

ZINC AVAILABILITY IN PROFILES OF SELECTED KANSAS SOILS

by

DAVID ORION TRAVIS

B. S., Oklahoma State University, 1963

A THESIS

submitted in partial fulfillment of the

requirements for the degree

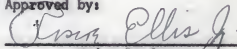
MASTER OF SCIENCE

Department of Agronomy

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

Approved by:


Major Professor

LD
2668
T4
1965
T782
C.2
Document

TABLE OF CONTENTS

INTRODUCTION	1
REVIEW OF LITERATURE	2
Reports of Zinc Deficiency	2
Zinc Toxicity Levels	6
Synthesis and Activity of Plant Auxin Cont as Affected by Zinc Concentration	7
Cellular Derangements and Other Growth Abnormalities as Affected by Zinc Content	10
The Effect of Nitrogen Carrier on Soil Reaction and Consequent Zinc Availability	11
The Effect of Phosphorus on Zinc Availability	12
Zinc Availability as Related to Carrier	15
Total and Available Zinc Content of Representative Soils	15
Estimation of Available Soil Zinc from Plant Concentrations	16
Analytical Methods for Zinc Analyses	17
EXPERIMENTAL PROCEDURES	17
Sampling	17
Analytical Procedures	18
RESULTS AND DISCUSSION	20
SUMMARY	34
ACKNOWLEDGMENTS	36
LITERATURE CITED	37
APPENDIX I	41
APPENDIX II.....	45

This thesis is affectionately dedicated to

my niece and nephew

Annette Darlene and Steven Brent Travis

INTRODUCTION

On a world basis zinc is the most commonly reported micronutrient element to be deficient in crop producing soils (2). Deficiencies have also been reported in 20 other countries (30). Within the United States 32 states report cases of zinc deficiency (2). Viets et al. (34) reported castorbeans, field beans, lima beans, sweet corn, field corn, Sudan grass, Concord grapes, hops, soybeans, flax and tomatoes as being susceptible to zinc deficiency while wheat, oats, barley, safflower, alfalfa, asparagus, mustard, peas, and grain sorghums were reported to be relatively nonsusceptible. Other research, however, has been reported in which zinc deficiency has occurred on some of these latter crops. Corn is the most commonly reported affected crop in the western states (2). Much research has indicated that zinc deficiencies may be induced by large applications of phosphorus and that the effects are more severe under cold, wet soil conditions.

Soil zinc deficiencies often result when the zinc containing "A" or organic horizon is removed by erosion or by grading in preparation for irrigation. Zinc is concentrated within the "A" horizon as it is continually redeposited here by decaying plant tissue. Over a period of years the lower horizons may become nearly depleted of their original available zinc supply. Therefore, plants being grown on depleted "B" horizons, due to erosion or surface soil removal by grading in preparation for irrigation, often show zinc deficiency symptoms and produce low yields. This situation has occurred in Kansas river valleys that have been recently placed under irrigation.

The objective of this research was to provide a means whereby the probability of zinc deficiencies occurring on a given soil when placed under irrigation and heavy fertilization for maximum yield could be predicted.

REVIEW OF LITERATURE

Reports of Zinc Deficiency

The proof of zinc as an essential plant nutrient and its dependence upon soil reaction for availability for plant absorption have been well established. Camp (12) reported that as soil pH increases, zinc availability decreases. He defined the critical pH value as ranging between 5.5 and 6.5. Thorne (31) reported that zinc deficiencies were first observed in citrus orchards of Florida growing on peat soils. He described zinc deficiency as occurring most commonly on fruit trees and listed sweet cherries, peaches, apricots, apples, pears, walnuts, citrus, tung and grapes as being highly susceptible. Fruit growers often report zinc deficiency as little leaf, rosette, die back, bronzing, yellows and white bud. Thorne (31) described visual zinc deficiency symptoms as a mottled yellow color appearing between the veins of leaves. As the severity increases the chlorosis becomes continuous from the midvein to the margin. Stem growth is retarded and the leaves are often small, narrow, and crinkled along the edges. Rosettes of leaves often appear at the ends of bare twigs. Death of stem tips and early fruiting maturity are characteristic of the deficiency. Peaches are often reported to be flattened or pointed and reduced in size. Lyman and Dean (19) reported a relatively decreased zinc

