal ash. The samples used were fly ash from Crawford Edison Plant, Chicago, Ill., and the Lewis and Clark Plant, Sidney, Mont.; and bottom ash from the Municipal Plant, Columbus, Ohio. All of the above treatments were arranged in a randomized complete block with three replications. The rates of application for the three ashes were based on their respective total and 1.0N HCl extractable Zn contents (Table I). The amendments required for the various treatments and the following

Table I. Total Zn and 1.0N HCl extractable Zn contents of several coal ash samples.

Source of Coal Ash		Total	1.0N HCl Ext.
Plant	Location	Zn	Zn
		ppm	
Big Sandy	Louisa, Ky.	51.0	7.0
Clinch River	Cleveland, Va.	54.7	11.4
Glen Lyn	Glen Lyn, Va.	36.4	3.9
Kanawha River	Glasgow, W. Va.	45.9	3.1
Muskingum River	Beverly, Ohio	37.2	33.9
Muskingum River	Beverly, Ohio	114.5	74.9
Philip Sporn	New Haven, W. Va.	87.3	8.2
Mt. Storm	Mt. Storm, W. Va.	378.2	9.4
Albright	Albright, W. Va.	29.7	1.5
Rivesville	Fairmont, W. Va.	12.9	3.5
Fort Martin	Maidsville, W. Va.	88.2	28.1
Crawford Edison	Chicago, Ill.	363.1	93.0
John Sevier	Rogersville, Tenn.	73.8	2.2
Ernest C. Gaston	Wilsonville, Ala.	186.4	8.5
Ernest C. Gaston	Wilsonville, Ala.	71.2	8.5
Municipal*	Columbus, Ohio	1,582.0	1,420.0
Hoot Lake	Fergus Falls, Minn.	85.7	3.0
Lewis and Clark	Sidney, Mont.	131.9	4.2

*Bottom ash.

nutrients were mixed in a twin shell blender with 2100g portions of the Frederick soil: 441 mg N, 225 mg P, 105 mg Mg, 147 mg K, 2.1 mg Cu, 5.3 mg Mn, 3.2 mg B, and 0.2 mg Mo (Appendix, Table I). The amended soils were placed in polyethylene lined pots, watered to approximate field moisture equivalent (2) with deionized H_2O, and allowed to incubate for two weeks while the polyethylene bags were closed. Following the equilibration period, two successive crops of 4 corn plants per pot were grown. The variety of corn was DeKalb XL-385. During the first growth period of 26 days, two applications each of 52.5 mg N were added to the soil surface 14 and 21 days after emergence. After the addition of 357 mg P and 162 mg N, a second crop of corn was grown for 34 days. The pots were watered daily to approximate field moisture equivalent (2) during each growth period.

Soil pH was determined on a Beckman Model G pH meter, using a 1:1 soil-water ratio and a 1-hour period of equilibration. Specific conductivity was determined using a 2:1 soil-water mixture according to the method described by Bower (16). Plant tissue was prepared for Zn analysis by drying at 70C for 48 hours and grinding in a stainless steel Wiley mill. A 1-g subsample of ground tissue was digested in a mixture of 10 ml of concentrated HNO_3 and 2 ml of concentrated $HClO_4$. The digested sample was diluted to 50 ml with 0.5<u>N</u> HCl, and the Zn in solution was determined by atomic adsorption spectrophotometry.

Results and Discussion

Zinc content of coal ash: The concentrations of total Zn and acid extractable Zn varied considerably (Table I). The sample of bottom ash from the Municipal plant was higher in both total and acid extractable Zn than the fly ash samples which varied from 12.9 to 378.2 ppm in total Zn and from 1.5 to 93.0 ppm in acid extractable Zn. Three of these samples, one bottom ash and two fly ashes that represented a cross section of the above samples, were selected for greenhouse and laboratory experiments. Those samples containing less than 100 ppm total Zn were excluded, since they would have to be added in extremely large amounts and might cause problems due to high soluble salt levels.

Soil pH and specific conductivity: Soil pH determined after two corn crops had been grown was increased by the addition of $CaCO_3$, all rates of Lewis and Clark fly ash, and high rates of Crawford Edison fly ash (Table II). The pH increases associated with the addition of these ash samples were due to their high neutralizing power. Doran[1] reported that for each gram of Crawford Edison, Municipal, and Lewis and Clark ash added, the respective amounts of acid required to obtain pH 6.5 were 1.33, 0.03, and 3.38 meq H_3O^+. Also responsible for the increases in soil pH were the large quantities of Crawford Edison and Lewis and Clark ashes added due to their low total Zn contents (Table I).

Application of both fly ash samples increased the soluble salt content of the soil to a high level (Table II). The highest specific conductivity was observed where the acid extract of Lewis and Clark fly ash was added to the soil. This can be attributed to the high

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[1] Doran, J. W. 1969. The availability of soil molybdenum as affected by fly ash applications and certain soil properties. M.S. Thesis, Virginia Polytechnic Institute, Blacksburg.

Table II. The effect of $ZnSO_4$, $CaCO_3$, and coal ash on the pH and specific conductivity of a Frederick silt loam.

Treatment				pH	Conductivity
Zn Source	Coal Ash	$CaCO_3$	Zn Rate		
	g/2.1 kg soil		mg/2.1 kg soil		mmhos/cm
Check	---	0.0	0.0	6.8ij*	0.413f
$ZnSO_4$	---	0.0	6.3	7.0hi	0.310f
$ZnSO_4$	---	0.0	12.6	6.8ij	0.307f
		4.2	0.0	7.0hi	0.537def
$ZnSO_4$	---	4.2	6.3	7.1gh	0.355f
$ZnSO_4$	---	4.2	12.6	7.1gh	0.372f
		8.4	0.0	7.1gh	0.484ef
$ZnSO_4$	---	8.4	6.3	7.3g	0.493ef
$ZnSO_4$	---	8.4	12.6	7.4f	0.336f
Crawford Edison[‡]	---	---	6.3	6.5k	0.782bcdef
Crawford Edison	17.3	---	6.3	6.8ij	0.538def
Crawford Edison	34.6	---	12.6	6.7j	0.847bcdef
Crawford Edison	69.2	---	25.2	7.1gh	1.373bcde
Crawford Edison	138.4	---	50.4	7.5f	1.583bc
Crawford Edison	276.8	---	100.8	7.9d	1.457bcd
Municipal[‡]	---	---	6.3	6.7j	0.334f
Municipal	4.0	---	6.3	6.9ij	0.177f
Municipal	8.0	---	12.6	6.7j	0.266f
Municipal	16.0	---	25.2	6.8ij	0.227f
Municipal	32.0	---	50.4	6.7j	0.321f
Municipal	64.0	---	100.8	6.7j	0.285f
Lewis and Clark[‡]	---	---	6.3	7.2gh	13.987a
Lewis and Clark	47.8	---	6.3	7.7e	0.795bcdef
Lewis and Clark	95.6	---	12.6	8.0d	0.759cdef
Lewis and Clark	191.2	---	25.2	8.6c	0.660cdef
Lewis and Clark	382.4	---	50.4	9.4b	0.863bcdef
Lewis and Clark	764.8	---	100.8	10.4a	1.692b

*Those means in each column not accompanied by the same letter are significantly different at the 0.05 level.

[‡] 1.0N HCl extract of the coal ash from the Crawford Edison, Municipal, and Lewis and Clark plants.

amounts of HCl extract required to obtain the desired Zn level. Although the acid extracts of all the samples were added in the dry form, the extract from the Lewis and Clark fly ash contained a high level of chloride. The Municipal plant bottom ash, which had the highest content of acid extractable Zn, also had the least effect on the soluble salt level. The effects of fly ash additions on the conductivity of soil observed here are similar to those noted by Holliday et al (45).

Corn yield: Yield of corn was increased by the addition of $ZnSO_4$ or Municipal plant bottom ash (Table III). The highest yields were obtained when Zn was added in the form of $ZnSO_4$ without $CaCO_3$ and of Municipal bottom ash at levels exceeding 12.6 mg Zn. Lime significantly decreased the overall yield with the lowest yields being observed where 8.4g $CaCO_3$ were added. Within lime treatments, corn yields were increased by the application of either 6.3 or 12.6 mg Zn. Application of both fly ash samples lowered the yield of corn in all cases (Table III). Yields were inversely related to the rates of the two fly ash samples. These yield decreases were apparently caused by decreased Zn availability at high pH levels and by high soluble salt levels obtained where either the Crawford Edison or Lewis and Clark fly ashes were added to the soil. Corn seeds did not germinate where the acid extract of Lewis and Clark fly ash was added.

Correlation and regression relationships between corn yield and the function $(\text{soil pH} - 6.3)^{-1}$ using data from the $ZnSO_4$, $CaCO_3$, or the unaltered ash treatments indicated that 59.9% ($r = 0.774^{**}$) of the variation in corn yield could be accounted for by variation in soil

Table III. The effect of $ZnSO_4$, $CaCO_3$, and coal ash on the total corn yield and average Zn uptake by corn grown on a Frederick silt loam.

Treatment				Total[†] Yield	Total[†] Zn Uptake
Zn Source	Coal Ash	$CaCO_3$	Zn Rate		
	g/2.1 kg soil		mg/2.1 kg soil	g/pot	µg/pot
Check	---	0.0	0.0	16.0cd[*]	155.9ij
$ZnSO_4$	---	0.0	6.3	18.0ab	343.6de
$ZnSO_4$	---	0.0	12.6	19.0a	377.5d
		4.2	0.0	10.3g	88.5lmn
$ZnSO_4$	---	4.2	6.3	12.9f	231.3gh
$ZnSO_4$	---	4.2	12.6	15.0de	310.4ef
		8.4	0.0	8.3h	84.1lmno
$ZnSO_4$	---	8.4	6.3	13.4p	187.2hi
$ZnSO_4$	---	8.4	12.6	14.1ef	262.7fg
Crawford Edison[‡]	---	---	6.3	13.3f	140.2ijk
Crawford Edison	17.3	---	6.3	12.5f	125.3jkl
Crawford Edison	34.6	---	12.6	9.7g	108.9jklm
Crawford Edison	69.2	---	25.2	6.4i	99.5klm
Crawford Edison	138.4	---	50.4	2.6k	44.1nopq
Crawford Edison	276.8	---	100.8	1.0lm	20.0pq
Municipal[‡]	---	---	6.3	15.9cd	154.1ij
Municipal	4.0	---	6.3	19.2a	285.1f
Municipal	8.0	---	12.6	17.1bc	357.9de
Municipal	16.0	---	25.2	19.2a	524.3c
Municipal	32.0	---	50.4	17.7ab	682.3b
Municipal	64.0	---	100.8	18.1ab	985.0a
Lewis and Clark[‡]	---	---	6.3	0.0m	0.0q
Lewis and Clark	47.8	---	6.3	6.6i	54.7mnop
Lewis and Clark	95.6	---	12.6	4.6j	39.1nopq
Lewis and Clark	191.2	---	25.2	3.1k	37.7nopq
Lewis and Clark	382.4	---	50.4	2.2kl	23.9pq
Lewis and Clark	764.8	---	100.8	1.6kl	15.7pq

[*] Those means in each column not accompanied by the same letter are significantly different at the 0.05 level.