content of the growing points of zinc deficient pineapple plants relative to the zinc content of other plant tissue. This decreased zinc content of growing points was shown to be related to the degree of zinc deficiency. Lyman and Dean further reported that meristematic tissues of normal plants contain the highest concentrations of zinc. Beawn and Viets (6) reported zinc deficiency occurring in Ranger alfalfa. The deficiency occurred on virgin Ritzville very fine sandy loam that had been leveled for irrigation. The deficient plants were noticeably shorter than nondeficient normal plants growing on adjacent uncut areas. The deficient plants gave a favorable response and resumed normal growth after receiving applications of either a 0.5% $ZnSO_4 \cdot 7H_2O$ spray or a $ZnCl_2$ spray of equal zinc concentration. The resumption of normal growth and color formation occurred within ten days after spraying. These effects were reported as consistent irregardless of the spray used. Riceman and Jones (26) observed zinc chlorosis on Subterranean clover (Trifolium subterraneum L.) 33 days after germination when grown in a zinc free culture solution. The plant dry weight at this time was less than 100 mg and the zinc content was less than 1.5 ug. The last deficiency symptoms observed occurred 162 days after germination with plant dry weight and zinc content each in excess of 35 g and 350 ug respectively. These researchers also reported that the zinc concentration of most affected plants on a plant dry matter basis lies between 15 and 20 ppm. Brown and Wilson (10) examined zinc deficiency effects on three cotton species: Gossypium barbadense L., Gossypium hirsutum L., and the diploid Gossypium arboreum L. Deficiency effects were most evident in depressed plant height. Control plants were 138% to 285% taller

than the no treatment plants. Chlorotic symptoms occurred as early as five weeks after emergence. These chlorotic symptoms were evident as tinges of yellow between leaf veins and small white spots on zinc deficient plants of all varieties, no squares being produced on G. barbadense. These authors observed that limited square formation may result on zinc deficient plants but these are shed before anthesis. Wood and Sibly (39) found that visual zinc deficiency symptoms occurred in oats when the zinc concentration was below 20 ppm at a time prior to exertion of the inflorescence. Viets et al. (35) reported zinc deficiency symptoms of interveinal chlorosis and death of leaf tissue in field grown Red Mexican beans. They found visual deficiency symptoms common in plants whose zinc content of mature leaves or plant tops were about 20 ppm. The chlorosis was restricted to the small veins and mesophyll when the zinc content of leaves was 12.8 ppm but when the zinc content was only 11.4 ppm chlorosis appeared in the midribs and petioles as well. Viets et al. (37) found zinc deficiency occurring in corn in central Washington on newly irrigated areas. Chlorosis and necrosis of the lower four or five leaves were common. These plants gave a significant yield increase to foliar applications of zinc. These researchers also reported that a zinc concentration of 15 ppm within the mature leaves (6th leaf from the base or 2nd leaf from node below upper ear node) when measured at time of pollen shedding was sufficient to produce yields ranging from 100 to 125 bushels per acre without showing deficiency symptoms. Barnette et al. (3) described zinc deficiencies of corn occurring in Florida. The deficiency was described as "white bud" and was reported to be corrected by applications of zinc sulfate or animal manures. Brown et

a1. (8) reported that sweet corn responded to zinc applications on 84% of the soils examined whose dithizone-extractable zinc content was less than or equal to 0.55 ppm. No response was obtained on 76% of the soils examined whose dithizone-extractable zinc content was greater than 0.55 ppm. Hiatt and Massey (15) found the zinc concentration of corn to be directly related to the amount of zinc available in the culture medium. By growing corn plants in cultures of varying zinc concentrations they found that plants exhibiting only slight deficiency and near normal growth contained the lowest zinc concentrations while plants exhibiting severe deficiency symptoms contained the highest zinc concentrations of the zinc deficient plants. However, total zinc uptake was always least for the plants exhibiting limited growth and high zinc concentration. Explanations were suggested but no explanation was regarded as adequate to explain the results. The explanations suggest that the zinc requirement of corn plants is higher during the early vegetative stages of growth. Therefore, a plant on a severely deficient soil would soon become stunted and growth might cease completely. The plant, however, may continue to absorb soil zinc and accumulate it in the nodal tissue. Therefore a high concentration might be expected with absence of growth and continual absorption. A plant growing on a less zinc deficient soil could be expected to exhibit a more nearly normal growth response but as available zinc becomes limiting the total zinc concentration would be less than in the stunted plant which continues to absorb zinc but fails to undergo further growth.