[†] Total of two harvests. Yields for individual harvests are given in the Appendix.

[‡] 1.0N HCl extract of the coal ash from the Crawford Edison, Municipal, and Lewis and Clark plants.

pH (Figure 1). Similarly, correlation of yield with the function (specific conductivity 0.3)$^{-1}$ indicated that 85.4% (r = 0.923**) of the variation in yield could be explained by the variation in specific conductivity (Figure 2). Partial correlation analyses of corn yield with the above-mentioned functions of pH and specific conductivity gave coefficients of 0.688** and 0.899** respectively, indicating that both factors had a significant effect on corn yield (Figure 3).

Total Zn uptake: Total Zn uptake by corn was increased over the check treatment by the addition of $ZnSO_4$, except where the $CaCO_3$ rate was 8.4g/2100g soil and the Zn rate was 6.3 mg/2100g soil (Table III). Both the 4.2 and 8.4 g/2100g rates of $CaCO_3$ decreased Zn uptake similarly. Amending the soil with both fly ash samples resulted in decreased total Zn uptake, except where the acid extract of Crawford Edison fly ash was added. Zinc uptake was inversely related to the level of fly ash application. The causes of decreased Zn uptake appear similar to those noted concerning yield; i.e., high pH and soluble salts. Zinc uptake varied directly with rates of Municipal bottom ash application, showing that the availability of Zn in this ash is high.

The use of ash as a soil amendment for the correction of Zn deficiency may be feasible, but there appear to be some limitations which must first be overcome. The total elemental content of an ash as well as the Zn content should be known to determine if there are any constituents present which might adversely affect Zn availability or plant growth. Indiscriminate use of coal ash as a Zn source could lead to highly undesirable chemical conditions in the soil which would be difficult to correct. Particular attention should be paid to the

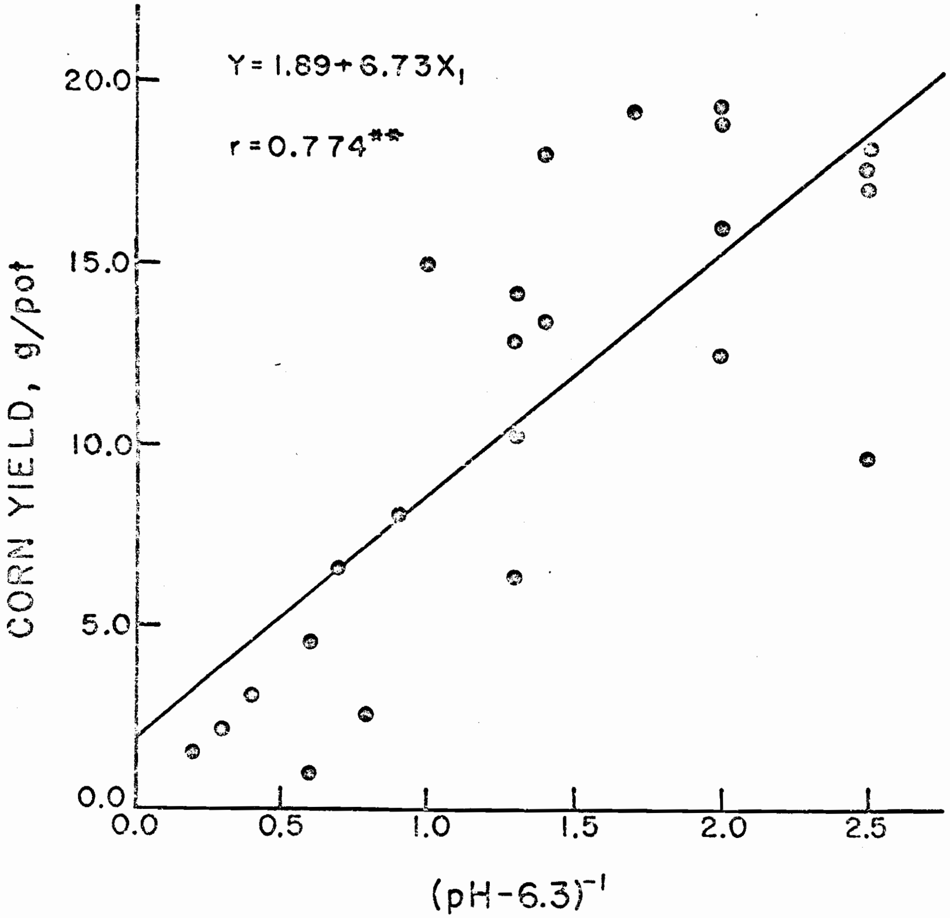

Fig. 1. The relationship between corn yield (Y) and pH $[X_1 = (pH - 6.3)^{-1}]$ of a Frederick silt loam amended with various rates of $ZnSO_4$, $CaCO_3$, and coal ash.

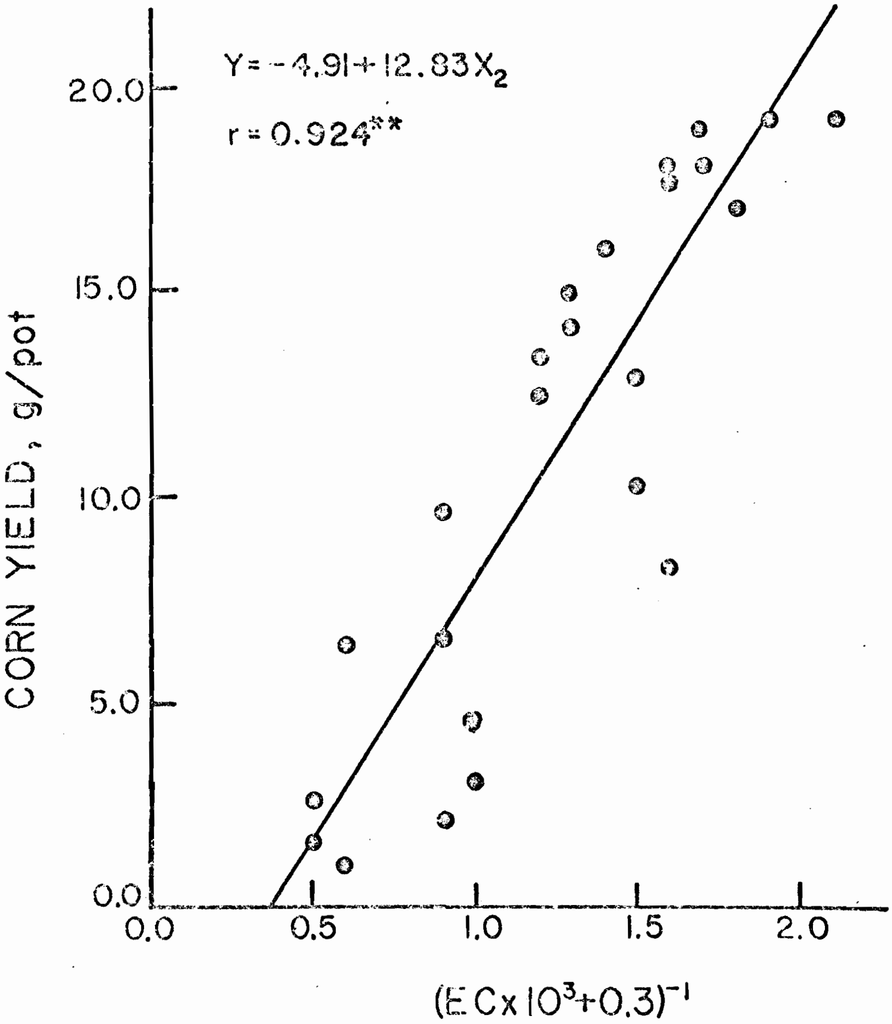

Fig. 2. The relationship between corn yield (Y) and specific conductivity [X_2 = (E.C. x 10^3 + $0.3)^{-1}$] of a Frederick silt loam amended with various rates of $ZnSO_4$, $CaCO_3$, and coal ash.

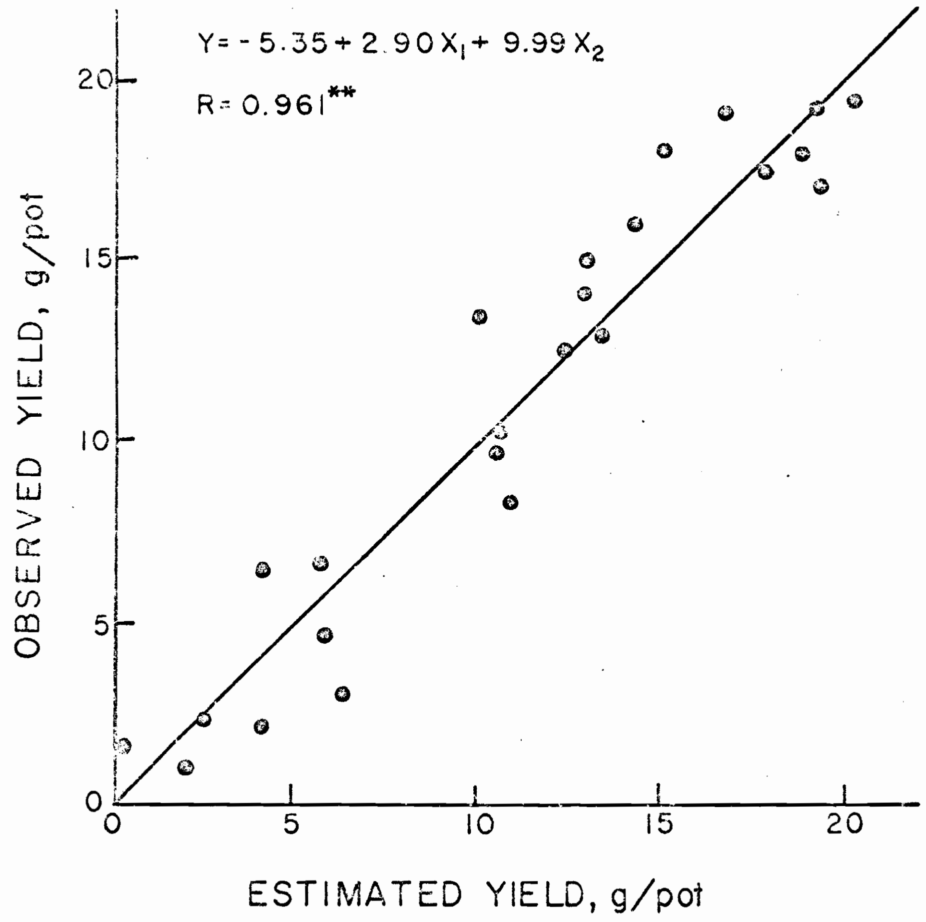

Fig. 3. The relationship between observed corn yield (Y) and corn yield predicted from pH [$X_1 = (pH - 6.3)^{-1}$] and specific conductivity [$X_2 = (E.C. \times 10^3 + 0.3)$] of a Frederick silt loam amended with various rates of $ZnSO_4$, $CaCO_3$, and coal ash.

acid or base content of the ash before its use as a Zn source for plants. Among the three ash samples investigated, only the Municipal plant bottom ash was a suitable Zn fertilizer, since it is high in Zn and has only a slightly alkaline reaction.