Zinc Toxicity Levels

Gall and Barnette (14) reported that mobile replaceable zinc may become toxic to plant growth at certain concentrations; however, water-insoluble forms seldom become toxic to plant growth. Greenhouse cultures of varying zinc concentrations were prepared from a Norfolk sand, an Orangeburg fine sandy loam and a Greenville clay loam. Portions of the samples collected were washed free of all soluble salts and then were zinc saturated. These zinc saturated samples were mixed at various concentrations with corresponding untreated soil to provide the desired culture media. Two crops of corn and cowpeas were grown for four weeks in rotation. It was concluded from the results that replaceable zinc became toxic to corn on the Norfolk sand at concentrations ranging from 0.688 to 1.376 me/100g (451-902 pounds zinc per acre), that replaceable zinc became toxic to corn on the Orangeburg fine sandy loam at concentrations ranging from 0.758 to 1.137 me/100 g (497-734 pounds zinc per acre), and that replaceable zinc became toxic to corn on the Greenville clay loam at concentrations ranging from 1.615 to 2.153 me/100g (1051-1402 pounds zinc per acre). The concentrations at which available zinc became toxic to cowpeas were found to range from 0.275 to 0.482 me/100g (181-316 pounds zinc per acre, 0.379 to 0.758 me/100g (246-497 pounds zinc per acre), and 0.538 to 1.077 me/100g (351-701 pounds per acre) for these three soils, respectively. Heavy applications of mono-calcium phosphate did not change the average zinc toxic limits on these soils but the phosphorus of the compound did act as a plant nutrient on the Orangeburg fine sandy loam and Greenville clay

loam. Test plant growth was stimulated on these soils while no such response was evident on the Norfolk sand. However, heavy applications of CaCO_3 greatly increased the concentration at which available zinc became toxic to corn and cowpeas and alleviated the toxic condition.

Synthesis and Activity of Plant Auxin Content as Affected by Zinc Concentration

Much research evidence suggests that the reduced growth of zinc deficient plants is related to the production or activity of the growth inducing plant auxins. Skoog (29) reported that only traces of auxin or no auxin could be extracted from zinc deficient plants by diffusion into agar blocks. Auxin was extractable from the foliar tissue of zinc deficient plants but in much smaller quantities than from the control plants. The auxin content of the control plants was in excess of that required for maximum stem elongation. The decrease of auxin in the zinc deficient plants took place before any visual zinc deficiency symptoms were apparent. Such plants when treated with zinc applications responded by synthesizing auxins in large concentrations within one to a few days, but resumption of normal growth was delayed for a longer period. Plants grown in copper- and manganese-deficient cultures responded quite differently with respect to auxin level. Under these conditions the auxin content remained near normal until after visual deficiency symptoms were apparent. It was concluded from these observations that with copper- and manganese-deficient plants the reduction in auxin content may be due to a secondary effect but with zinc-deficient plants the reduction in auxin content can only be attributed to the primary effects of zinc deficiency independent of the decreased vigor of

deficient plants. Zinc-deficient plants inactivated indole-3-acetic acid more rapidly than control plants. Also a higher oxidation capacity in zinc deficient plants was noted which was believed to be correlated with and causally related to the auxin destruction property. The decrease in stem elongation was noted to a much less degree when plants were growing in red or weak light. The decreases in stem elongation were readily apparent in those plants growing in blue light. Foliar applications of indole acetic acid often stimulated stem elongation but did not replace zinc as a plant nutrient. Such applications of auxin appeared only to increase the plants' utilization of available zinc and did not act as a substitution for natural plant synthesized auxin. Skoog (29) concluded that zinc is required for the maintenance of auxin in an active state rather than for its synthesis. Tsui (33), who also studied auxin content in relation to zinc deficient plants, noticed many of these same results with tomato plants, Lycopersicon esculentum Mill. var. John Baer. Auxin content of zinc deficient plants again decreased significantly before any visual deficiency symptoms were apparent. However, when bound auxins were released from dried material by treatments with NaOH, HCl and trypsin, Tsui found two kinds of auxins. He labeled these as acid-stable and alkali-labile, and alkali-stable and acid-labile. Each type was reported to decrease as the zinc concentration of the plant decreased but in normal plants the acid-stable and alkali-labile types increased as the plant matured while the alkali-stable and acid-labile type remained nearly constant. Also prior to the appearance of visual deficiency symptoms the tryptophane content of the zinc deficient plants greatly decreased. An

increase in tryptophane content was delayed by three days after an addition of zinc to the zinc deficient plants. From these observations this author concluded that zinc is required directly for synthesis of tryptophane and indirectly for the synthesis of auxins. Results from research by Quinlan-Watson (23) indicated that the effect of zinc and copper deficiency on aldolase activity are similar to the same deficiency effects on auxin as reported by Skoog (29) and Tsui (33). With oats (Avena sativa var. Algerian) and subterranean clover (Trifolium subterraneum L.) as test plants, Quinlan-Watson (23) found that the aldolase activity of the copper deficient plants remained nearly normal in each of the test plants until after deficiency was severe and visual symptoms were apparent. As noticed before in relation to auxin activity and zinc deficiency this research demonstrated a sharp decrease in aldolase activity due to zinc deficiency in oat and clover plants before visual zinc deficiency symptoms were apparent. Aldolase is the enzyme which catalyses the reversible reaction between hexose diphosphate and triose phosphate.

In addition to his research demonstrating the essentiality of zinc for synthesis of tryptophane from which auxin is synthesized, Tsui (32) also examined water relations and osmotic pressures of zinc deficient plants. A greatly decreased water content occurred simultaneously with retarded growth of zinc deficient plants. Within two days after zinc application to these plants the water content and the osmotic pressure of the plant tops increased, the latter increasing from 5 to 9 atmospheres. This increased water content was accompanied by a resumption in growth.

Cellular Derangements and Other Growth Abnormalities
as Affected by Zinc Content

As earlier recorded from Thorne (31), the occurrence of rosette in orchards growing in available zinc deficient soils, especially in peach and apricot orchards, is very common in the West and other parts of the country. Reed (25) observed that the earliest detection of abnormalities in zinc deficient apricot buds is noted by the strong affinity of certain meristematic cells for dyes, followed later by premature vacuolization and polarization. These hypoplastic conditions were clearly evident in late winter before bud emergence. The initial derangements in peach buds were evident as vacuolization with less emphasis on hyperchromatization of the meristematic cells.

Reed (25) stated that abnormalities of shoot growth and appearance can in part be explained by the appearance and disappearance of phenolic compounds. With zinc deficient plants it was apparent that in early spring when shoot growth was most rapid, substances believed to be tannins were replaced by phloroglucinol, especially in the more active cells. As the tissues entered differentiation, tannic material reappeared in certain cells and resulted in the conspicuous enlargement of the cells and retarded cellular mitosis. At the same time the cells of the apical meristems of these same stems exhibited normal multiplication and enlargement. The cells of these normally appearing apical meristems were free of phenolic compounds. Normally the concentration of phenolic materials in buds of healthy plants is a minimum in the early spring during rapid growth and reaches a maximum in the fall prior to the resting period. However, in

zinc deficient plants this accumulation of phenolic compounds appears earlier and in heavier concentrations. Reed further reported the principal effects of zinc deficiency on deficient trees appeared to be reflected in the condition of hypoplasia created, the polarization of cell contents, and the restriction of cell multiplication in the apical region. The accumulation of phenolic substances in the vacuoles of zinc deficient plants is reported to have resulted in increased cell size, but was not associated with necrosis.

The importance of nutrient element balance was demonstrated by Brown and Tifflin (9) on a Tulare clay. This is a known zinc deficient and potentially iron deficient soil that developed from an old lake bed. Of some 14 plant species grown on this soil, zinc deficiencies became evident on red kidney beans, okra, tomatoes, dill, cotton and corn. No deficiency symptoms were apparent on barley, wheat, Hawkeye soybeans or millet. Iron chlorosis was evident on both PI-54619-5-1 soybeans and *Sesuvium portulacastrum* when growing on both zinc-treated and untreated soil. When applications of zinc were applied to plants growing on zinc deficient soil, iron chlorosis appeared on corn and millet plants. This apparently zinc-induced iron chlorosis was not evident on any other plants.