COAL ASH AS A SOIL AMENDMENT FOR THE CORRECTION OF ZINC DEFICIENCY IN CORN: II. BOTTOM ASH AND NEAR NEUTRAL FLY ASH

It appears that several factors other than the total Zn content of coal ash have an effect on the availability of Zn contained in this material. As shown in the preceeding investigation, increases in both soil pH and specific conductivity caused by coal ash application resulted in decreased corn yield. In this study, low rates of coal ashes that were acidic or slightly alkaline in reaction were used in an attempt to prevent increases in soil pH and specific conductivity. One objective of this investigation was to evaluate the availability of Zn contained in these less-alkaline coal ashes to plants in the greenhouse. Coal ash contains a high amount of SiO_2 (54), and amorphous SiO_2 has been found to affect the solubility of soil Zn (54, 78). A second objective of this study was to determine the effect of soluble SiO_2 in soil solution, as altered by coal ash application, on Zn availability.

Experimental Methods

Soil from the 0- to 15-cm layer of a Frederick silt loam described previously (Page 12) and a Tatum silt loam (Typic Hapludult; clayey, mixed, thermic), known to be deficient in Zn for the growth of corn under greenhouse conditions, was used for this experiment. The soils were air dried and passed through a stainless steel screen having 1-cm openings in preparation for the greenhouse experiment. The following nutrients were mixed with the equivalent of 2100g of oven dry soil: 440 mg N, 450 mg P, 105 mg Mg, 147 mg K, 2.1 mg Cu, 5.3 mg Mn, 3.2 mg B, and 0.25 mg Mo (Appendix, Table I). Treatments in the experiment consisted of a check, one rate of $ZnSO_4$, and two rates of five different coal ash samples. The $ZnSO_4$ was applied at a rate of 0.0 and 12.6 mg Zn, and the coal ashes were applied at rates equivalent to 6.3 and 12.6 mg Zn based on their total Zn contents (Table I). The fly ash samples were obtained from the following plants: Muskingum River, Beverly, Ohio; Philip Sporn, New Haven, W. Va.; Mt. Storm, Mt. Storm, W. Va.; and John Sevier, Rogersville, Tenn.; and the bottom ash sample from the Municipal plant, Columbus, Ohio. The samples were either acid or slightly alkaline in reaction[1]. All fertilizer and coal ashes were mixed with the soils in a twin shell bulk blender.

Eight corn seeds (Var. DeKalb XL-385) were planted in each pot, and 1 week after germination the corn was thinned to four plants per pot. The growth periods on the Frederick and Tatum soils were 31 and 36 days, respectively. The pots were watered to approximate field capacity (2) daily with deionized water, and two supplemental N applications of 52.5 mg each were added to all pots 14 and 21 days after emergence. The aerial portions of the plants were harvested, and their Zn content determined (see Page 14).

Samples of the Tatum soil taken before corn was planted were used for soluble SiO_2 and available Zn determinations, whereas pH was determined on both soils after corn had been harvested. Soluble SiO_2 was extracted from the Tatum soil that was equilibrated at approximate field moisture capacity (2) for 7 days. A 1:1 soil-to-deionized water ratio was then shaken for 24 hours, centrifuged, and the supernatant liquid filtered. Monosilicic acid in solution was determined by the molybdenum blue method as described by Govett (34). Extractable Zn in the Tatum soil was obtained by shaking 5g of the soil with 20 ml of a mixture of 0.05N HCl and 0.025N H_2SO_4 for 5 minutes (68). Zinc in solution was determined by atomic adsorption spectrophotometry. Soil pH was determined as described previously (Page 14).

Results and Discussion

Soil pH: Only the Muskingum River fly ash influenced pH of either soil appreciably (Figure 4). The pH of the Tatum soil was decreased from 6.1 to 5.8 or 5.6, depending on the amount of this fly ash added, whereas the pH of the Frederick soil was decreased from 6.9 to 6.5. The lack of change in pH from the addition of the other samples corroborates their low acid or base contents as reported by Doran[1].

Corn yield and Zn uptake: Corn yields on both the Tatum and Frederick soils were increased by the addition of $ZnSO_4$, Muskingum River fly ash, or Municipal bottom ash (Figure 5). Also a yield increase was obtained on the Frederick soil due to the application of 12.6 mg Zn as Philip Sporn fly ash. Apparently, the Zn contained in the Philip Sporn, Mt. Storm, or John Sevier fly ash was unavailable to plants in most cases.

Zinc uptake by corn was well correlated with yield response data (Figure 6) and was increased on both soils when $ZnSO_4$, Muskingum River fly ash, or the 12.6 mg Zn rate of Municipal bottom ash was applied. All other fly ash treatments did not alter Zn uptake significantly. The application of 12.6 mg Zn as Muskingum River fly ash increased Zn

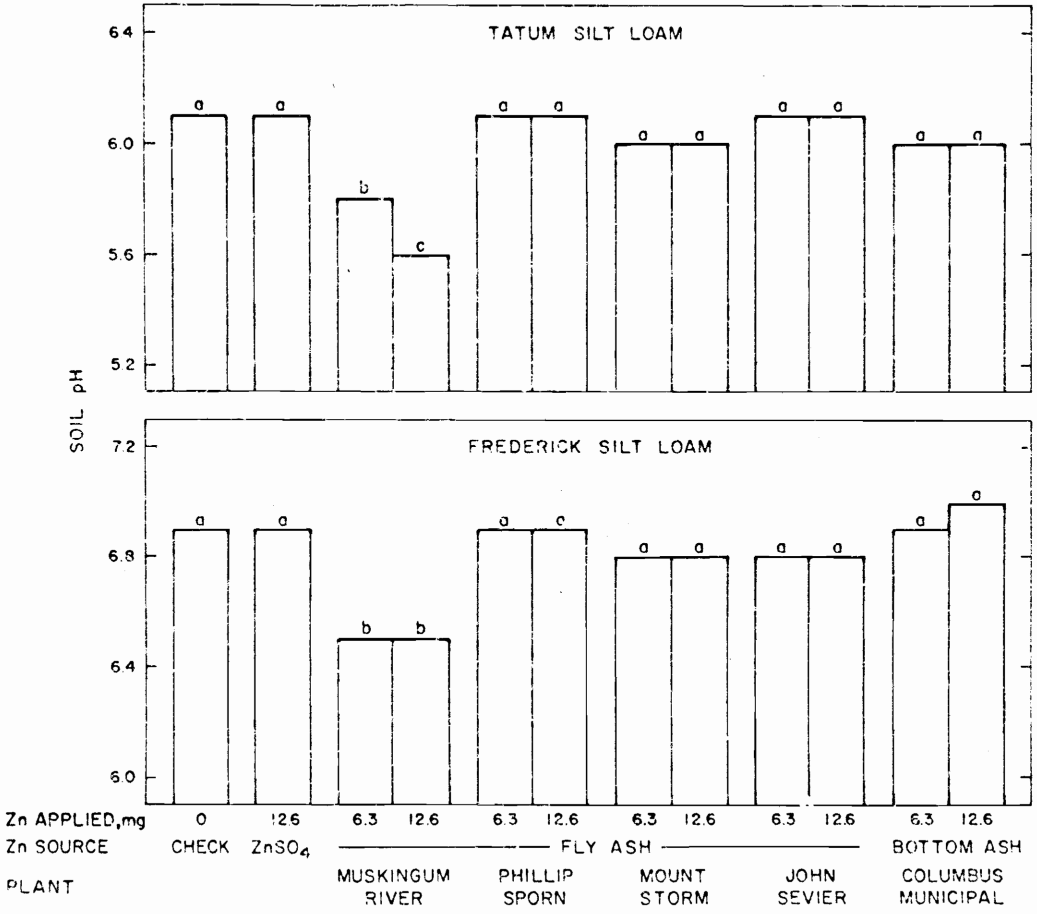

Fig. 4. The effect of $ZnSO_4$ and coal ash application on the pH of a Tatum silt loam and a Frederick silt loam.

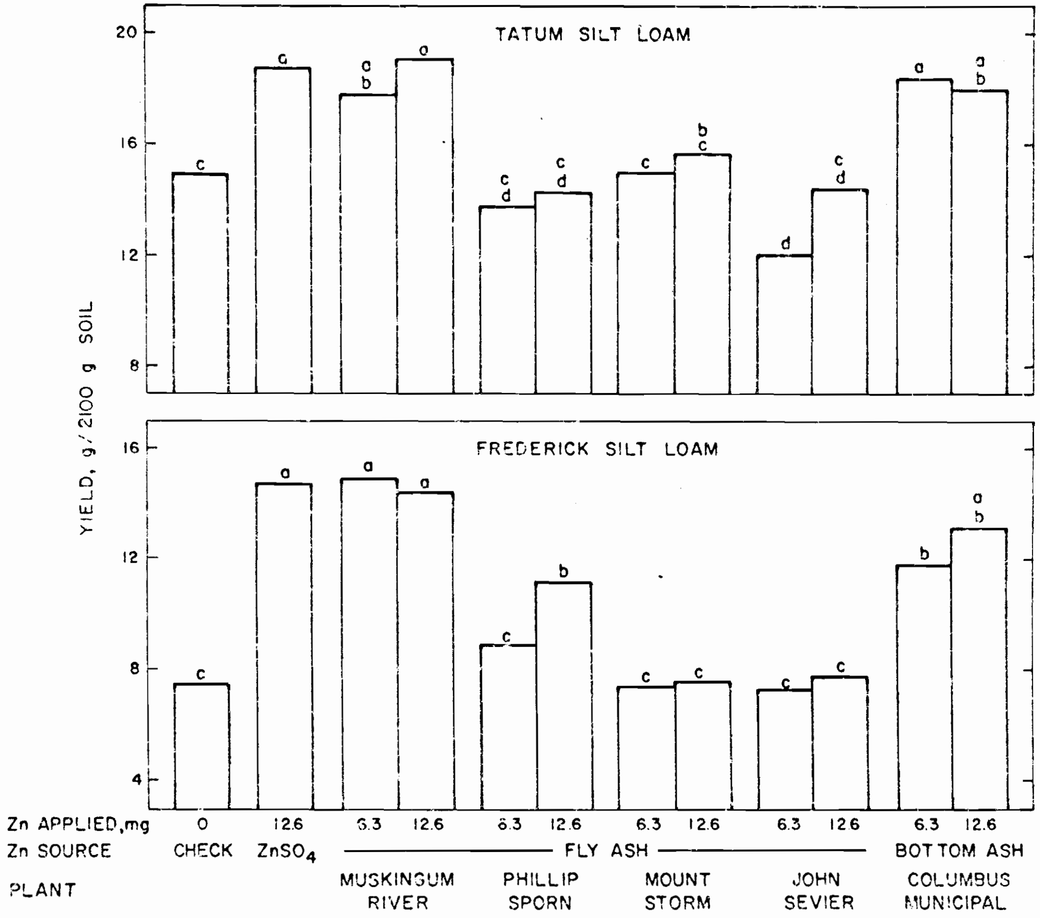

Fig. 5. Corn yields on a Tatum silt loam and a Frederick silt loam as affected by $ZnSO_4$ and coal ash application.

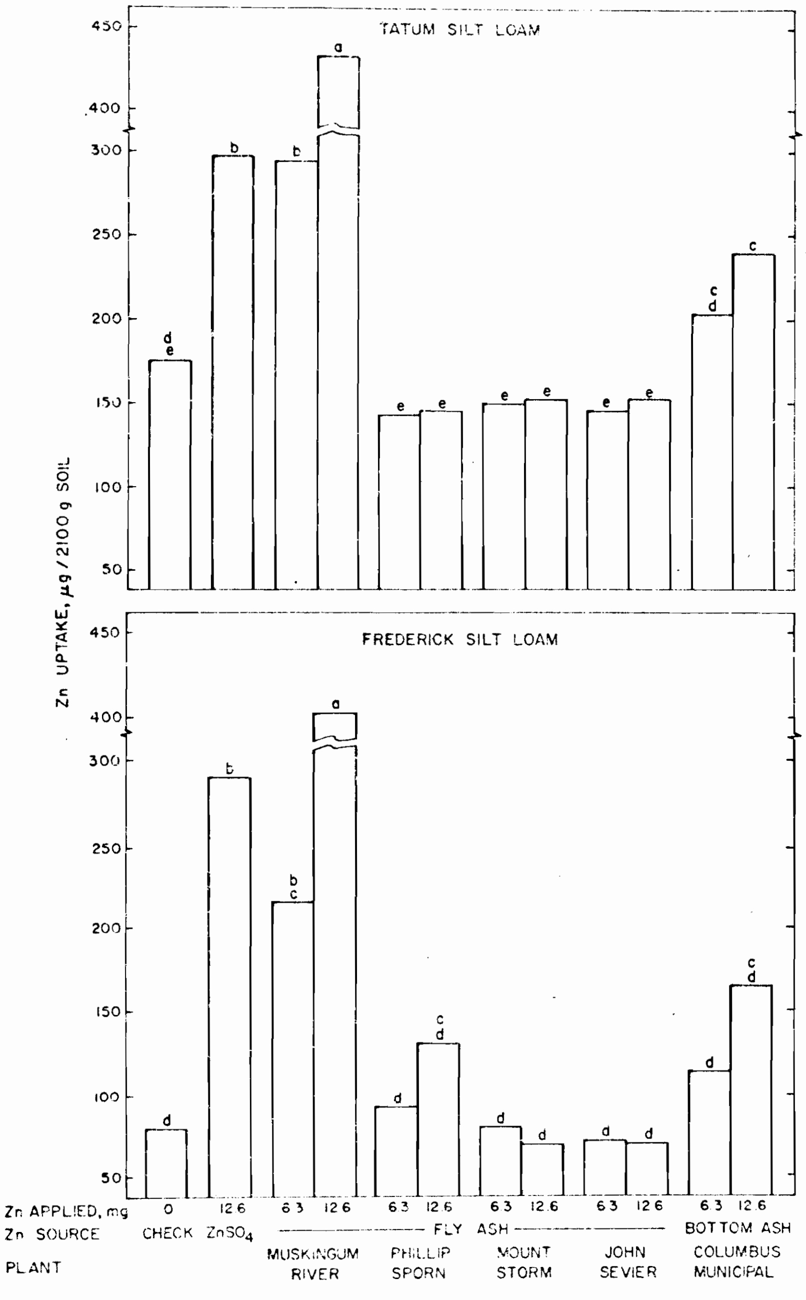

Fig. 6. Total Zn uptake by corn grown on a Tatum silt loam and a Frederick silt loam as affected by $ZnSO_4$ and coal ash application.

uptake markedly. Hence, the Zn present in this fly ash appeared to be more available than an equal amount of Zn applied as $ZnSO_4$. However, the increased Zn availability noted in this case may have been due to a combination of soluble Zn in the fly ash and a larger amount of available indigenous soil Zn caused by a decrease in soil pH. In soils where lime must be used to maintain a soil pH favorable for crop growth, the use of Muskingum River fly ash may not be feasible. However, where Zn deficiencies occur on soils with naturally high pH levels, this material may be a suitable Zn fertilizer. Municipal bottom ash probably can be used to correct Zn deficiency under most soil conditions, especially where changes in soil pH are undesirable.

Silica-Zn relationship: The relationship between soluble SiO_2 and Zn availability was studied on the Tatum soil, exclusive of Muskingum River fly ash treated samples to preclude pH effects. These coal ash-soil mixtures varied from 12-26 ppm soluble SiO_2 and from 1.2 to 3.0 ppm dilute acid extractable Zn. The coefficient of simple correlation (r = 0.706**) shows that 49.8% of the variation in yield was accounted for by variations in dilute acid extractable Zn (Figure 7). Similarly, correlation of yield with soluble SiO_2 indicates that 61.4% (r = 0.784**) of the yield variations could be explained by variation in soluble SiO_2 levels (Figure 8). It appears that neither of the above relationships gave an adequate index of yield when used alone.

Partial correlation analyses of corn yield with both extractable Zn and soluble SiO_2 gave coefficients of 0.833** and -0.875** respectively, indicating that both factors had a significant effect on corn yield (Figure 9). This relationship suggests that although the

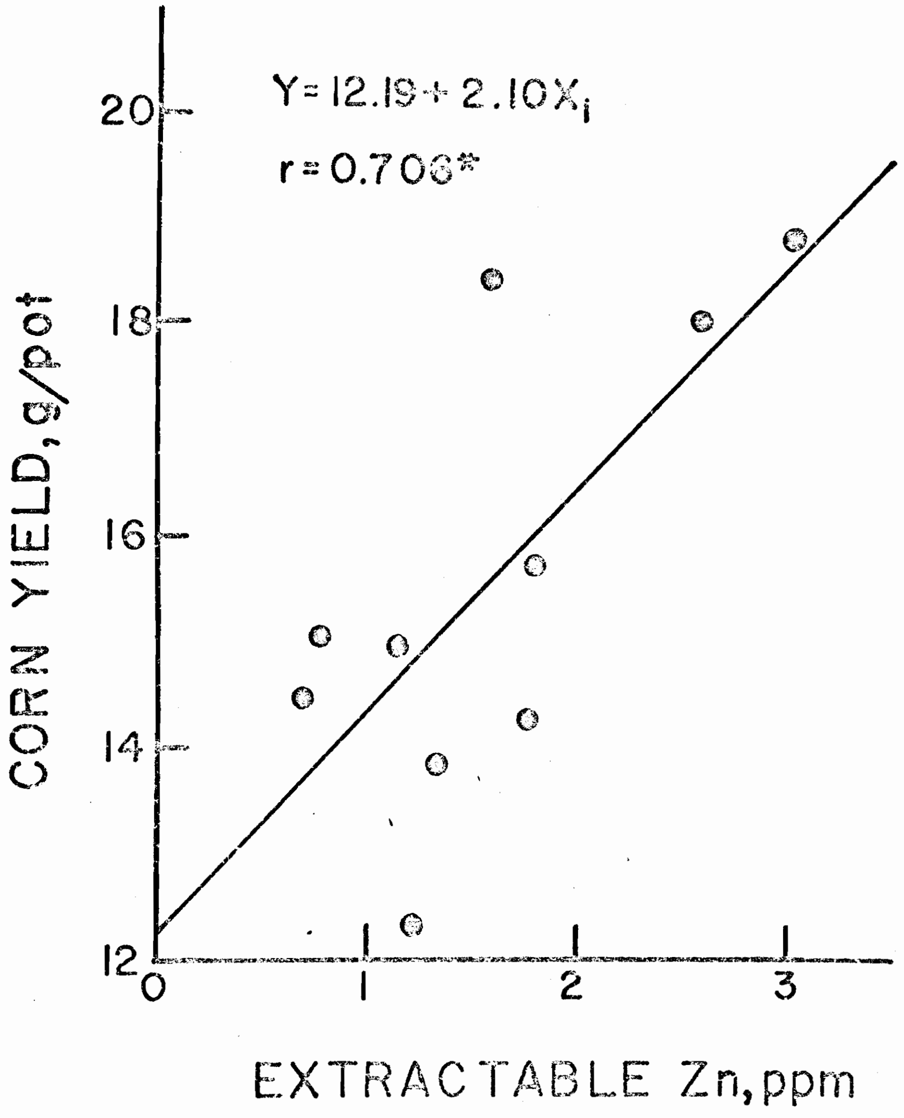

Fig. 7. The relationship between corn yield (Y) and dilute acid extractable Zn (X_1) of a Tatum silt loam amended with $ZnSO_4$ and coal ash.