The Effect of Nitrogen Carrier on Soil Reaction and Consequent Zinc Availability

In relation to the influence of nitrogen carrier on soil pH and zinc availability, research has been conducted by Viets et al. (36) on a Ritzville fine sandy loam. The research examined the effects of nitrogen carrier upon native soil zinc uptake by plants. Nitrogen was applied to

the test plants, milo and Ladino clover, as NaNO_3 and as $(\text{NH}_4)\text{SO}_4 \cdot 7\text{H}_2\text{O}$. After two croppings the soil pH ranged from 5 to 7.3 depending upon the nitrogen carrier used. The use of NaNO_3 resulted in a higher soil pH and reduced zinc availability. Four pounds of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ applied to the pots receiving NaNO_3 gave the same response as the uptake of native soil zinc from the pots receiving applications of $(\text{NH}_4)\text{SO}_4$.

The Effect of Phosphorus on Zinc Availability

The inability of zinc deficient plants to cope with heavy applications of soil phosphorus has long been recognized. Reed (24) reported that the extrastelar region and the phloem of the stems of zinc deficient plants contained greater amounts of inorganic phosphate and phenoloxidase than normal non-deficient plants. Normal cellular activity within these zinc deficient plants was profoundly disrupted due to an altered phosphate turnover. Leaves of zinc deficient plants contained less sucrose and starch than normal non-deficient leaves but they contained more reducing sugars. This was taken as evidence that one of the essential enzyme systems had failed or was blocked within these zinc deficient plants.

There is evidence to suggest the effect of phosphorus applications on available soil zinc depends upon the soil reaction. Bingham (5) suggested that phosphorus applied on an acid soil results in reduced zinc absorption while application on an alkaline soil results in increased zinc solubility.

The effect of excess phosphorus on available soil zinc at higher pH values is uncertain but some insight into this is presented by Jurinak and Inouye (17). They obtained zinc orthophosphate $Zn_3(PO_4)_2 \cdot 4H_2O$ by titrating a solution of zinc and KH_2PO_4 with NaOH. The pK_{sp} calculated from the dissociation of this orthophosphate at its isoelectric pH value was 47.9. It was noticed that as the solution pH reached and surpassed 8.63 the zinc tended to become more soluble. This was believed to be due to the zinc-orthophosphate precipitate changing from a granular to a gelatinous form. At this point analyses became uncertain and zinc concentrations reported above 8.63 must be regarded with caution.

There is much evidence to suggest phosphorus induced zinc deficiency. This has been demonstrated by Burleson et al. (11) using red kidney beans (Phaseolus vulgaris) as test plants in greenhouse experiments. Applications of phosphorus resulted in increasing phosphorus absorption and decreasing zinc absorption. Likewise applications of zinc resulted in increasing zinc absorption and decreasing phosphorus absorption. When both phosphorus and zinc were applied simultaneously absorption of both phosphorus and zinc was depressed. Similar results were reported by Rogers and Wu (27) who were working with Florida 167 variety of oats on a virgin Lakeland fine sand. They found that the zinc content of oats decreased to an almost constant value with increasing rates of phosphorus applications, while such phosphorus applications increased phosphorus content. An increase in zinc absorption resulted from applications of zinc. Native soil zinc absorption was decreased by both applications of phosphorus and lime. Burleson et al.

concluded that phosphorus may induce zinc deficiencies on some crops under certain soil and climatic conditions. Direct evidence of this conclusion was presented by Ellis et al. (13). Clear evidence of phosphorus induced zinc deficiency was indicated by the presence of visual zinc deficiency symptoms and reduction in growth of field beans following sugar beets on a calcareous Wisner clay loam. The preceding crop of sugar beets had received heavy applications of phosphorus and a high residual phosphorus content remained in the soil. From greenhouse investigations it was also evident that zinc deficiencies can be expected to be more severe on cold, wet soils such as are encountered during the early part of the growing season. Michigan hybrid corn, number 250, was transplanted to pots under controlled temperatures of 75° and 55° and after 36 days of additional growth were analyzed for total zinc and phosphorus contents. This decrease in temperature from 75° to 55° F decreased zinc concentration of the corn tops from 310 to 73 ug per pot. The phosphorus concentrations were not nearly so significantly affected. Although these zinc contents were abnormally high due to contamination of the soil during processing, the effect of decreased temperature was apparent in decreasing zinc uptake by the corn plants.