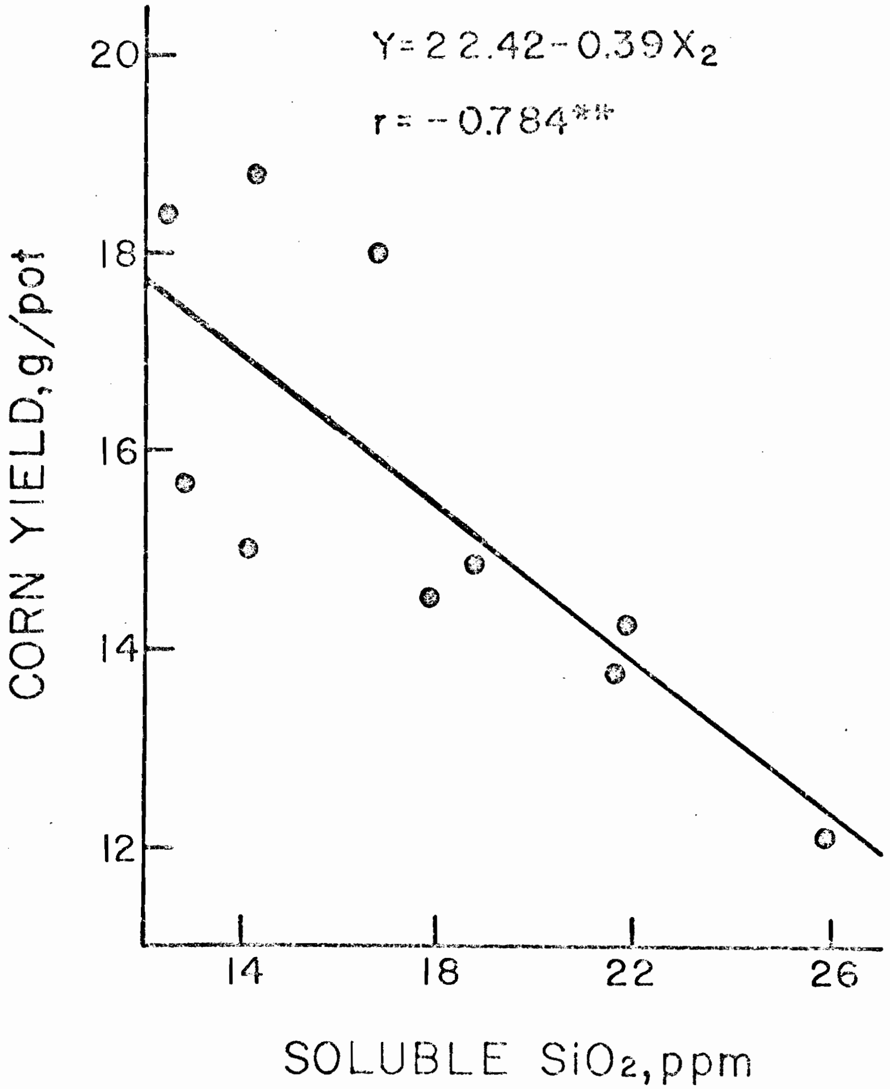

Fig. 8. The relationship between corn yield (Y) and soluble SiO_2 (X_2) of a Tatum silt loam amended with $ZnSO_4$ and coal ash.

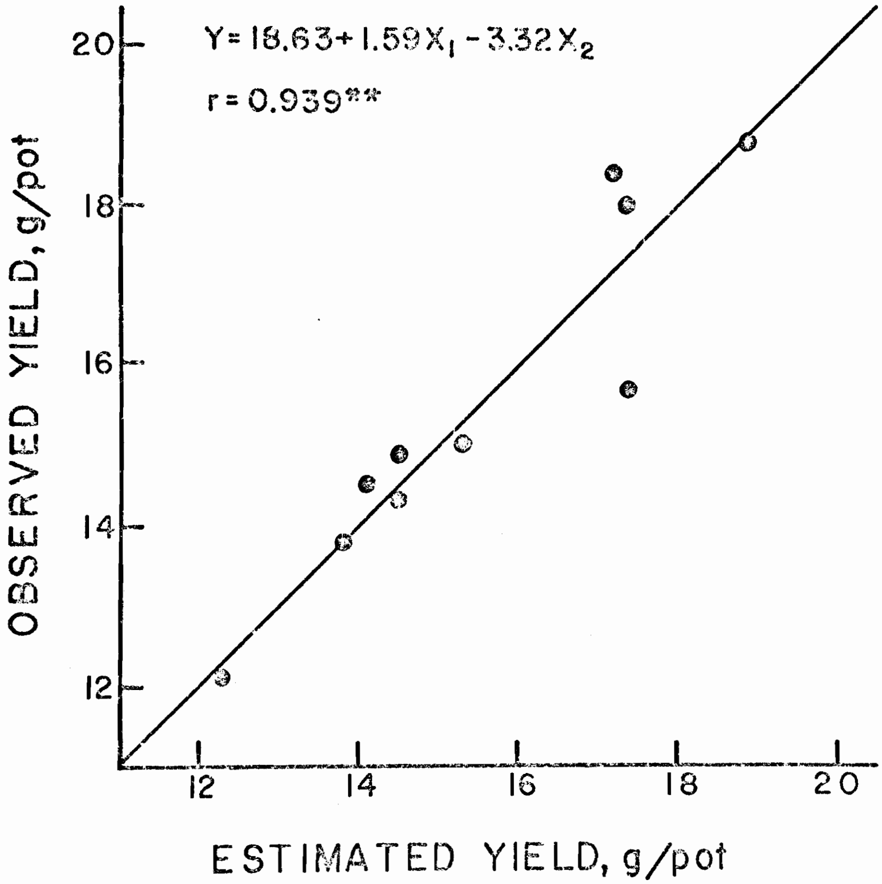

Fig. 9. The relationship between observed corn yield (Y) and corn yield predicted from dilute acid extractable Zn (X_1) and soluble SiO_2 (X_2) of a Tatum silt loam amended with $ZnSO_4$ and coal ash.

Philip Sporn, Mt. Storm, and John Sevier fly ashes contributed Zn to the soil, it may have been rendered unavailable due to the high soluble SiO_2 levels. On the basis of the high multiple correlation coefficient seen in Figure 9 (r = 0.939**), it seems likely that the use of soluble SiO_2 as well as extractable Zn might provide an adequate index of Zn availability from coal ash.

RESPONSE OF CORN TO Zn-EDTA AND $ZnSO_4$ in FIELD INVESTIGATIONS

In the two previous studies and as reported by other investigators, $ZnSO_4$ appears to be a suitable source of Zn for plants (4, 5, 29, 66, 83, 95). Greenhouse research has shown that Zn deficiency of corn plants can be corrected by a lower rate of Zn application as Zn-EDTA than as $ZnSO_4$ (13, 19, 24, 74). Very little research has been conducted in the Southeastern states using these two Zn sources under field conditions. It was necessary, therefore, to determine the rates of $ZnSO_4$ and Zn-EDTA that would be most effective in correcting Zn deficiency of corn grown in the field. The two soils used in the investigation were Litz silt loam and Norfolk loamy fine sand. The effect of placement of Zn-EDTA on grain yield and Zn content of corn plants grown on a Norfolk loamy fine sand was also evaluated.

Experimental Methods

Field experiments were conducted in 1968 on a Norfolk loamy fine sand located in the Coastal Plain and on a Litz silt loam located in the Allegheny Mountains. The Norfolk loamy fine sand is a Typic Paleudult (fine loamy, siliceous, thermic) derived from unconsolidated marine sediments of intermediate texture. The Litz silt loam is a Ruptic Ultic Dystrochrept (loamy skeletal, mixed, mesic) derived from non-calcareous shale with widely spaced thin strata of limestone or calcareous shales. Certain chemical properties of samples from the 0- to 15-cm layer of the experimental areas are shown in Table IV. Soil pH was determined as mentioned previously (Page 14). Available P was determined by the Mehlich procedure as outlined by Rich (68). The

Table IV. Properties of the 0- to 15-cm layer of Litz silt loam and Norfolk loamy fine sand.

Property	Litz sil	Norfolk lfs
Soil pH	7.2	6.3
Available P, ppm	98.2	96.0
0.1N HCl extractable Zn, ppm	1.9	1.2
Total Zn, ppm	77.0	13.0

extraction procedure devised by Wear and Sommer was used for 0.1N HCl extractable Zn analyses (91), and the Na_2CO_3 fusion procedure outlined by Kanehiro and Sherman (48) was followed for total Zn analyses. Zinc in solution from both analyses was determined by atomic adsorption spectrophotometry.

Two methods of application of $ZnSO_4$ and Zn-EDTA were used in the field experiments. Solutions of the Zn sources were either sprayed on the soil surface and disked into soil to a depth of approximately 8 cm or sprayed in the furrow directly in front of the press wheel of the corn planter. Hereafter, the respective methods of Zn application will be referred to as broadcast and band placements.

Treatments of the field experiments on the Norfolk soil consisted of a check; 7, 14, and 28 kg Zn/ha as broadcast $ZnSO_4$; 1.12, 2.24, and 4.48 kg Zn/ha as broadcast Zn-EDTA; and 0.28, 0.56, and 1.12 kg Zn/ha as banded Zn-EDTA. Treatments on the Litz soil consisted of a check; 7 and 14 kg Zn/ha as broadcast $ZnSO_4$; and 2.24 and 4.48 kg Zn/ha as broadcast Zn-EDTA. These treatments were arranged in a randomized complete block design with four replications on the Norfolk soil and five replications on the Litz soil. The plot dimensions were 15.24 m in length on both soils with a width of 3.68 m (4 rows) on the Norfolk soil and of 3.06 m (3 rows) on the Litz soil.

Macronutrients were applied at rates of 158 kg N, 49.6 kg P, and 152 kg K/ha to the Norfolk soil and of 168 kg N, 19.3 kg P, and 55.1 kg K/ha to the Litz soil. Diazinon was applied on the Norfolk soil at a rate of 4.48 kg/ha for insect control, and Atrazine was applied on both soils at a rate of 3.5 kg/ha for weed control. Pioneer 312 and

DeKalb XL-385 varieties of corn were planted in the Norfolk and Litz soils, respectively, at a rate of 44,500 seeds/ha. The dates of planting were April 16 on the Norfolk soil and May 1 on the Litz soil.

Tissue samples were taken in mid-June and again during the silk stage. The tissue samples in mid-June consisted of the sixth leaf of plants on the Norfolk soil and of the whole plant on the Litz soil. The leaf opposite and below the ear was sampled during the silk stage. The method of determining Zn in plant tissue was outlined earlier (Page 14). Height of corn plants was measured in mid-June. A 12.19 m portion of the center rows of plots on the Norfolk soil and of the middle row of the plots on the Litz soil was harvested for corn grain yield. The yield values obtained were corrected to 15.5% moisture.

Results and Discussion

Height of corn: Heights of young corn plants on the Litz silt loam and Norfolk loamy fine sand were increased by broadcast application of 7 and 14 kg Zn/ha as $ZnSO_4$ and of 2.24 and 4.48 kg Zn/ha as Zn-EDTA (Tables V and VI). Plants grown on the check plots of the Litz soil were stunted throughout the growing season and frequently failed to develop ears (Figure 10). In contrast, plants on the check plots of the Norfolk soil exhibited Zn deficiency symptoms in mid-June but not at the silk stage.

Broadcast applications of 7 and 14 kg Zn/ha as $ZnSO_4$ and of 4.48 kg Zn/ha as Zn-EDTA increased corn grain yield on the Litz silt loam (Table V). A lower rate of 2.24 kg Zn/ha as Zn-EDTA was inadequate to increase corn grain yield. The corn grain yield was higher where $ZnSO_4$

Table V. The effect of rate and source of Zn fertilization on Zn content, yield, and height of corn grown on Litz silt loam.

Zn Fertilization		Zn Content of Tissue Sampling Date		Yield of corn grain	Plant Height
Rate	Source	6/13/68	8/22/68		6/13/68
kg/ha		ppm	ppm	kg/ha	cm
0.00	------	16.1b*	10.8a*	314c*	20.4c*
7.00	$ZnSO_4$	18.5b	10.4a	3395ab	30.7ab
14.00	$ZnSO_4$	26.6a	10.5a	4265a	33.6a
2.24	Zn-EDTA	16.1b	9.6a	1348c	27.6b
4.48	Zn-EDTA	19.8b	10.0a	2846b	31.1ab

*The means in each column not accompanied by the same letter are significantly different at the .05 level of probability.