Loneragan (18) reported that visual zinc deficiency symptoms appeared within four weeks on flax plants growing in a Jojonup gravelly sand which had received heavy applications of phosphorus. After six weeks the deficiency symptoms were at a maximum and were present in all pots which had received phosphorus applications. After this maximum appearance of deficiency symptoms the plants appeared to grow out of the deficiency or

recover. Increased rates of phosphorus application decreased both relative and absolute zinc contents of the plants. Greatest severity of zinc deficiency and maximum response to zinc application resulted at the highest level of phosphorus application.

Zinc Availability as Related to Carrier

Boawn et al. (7) found plant absorption from a zinc chelate to be greater than absorption from $ZnSO_4 \cdot 7H_2O$, a stripping acid residue, ZnO , $Zn_3(PO_4)_2$, $ZnCO_3$, blast furnace slag, zinc frits, and zinc granules. The zinc chelate used was Sequestrene NA27_n (disodium zinc ethylenediaminetetraacetate) manufactured by the Alrose Chemical Company. This was determined by growing grain sorghum in pots containing Ritzville fine sandy loam. Plant absorption of zinc from the stripping acid residue, ZnO , $Zn_3(PO_4)_2$, and $ZnCO_3$ was found to be comparable to the absorption with $ZnSO_4 \cdot 7H_2O$. Only a slight response was obtained by use of blast furnace slag and no response was obtained by the use of three frit materials. Plant absorption from the zinc granules was found to equal or to be only slightly less than absorption from $ZnSO_4 \cdot 7H_2O$.

Total and Available Zinc Content of Representative Soils

Only limited research has been conducted in determining the total and available zinc contents of soils. Woltz et al. (38) reported soil zinc analyses of twenty important agricultural soils of New Jersey. They found that the total zinc content of 13 soils selected from the Appalachian Province averaged 100 ppm and the total zinc content of seven soils of the

Coastal Plain averaged 41 ppm. The average concentration of extractable zinc in these soils was found to be 4 ppm and 1.8 ppm for the Appalachian Province and Coastal Plain, respectively. Alben and Boggs (1) determined the total zinc content of six calcareous pecan soils, four acid pecan soils, and six pecan soils which have both basic and acid horizons. The total zinc content of the surface 6 inches of the calcareous soils ranged between 76 and 146 pounds per acre with a mean of 107.7 pounds zinc per acre. The total zinc content of the surface 6 inches of the acid soils ranged from 18 to 66 pounds per acre with a mean of 32 pounds zinc per acre. The total zinc content of the surface 6 inches of the soils having both basic and acid horizons ranged from 8 to 126 pounds per acre with a mean of 51 pounds of zinc per acre. Lyman and Dean (19) determined the zinc content of five pineapple producing soils of Hawaii. These soils were found to contain from 0.5 to 3.9 ppm ammonium acetate soluble zinc at pH 4.6 with a mean of 1.42 ppm. The dithizone-extractable zinc content of 34 Kentucky soils ranged from 0.2 to 4.2 ppm with a mean of 1.24 ppm zinc (Massey (20)). Viets et al. (34) determined the NH_4Ac -dithizone extractable zinc content of a known zinc deficient soil of central Washington. Two profiles were sampled, one from an uncut area and one from an adjacent cut area. The extractable zinc content of the surface foot of these two profiles was 0.17 ppm and 0.04 ppm, respectively.

Estimation of Available Soil Zinc from Plant Concentrations

Nearpass (21) related available zinc in soil to yield-of-zinc curves. These curves were obtained by plotting total uptake of zinc in the aerial

portions of plants against the combined concentrations of available and fertilizer zinc in the soil, and could be described by logarithmic or parabolic equations. The estimated available soil zinc determined by solving the logarithmic equation was found to be positively correlated with the zinc contents of the control plants. The correlation coefficient was +0.800. The choice of plants affected the estimates of available zinc in other soils. Smaller values were obtained for these estimates when millet was selected than when oats or tomato plants were selected.