Table VI. The effect of rate, source, and method of Zn fertilization on Zn content, yield, and height of corn grown on Norfolk loamy fine sand.

Zn Fertilization			Zn Content of Tissue Sampling Date		Yield of Corn Grain	Plant Height 6/11/68
Rate	Source	Method	6/11/68	7/11/68		
kg/ha			ppm		kg/ha	cm
0.00	-----	-----	20.2b*	12.4b*	8475c†	118.5b*
7.00	$ZnSO_4$	broadcast	22.5b	14.0b	9620a	134.4a
14.00	$ZnSO_4$	broadcast	26.6b	13.3b	9925a	134.9a
28.00	$ZnSO_4$	broadcast	35.7a	20.8a	8985abc	127.9b
1.12	Zn-EDTA	broadcast	23.0b	12.2b	8397c	125.6b
2.24	Zn-EDTA	broadcast	20.5b	11.3b	9596ab	139.0a
4.48	Zn-EDTA	broadcast	26.3b	14.9b	8726bc	134.8a
0.28	Zn-EDTA	band	21.6b	12.0b	9204abc	125.0b
0.56	Zn-EDTA	band	26.6b	11.5b	9165abc	124.4b
1.12	Zn-EDTA	band	27.0b	11.7b	9432ab	129.0ab

*The means in each column not accompanied by the same letter are significantly different at the .05 level of probability.

†The means in each column not accompanied by the same letter are significantly different at the .10 level of probability.

Fig. 10. Effect of Zn fertilization on corn growth and development on Litz silt loam. The stunted plants did not receive Zn fertilization, whereas the tallest plants received 14 kg Zn/ha as broadcast $ZnSO_4$.

was broadcast at a rate of 14 kg Zn/ha than where Zn-EDTA was broadcast at a rate of 4.48 kg Zn/ha. The very high available P content and slightly alkaline pH of the Litz soil (Table IV) probably were responsible for the incomplete correction of Zn deficiency where Zn-EDTA was broadcast at a rate of 4.48 kg Zn/ha (25, 90).

Corn yield: Corn grain yield increases on the Norfolk loamy fine sand resulted from broadcast application of 7 and 14 kg Zn/ha as $ZnSO_4$ and of 2.24 kg Zn/ha as Zn-EDTA (Table VI). A lower rate of banded Zn-EDTA of 1.12 kg Zn/ha also increased corn grain yield. These data show that band method of applying Zn-EDTA was more efficient in supplying Zn to corn plants than the broadcast method. Yield responses to Zn application were obtained on the Norfolk soil, although plants appeared to recover from Zn deficiency. It seems, therefore, that Zn application might increase yields on other soils where temporary Zn deficiency symptoms occur early in the growing season.

The contents of 0.1N HCl extractable Zn and total Zn in the Litz silt loam and Norfolk loamy fine sand (Table IV) were not abnormally low as compared to other soils (80, 91). This observation implies that the Zn deficiency of corn plants on the two soils cannot be attributed to a low content of indigenous soil Zn. Neither the available P contents nor the pH levels in the two soils is naturally as high as occurred in the experimental areas (Table IV). It can be assumed, therefore, that liberal applications of limestone and P established these conditions in the soils. The high pH levels and available P contents probably were responsible for the low plant availability of Zn, since both factors are known to induce Zn deficiency (21, 25, 37, 52, 89, 90).

Zinc content of corn: Only the 14 kg Zn/ha rate of broadcast $ZnSO_4$ increased the Zn content of above-ground portions of corn plants on the Litz soil early in the growing season (Table V). The Zn content of ear leaves of plants on the Litz soil was not increased during the silk stage by either $ZnSO_4$ or Zn-EDTA application. On the Norfolk soil, only the highest rate of broadcast $ZnSO_4$ of 28 kg Zn/ha increased the Zn content of the sixth leaf of plants early in the growing season and of the ear leaf during the silk stage (Table VI). The small increases in Zn content of tissue due to Zn application probably resulted from the dilution effect which has been explained by Hiatt and Massey (38).

The ear leaves of corn plants on check plots of the Litz and Norfolk soils contained 10.8 and 12.4 ppm Zn, respectively, during the silk stage (Tables V and VI). The tissue samples of plants on check plots of the two soils contained approximately 20 ppm Zn early in the growing season. In most cases, a yield response was obtained due to Zn application without an accompanying increase in Zn content of tissue. It appears from these data that combinations of sampling times and plant portions other than those used in the present investigation should be selected for diagnosis of Zn deficiency of corn by tissue analysis.

RESPONSE OF CORN TO RESIDUAL AND ANNUAL APPLICATIONS OF Zn-EDTA AND $ZnSO_4$ IN FIELD INVESTIGATIONS

Associated with the problem of initially correcting Zn deficiency of corn in the field is that of preventing it from recurring in subsequent years, especially where continuous corn is grown. The research reported herein was designed to determine the residual effects of $ZnSO_4$ and Zn-EDTA applied in 1968 on the yield of corn grown the following year. A second aspect of this investigation was to compare the effect of small annual Zn applications on the correction of Zn deficiency of corn to that of a single large application.

Experimental Methods

Field experiments were conducted in 1969 on a Norfolk loamy fine sand and on a Litz silt loam described previously (Page 35). The pH and contents of available P, 0.1N HCl extractable Zn, and total Zn in soil samples from the 0- to 15-cm layer of the experimental areas on the two soils taken at the time that the study was initiated in 1968 were reported previously (Table IV).

In an initial study conducted on these plots, two methods of $ZnSO_4$ and Zn-EDTA application were used. Solutions of the Zn sources were either sprayed on the soil surface and disked into the soil to a depth of approximately 8 cm or sprayed in a 5-cm band directly in front of the press wheel of the corn planter. Hereafter, the respective methods of Zn application will be referred to as broadcast and band placements.

Treatments of the field experiment on the Norfolk soil consisted of a check; 7, 14, and 28 kg Zn/ha as broadcast $ZnSO_4$; 1.12, 2.24, and 4.48 kg Zn/ha as broadcast Zn-EDTA; and 0.28, 0.56, and 1.12 kg Zn/ha as banded Zn-EDTA. Treatments on the Litz soil were all broadcast and consisted of a check; 7 and 14 kg Zn/ha as $ZnSO_4$; and 2.24 and 4.48 kg Zn/ha as Zn-EDTA. Treatments of both field experiments were arranged in a randomized complete block design with four replications on the Norfolk soil and five replications on the Litz soil. In 1969, each plot was divided with one half of the plot receiving the same treatment as in 1968 and the other receiving no Zn treatment. The sub plot of the check treatment on the Norfolk soil received 3.5 kg Zn/ha, and 28 kg Zn/ha was applied to the corresponding plot on the Litz soil, all as broadcast $ZnSO_4$. The sub plot size was 7.62 m in length on both soils with a width of 3.68 m (4 rows) on the Norfolk soil and 3.06 m (3 rows) on the Litz soil.

Macronutrients applied to both soils in 1969 were 158 kg N, 19.3 kg P, and 55.1 kg K/ha. For weed control 1.68 kg/ha each of Atrazine and Simazine were applied to the Norfolk soil, and 3.5 kg/ha Atrazine was applied to the Litz soil. The corn variety DeKalb XL-45 was planted at a rate of 62,000 seeds/ha, and Southern States 820S variety of corn was planted at a rate of 44,500 seeds/ha on the Norfolk and Litz soils respectively. The dates of planting were April 18 on the Norfolk and May 8 on the Litz soil.

Plant height measurements of corn grown in the field experiments were made in mid-June. Tissue samples consisting of the sixth leaf of plants were taken in mid-June on the Norfolk plots. The leaf opposite and below the ear was sampled during the silk stage on the Litz soil. Total Zn in plant tissue was determined as described earlier (Page 14).

Statistical analyses were conducted on the data using the residual treatments as a randomized complete block design. A split plot analysis was used on all treatments except the check to determine the overall effects of both annual and biennial Zn applications. Paired t-tests were calculated between the sub plots for each Zn level, carrier, and type of placement (53).

Results and Discussion

Height of corn: Plant height on the Litz silt loam was increased by both high residual Zn levels and by application of supplemental Zn in 1969 (Table VII). Increases in plant height occurred where Zn was applied at rates of 7 and 14 kg Zn/ha as $ZnSO_4$ or 4.48 kg Zn/ha as Zn-EDTA only in 1968. These data indicate that residual Zn from $ZnSO_4$ and Zn-EDTA is available to plants for more than one growing season, although only the highest rate of Zn-EDTA exerted this effect. Average plant heights obtained for both sub plots at each Zn level were greater for both 14 kg Zn/ha as $ZnSO_4$ and 4.48 kg Zn/ha as Zn-EDTA than for the 2.24 kg Zn/ha as Zn-EDTA rate. Comparisons between the sub plots at each Zn level indicated that plant height was increased by the addition of 28 kg Zn/ha as $ZnSO_4$ to the check treatment or second application of 14 kg Zn/ha as $ZnSO_4$ and 2.24 kg Zn/ha as Zn-EDTA. The heights of corn plants were not affected by either residual Zn or additional Zn applied in 1969 on the Norfolk loamy fine sand (Table VIII).

Table VII. The effect of rate and source of Zn fertilization on plant height, Zn content, and yield of corn grown on a Litz silt loam.

Treatment		Plant Height			Zn Content of Plants			Corn Grain Yield		
		Zn Applied			Zn Applied			Zn Applied		
Zn Source	Zn Rate	1968	1968 and 1969	Avg.	1968	1968 and 1969	Avg.	1968	1968 and 1969	Avg.
	kg/ha	cm			ppm			ppm		
Check	0.00	25b[1]	35[2]**		11a[1]	17[2]**		933c[1]	6680[2]**	
$ZnSO_4$	7.00	34a	35	34bc[1]	12a	14	13b[1]	5018ab	5700	5359b[1]
$ZnSO_4$	14.00	34a	37*	36a	13a	19†	16a	6100a	6539	6320a
Zn-EDTA	2.24	26b	31*	38c	10a	11	11b	1325c	4202*	2764c
Zn-EDTA	4.48	33a	37	35ab	12a	13	12b	3763b	5747†	4755b

[1] Those means in each column not followed by the same letter or letters are significantly different at the 0.05 level where applicable.

[2] 28.00 kg Zn/ha as $ZnSO_4$ broadcast in 1969.

**, *, † Indicates significant differences according to paired t-tests at the 0.01, 0.05, and 0.10 levels respectively.

Table VIII. The effect of rate and source of Zn applied by broadcast (Bc) and band (Ba) application on plant height, Zn content, and yield of corn grown on a Norfolk loamy fine sand.

Treatment			Plant Height			Zn Content of Plants			Corn Grain Yield		
			Zn Applied			Zn Applied			Zn Applied		
Zn Source	Method	Zn Rate	1968	1968 and 1969	Avg.	1968	1968 and 1969	Avg.	1968	1968 and 1969	Avg.
		kg/ha	cm			ppm			kg/ha		
Check	--	0.0	97a[1]	99[2]		17b[1]	26[2]*		7668a[1]	7793[2]	
$ZnSO_4$	Bc	17.00	99a	96	97a[1]	29b	59**	44bc[1]	7644a	7793	7719a[1]
$ZnSO_4$	Bc	14.00	104a	101	102a	30b	96**	63b	8193a	7777*	7985a
$ZnSO_4$	Bc	28.00	104a	90	97a	54a	149†	102a	7511a	8185	7848a
Zn-EDTA	Bc	1.12	95a	89	96a	22b	33†	27c	7432a	7503	7468a
Zn-EDTA	Bc	2.24	104a	103	103a	23b	31*	27c	7809a	8499	8154a
Zn-EDTA	Bc	4.48	106a	109	107a	21b	37†	29c	7064a	7652	7358a
Zn-EDTA	Ba	0.28	100a	97	98a	22b	20	21c	7668a	7440	7554a
Zn-EDTA	Ba	0.56	98a	97	98a	18b	21	20c	7064a	7628	7346a
Zn-EDTA	Ba	1.12	97a	98	97a	19b	23	21c	7785a	8232	8008a

[1] Those means in each column not followed by the same letter or letters are significantly different at the 0.05 level where applicable.

[2] 3.5 kg Zn/ha as $ZnSO_4$ broadcast in 1969.

**, *, † Indicates significant differences according to paired t-tests at the 0.01, 0.05, and 0.10 levels respectively.

Zinc content of corn: The Zn content of corn grown on the Litz soil was not affected by residual Zn (Table VII). These results are similar to those reported previously and might indicate that very little of the residual Zn was available for plant growth. However, it appears that the lack of differences was probably due to the dilution effect noted by Hiatt and Massey (38), since plant size was highly affected by Zn rate, especially in the later stages of growth when the tissue samples were taken. Comparison of the means for whole plots indicated that only the 14 kg Zn/ha rate as $ZnSO_4$ resulted in an increase in the Zn content over those plants grown on plots which had received Zn. Zinc content was increased by the application of $ZnSO_4$ either at the rate of 28 kg Zn/ha to the check plot or annual applications of 14 kg Zn/ha. Apparently, large applications of Zn are required to overcome the Zn "fixing" capacity of the Litz soil.

Zinc remaining in the Norfolk soil from 1968 applications had little effect on the Zn content of corn except in the case of the 28 kg Zn/ha rate as $ZnSO_4$ where it was increased significantly over all other treatments (Table VIII). This indicates that there was a high amount of available Zn due to the addition of high amounts of $ZnSO_4$. The means for whole plots indicated that applications of 14 or 28 kg Zn/ha as $ZnSO_4$ increased the Zn content over all other treatments. Comparisons between sub plots at each Zn level revealed that Zn contents were increased by all treatments except those where Zn-EDTA was banded. It would seem likely that there was luxury consumption of Zn, especially in the case of the two yearly applications of 28 kg Zn/ha as $ZnSO_4$ where the Zn content was 149.4 ppm.

Corn yield: Corn grain yield on the Litz soil was increased significantly by both residual and annual applications of Zn. Comparisons of the means where residual Zn only was available indicated that both rates of $ZnSO_4$ gave the highest yields, while the 2.24 kg Zn/ha as Zn-EDTA and the check were the lowest. The averages for the sub plots of each Zn level showed a similar trend, except that the 14 kg Zn/ha as $ZnSO_4$ gave the highest yield. Two applications of 4.48 kg Zn/ha as Zn-EDTA were needed to obtain maximum grain yield, and yield was increased in both cases where Zn-EDTA was added the second year. These increases reflect the low availability of residual Zn applied to the Litz soil in the chelate form. Corn yield was also increased by the application of 28 kg Zn/ha to the check plot.

Corn grain yield was not affected by Zn application on the Norfolk soil. Response to Zn fertilizers on this soil seems to depend largely on the weather conditions during the growing season. The spring of 1969 was somewhat warmer and drier than in 1968 when Zn deficiency was previously noted on this soil. Comparison of the sub plot values at each Zn level indicated that there was a decrease in yield due to the second application of 14 kg Zn/ha as $ZnSO_4$. The possibility that a Zn toxicity existed was not borne out by the next highest $ZnSO_4$ rate. It would seem likely that if a toxicity were to exist, that the annual application of 28 kg Zn/ha as $ZnSO_4$ would also have decreased yield.

RESPONSE OF CORN TO ZINC APPLIED AS CHELATE OR SULFATE IN A FIELD INVESTIGATION ON A LITZ SILT LOAM

In a previous experiment on a Litz silt loam, it was found that Zn-EDTA was not as effective as $ZnSO_4$ in correcting the Zn deficiency of corn when applied in a 1:3 ratio of Zn as chelate to Zn as sulfate. Due to the high pH of this soil, it was felt that the Zn-EDTA complex may have been unstable, thereby precluding any advantage of adding Zn in the chelated form. In contrast to Zn-EDTA, Zn-DTPA has been shown to have greater stability at high pH levels in laboratory research (60). The objective of this study was to determine the effect of various rates of surface applied Zn-EDTA, Zn-DTPA, and $ZnSO_4$ and foliar applied Zn-EDTA on the grain yield and Zn content of corn grown on a Litz silt loam.

Experimental Methods

A field experiment was conducted in 1969 on a Litz silt loam described earlier (Page 35). Treatments of the field experiment consisted of a check, 0.56 and 1.12 kg Zn/ha as Zn-DTPA, 0.56 and 1.12 kg Zn/ha as Zn-EDTA, and 1.12 and 4.48 kg Zn/ha as $ZnSO_4$. All treatments except the foliar application were sprayed in a 6-cm band immediately over the row after the corn had been planted. An additional treatment consisting of foliar applied Zn-EDTA was made at a rate of 0.56 kg Zn/ha in mid-June after Zn deficient corn plants were observed and prior to tissue sampling. The treatments were arranged in a randomized complete block with five replications. Macronutrients were applied at the rates of 158 kg N, 19.3 kg P, and 55.1 kg K/ha. Atrazine was applied at a rate of 3.5 kg/ha for weed control to the soil. The Southern States 820S variety of corn was planted at a rate of 44,500 seeds/ha on May 8, 1969. Plant height measurements and tissue samples consisting of the aerial portion of the plants were taken in mid-June. The method for determining Zn in plant tissue is described elsewhere (Page 14).

Results and Discussion

Zinc deficiency of the corn plants was observed but was not sufficiently severe to stunt the plants (Table IX). There was a general chlorosis and in some instances "white bud" occurred. It was observed that after applying the Zn-EDTA to the plants, the newly-emerged leaves remained chlorotic, while those leaves which had been in direct contact with the spray appeared dark green. This would indicate a lack of mobility of foliar applied Zn in the plant.

Plant height, Zn content, and corn grain yield were not affected by any method of application or rate of the three Zn sources (Table IX). The lack of response may be attributed to the methods of Zn application. According to Lindsay et al. (54), the stability of Zn-EDTA decreases rapidly above pH 7.0, while that of Zn-DTPA decreases above pH 7.3. It is possible that although the Zn was added in the chelated form, the Zn was released from the complex due to competition from other ions such as Ca^{2+}, since the soil pH was 7.1. If this were the case, the chelated Zn may have reverted to the inorganic form. The mobility of inorganic Zn in soil is usually quite limited, as shown by Mortvedt and Giordano (57). They found that Zn applied as $ZnSO_4$ to a soil

Table IX. Plant height, zinc content, and yield of corn grown with several levels of three zinc sources on a Litz silt loam.

Zn Treatment		Plant Height	Zn Content of Tissue	Yield of Corn Grain
Source	Rate			
	kg/ha	cm	ppm	kg/ha
Check	0.0	32.2a*	24.3a*	6217a*
Zn-DTPA	0.56	32.5a	25.3a	6052a
Zn-DTPA	1.12	32.0a	27.1a	6186a
Zn-EDTA	0.56	31.5a	27.9a	6421a
Zn-EDTA	1.12	34.5a	27.8a	6350a
$ZnSO_4$	1.12	32.2a	25.6a	6021a
$ZnSO_4$	4.48	32.2a	28.8a	5425a
Zn-EDTA†	0.56	32.5a	24.8a	5355a

*Those means in each column not followed by the same letter or letters are significantly different at the 0.05 level.

†Foliar application.

having a pH of 7.1 moved 0.75 cm after 8 weeks of equilibration. It seems probable that the surface applied Zn did not move downward into the root zone to supply adequate Zn for optimum corn yield.

SUMMARY AND CONCLUSIONS

This investigation was conducted to determine the efficacy of several Zn bearing materials for correction of Zn deficiency of corn and to evaluate the effect of certain soil factors on the availability of Zn from these sources. The soil amendments considered during the course of the investigation were coal ash, $ZnSO_4$, Zn-EDTA, and Zn-DTPA. The soil factors under study were pH, specific conductivity, and soluble SiO_2 levels as altered by coal ash application.

Coal ash, a by-product of the coal burning electric power industry, was analyzed for total and 1.0N HCl extractable Zn. Seventeen fly ash samples were found to contain from 13 to 378 ppm in total Zn and from 2 to 93 ppm in acid extractable Zn. Only one of seven fly ash samples used corrected Zn deficiency of corn in greenhouse studies on Tatum and Frederick silt loams. The increase in Zn availability due to the addition of this fly ash was attributed to a decrease in soil pH, which made indigenous soil Zn more available. Several of the fly ashes that were alkaline in reaction caused a decrease in corn growth due to increased soil pH and soluble salt levels. A sample of bottom ash that contained 1582 ppm total Zn was effective in correcting Zn deficiency of corn plants grown on both the Frederick and Tatum soils. These studies indicated that coal ash can be an effective source of Zn for plants if it contains a high amount of Zn and if it does not significantly alter the soil pH or soluble salt level.

The relationship between corn yield and soluble SiO_2 levels induced by application of coal ash to the Tatum soil was studied.

Corn yield was found to be directly related to weak acid extractable soil Zn and inversely related to soluble SiO_2 levels. It was shown in this study that, although a particular coal ash sample contains a relatively high amount of Zn, the by-product may also contribute soluble and amorphous SiO_2 to the soil, thereby decreasing Zn availability.

In field studies, $ZnSO_4$, Zn-DTPA, and Zn-EDTA were applied by various methods to a Litz silt loam and a Norfolk loamy fine sand. Both $ZnSO_4$ and Zn-EDTA were found to increase corn yield on these two soils in 1968. On the Norfolk soil, the most effective correction of Zn deficiency was accomplished by the application of 7.00 kg Zn/ha as broadcast $ZnSO_4$, 2.24 kg Zn/ha as broadcast Zn-EDTA, or 1.12 kg Zn/ha as banded Zn-EDTA.

In a 1969 field study on the Norfolk soil, residual or multiple applications of Zn did not increase corn yield. It appears that response to Zn fertilizers on this soil depends largely on weather conditions during the growing season. Zinc deficiency of corn was corrected on the Litz soil by broadcast application of both $ZnSO_4$ and Zn-EDTA. The largest increase in yield occurred where $ZnSO_4$ was applied at the rate of 14 kg Zn/ha. Corn grain yield was increased by both residual and annual applications of Zn on the Litz soil in 1969.

A second field study on the Litz soil consisted of spraying $ZnSO_4$, Zn-EDTA, and Zn-DTPA directly over the corn row immediately after the corn was planted. Zinc-EDTA was also applied as a foliar spray. Although Zn deficiency symptoms were observed, corn grain yield was not increased by any of the treatments used. These results demonstrated that surface or foliar application of Zn fertilizers was not effective in the correction of Zn deficiency on the Litz soil.

It was concluded that the correction of Zn deficiency of corn can be accomplished by the application of coal ash, $ZnSO_4$, or Zn-EDTA to soil. However, there are several limitations to the use of coal ash as a Zn source to plants. The total elemental content of an ash as well as the Zn content should be known to determine if there are constituents present which would adversely affect Zn availability or plant growth. The testing of a coal ash that might be a potential Zn source would involve an extensive quality control system to evaluate such factors as total Zn content, soluble SiO_2 content, and pH. If coal ashes can be found that have comparable properties to those of the Municipal bottom ash from Columbus, Ohio, they would probably be adequate and inexpensive sources of Zn to plants. This has yet to be tested in field studies. With regard to the several commercially produced Zn sources tested, both $ZnSO_4$ and Zn-EDTA may be suitable sources of Zn to plants. Due to the cost of Zn-EDTA, the most economically feasible method of application would be that of banding at low rates. Zinc sulfate can be very effective and economical when it is premixed with a macronutrient fertilizer, broadcast, and mixed with the soil during tillage operations. More extensive field research is required before the feasibility of using Zn-DTPA as a source of Zn to plants can be fully evaluated.

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APPENDIX

Table I. Reagent grade chemicals applied to soils in greenhouse studies.

Element	Source
N	NH_4NO_3
P	$Ca(H_2PO_4)_2 \cdot H_2O$
Mg	$MgSO_4 \cdot 7H_2O$
K	KCl
Cu	$CuSO_4 \cdot 5H_2O$
Mn	$MnSO_4 \cdot H_2O$
B	$Na_2B_4O_7 \cdot 10H_2O$
Mo	$Na_2MoO_4 \cdot 2H_2O$
Zn	$ZnSO_4 \cdot 7H_2O$

Table II. The effect of $ZnSO_4$, $CaCO_3$, and coal ash on corn yield and Zn uptake by corn grown on a Frederick silt loam (sampled 10/19/68).

Treatment				Corn Yield	Zn Uptake
Zn Source	Coal Ash	$CaCO_3$	Zn Rate		
	g/2.1 kg soil		mg/2.1 kg soil	g/pot	µg/pot
Check	---	0.0	0.0	10.6ab*	104.7fghi
$ZnSO_4$	---	0.0	6.3	10.5ab	211.3d
$ZnSO_4$	---	0.0	12.6	12.0a	196.5de
		4.2	0.0	5.3defg	41.2hij
$ZnSO_4$	---	4.2	6.3	5.7def	111.7fgh
$ZnSO_4$	---	4.2	12.6	6.8de	135.9efg
		8.4	0.0	4.0fghi	37.0hij
$ZnSO_4$	---	8.4	6.3	5.8def	74.5ghij
$ZnSO_4$	---	8.4	12.6	6.2de	100.1fghi
Crawford Edison[‡]	---	---	6.3	6.8de	74.3ghij
Crawford Edison	17.3	---	6.3	7.2cd	70.7ghij
Crawford Edison	34.6	---	12.6	4.8efgh	54.7ghij
Crawford Edison	69.2	---	25.2	3.2hij	40.5hij
Crawford Edison	138.4	---	50.4	1.2k	18.8j
Crawford Edison	276.8	---	100.8	1.0k	20.0j
Municipal[‡]	---	---	6.3	9.5b	95.6fghi
Municipal	4.0	---	6.3	9.6b	161.6def
Municipal	8.0	---	12.6	9.5b	229.3cd
Municipal	16.0	---	25.2	9.6b	294.0c
Municipal	32.0	---	50.4	8.6bc	411.6b
Municipal	64.0	---	100.8	9.2b	548.0a
Lewis and Clark[‡]	---	---	6.3	0.0k	0.0j
Lewis and Clark	47.8	---	6.3	3.5ghij	29.6ij
Lewis and Clark	95.6	---	12.6	2.0ijk	16.0j
Lewis and Clark	191.2	---	25.2	1.6jk	14.1j
Lewis and Clark	382.4	---	50.4	1.6jk	12.7j
Lewis and Clark	764.8	---	100.8	1.2k	12.1j

*Those means in each column not accompanied by the same letter are significantly different at the 0.05 level.

[‡] 1.0$\underline{N}$ HCl extract of the coal ash from the Crawford Edison, Municipal, and Lewis and Clark plants.

Table III. The effect of $ZnSO_4$, $CaCO_3$, and coal ash on corn yield and Zn uptake by corn grown on a Frederick silt loam (sampled 11/25/68).

Treatment				Corn Yield	Zn Uptake
Zn Source	Coal Ash	$CaCO_3$	Zn Rate		
	g/2.1 kg soil	g/2.1 kg soil	mg/2.1 kg soil	g/pot	μg/pot
Check	---	0.0	0.0	5.3g	51.2fg
$ZnSO_4$	---	0.0	6.3	7.5def	132.3e
$ZnSO_4$	---	0.0	12.6	7.0ef	181.0d
		4.2	0.0	5.0g	47.3fg
$ZnSO_4$	---	4.2	6.3	7.2def	119.6e
$ZnSO_4$	---	4.2	12.6	8.3bcd	174.5d
		8.4	0.0	4.4g	47.1gh
$ZnSO_4$	---	8.4	6.3	7.6def	112.7e
$ZnSO_4$	---	8.4	12.6	7.9cde	162.6d
Crawford Edison‡	---	---	6.3	6.4f	65.9f
Crawford Edison	17.3	---	6.3	5.3g	54.6fg
Crawford Edison	34.6	---	12.6	4.9g	54.2fh
Crawford Edison	69.2	---	25.2	3.2h	59.0f
Crawford Edison	138.4	---	50.4	1.4i	25.3gh
Crawford Edison	276.8	---	100.8	0.0j	0.0h
Municipal‡	---	---	6.3	6.5f	58.5f
Municipal	4.0	---	6.3	9.6a	123.5e
Municipal	8.0	---	12.6	7.6def	128.6e
Municipal	16.0	---	25.2	9.6a	230.3c
Municipal	32.0	---	50.4	9.0ab	270.7b
Municipal	64.0	---	100.8	8.9abc	437.0a
Lewis and Clark‡	---	---	6.3	0.0j	0.0h
Lewis and Clark	47.8	---	6.3	3.2h	25.1gh
Lewis and Clark	95.6	---	12.6	2.6h	23.1gh
Lewis and Clark	191.2	---	25.2	1.5i	23.6gh
Lewis and Clark	382.4	---	50.4	0.7ij	11.2h
Lewis and Clark	764.8	---	100.8	0.4ij	3.6h

*Those means in each column not accompanied by the same letter are significantly different at the 0.05 level.

‡1.0N HCl extract of the coal ash from the Crawford Edison, Municipal, and Lewis and Clark plants.

VITA

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Melvin G. Schnappinger Jr

Zinc Deficiency Correction in Corn as Affected by Certain Properties of Four Virginia Soils, and the Application of Zinc Sulfate, Zinc Chelates, and Coal Ash

by

Melvin G. Schnappinger

ABSTRACT

Coal ash, $ZnSO_4$, Zn-EDTA, and Zn-DTPA were evaluated as sources of Zn in greenhouse and field experiments on four soils known to supply inadequate amounts of Zn for corn (*Zea mays* L.) growth. Coal ashes from eighteen sources contained from 13 to 1582 ppm in total Zn and from 1.5 to 1420.0 ppm in 1.0*N* HCl extractable Zn. In a greenhouse experiment on a Frederick silt loam, applications of coal ash from one source increased corn yield, while that from two other sources decreased plant growth. The decrease in yield was found to be related to high soil pH and soluble salt levels induced by application of the coal ashes.

In a second greenhouse study, corn yield on Frederick and Tatum silt loam was increased by coal ash from two of the five sources applied. The increase was attributed to a high amount of available Zn from a bottom ash and to an acid reaction caused by application of a fly ash. This acid reaction may have increased the availability of indigenous and applied Zn. Corn yield on the Tatum soil was inversely related to soluble SiO_2, indicating that high levels of SiO_2 may decrease Zn availability to plants.

Field experiments were conducted in 1968 in which $ZnSO_4$ and Zn-EDTA were broadcast at various rates to a Litz silt loam and a

Norfolk loamy fine sand. Broadcast and band methods of Zn-EDTA placement were also used on the Norfolk soil. Highest corn grain yield occurred on both soils where 14 kg Zn/ha as $ZnSO_4$ was broadcast. Zinc-EDTA broadcast at 2.24 kg Zn/ha or banded at 1.12 kg Zn/ha also increased corn yield on the Norfolk soil. On the Litz soil, 4.48 kg Zn/ha as Zn-EDTA was required to increase corn yield. The ear leaves of corn plants on check plots of the Litz and Norfolk soils contained 10.8 and 12.4 ppm Zn respectively.

In 1969, a split plot design was superimposed on the 1968 experimental areas on the two soils in which the subplots received either the same rate of Zn or were untreated. Corn yield was not increased by any treatment on the Norfolk soil, but was increased on the Litz soil by residual Zn from previous applications of 7.0 and 14.0 kg Zn/ha as $ZnSO_4$ and 4.48 kg Zn/ha as Zn-EDTA. Two annual applications of 2.24 and 4.48 kg Zn/ha as Zn-EDTA resulted in increased corn yields as compared to one application of Zn at the same rate. Equivalent corn yields on the Litz soil occurred from either one or two annual applications of $ZnSO_4$ at the rates of 7 and 14 kg Zn/ha.

In a second field study on the Litz soil, $ZnSO_4$, Zn-EDTA, and Zn-DTPA were applied to the soil surface, and Zn-EDTA was also applied to the foliage. Corn grain yield was not increased by any of these treatments, although Zn deficient corn plants were observed throughout the experimental area. The lack of increases in corn yield were attributed to non-mobility of the surface applied Zn.