Analytical Methods for Zinc Analyses

Several analytical procedures for determining the zinc content of plant and soil samples have been proposed. A polarographic method has been reported by Barrows and Dresdoff (4). Perhaps the most widely accepted method is the dithizone (diphenylthiocarbazone) extraction method of Shaw and Dean (28). A simpler method requiring fewer mechanical operations is presented by Johnson and Ulrich (16). This latter method or "Zincon" method is meeting with increasing favor for analyses on both calcareous and noncalcareous soils.

EXPERIMENTAL PROCEDURES

Sampling

Seventy-eight soil samples were collected either from known zinc deficient Kansas soil profiles or from profiles suspected of being zinc deficient. These included noncalcareous samples from northeastern Kansas

and calcareous samples from northcentral and western Kansas. Samples of three profiles and six surface samples were collected from Shawnee county within the Kansas River valley. One profile was sampled within the Republican river valley in Geary county. Two surface samples were collected from Brown county and one surface sample from Pottawatomie county. In north-central Kansas six profiles were sampled in Osborne county and one profile was sampled in Smith county. The samples were taken at various depths within the profiles. Thirty samples were obtained from western Kansas by Dr. N. L. Nossaman of the Garden City Branch Experiment Station representing the Richfield silt loam soils of Lane, Wichita, Hamilton, Haskell, and Morton counties. In addition one surface sample was collected from Stafford county in central Kansas. The legal descriptions and sampling depths of the samples collected for this research are presented in Table 1.

Analytical Procedures

The profile samples were collected in cardboard containers and brought to the laboratory for processing and analyses. As a precaution against possible zinc contamination the samples were processed using a wooden roller and a 40-mesh stainless steel sieve. Five grams of processed soil were extracted in 100 ml polyethylene centrifuge tubes using 50 ml of 0.2 N HCl as the extractant. After stirring, the samples and extractant were stoppered with polyethylene stoppers and placed on a shaker for a minimum of one hour in order to insure that all free carbonates had reacted and that equilibrium had been reached. At this point a small amount of the extractant was removed and its pH determined. In order to insure complete extraction of available

zinc the equilibrium pH of the extracting solution must be below pH 5. With certain highly calcareous soils it was necessary to extract with 0.4 N HCl in order to obtain an equilibrium pH below 5. The samples were then centrifuged until the supernatant liquid was clear. A 25 ml aliquot of the supernatant liquid was withdrawn and taken to dryness. The residue was brought into solution by adding 5 ml of 2.0 N HCl. Zinc analysis was then conducted by the "Zincon" method as presented by Johnson and Ulrich (16) and as modified by Ellis (13). In accordance with this procedure, the residue, after being brought into solution by the addition of 5 ml of 2 N HCl, was passed through an anion exchange resin column. The resin column is saturated with chloride ions by passing 5 ml of 2 N HCl through the column prior to the passage of the sample. The zinc ions form a complex anion believed to be $ZnCl_4^{=}$ which is quantitatively adsorbed by the resin. Interfering ions were removed from the column by three successive 20 ml washings of normal KCl and the effluent was discarded. Fifty ml volumetric flasks were then placed under the resin columns and the zinc was extracted and collected by two successive 20 ml additions of 0.1 N $NaNO_3$. The 50 ml volumetric flasks were then removed and the resin columns were regenerated by passing 35 ml of 2 N HCl through them. This re-saturates the resin column with chloride ions. Immediately before the next determination 5 ml of 2 N HCl were passed through the resin columns. Five ml of zincon-buffer solution were then added to the 40 ml $NaNO_3$ filtrate and the solution was made to volume by the addition of re-distilled water or distilled water that had been passed through a resin column. The

optical density was then determined by use of a Coleman junior spectrophotometer. The absorbance was read at a wavelength setting of 620 mu. The zinc concentration of the solution was obtained from the standard curve. The preparation of the resin columns, standard curve, zincon-buffer solution, and other solutions and materials necessary for the analysis is presented in Appendix II.

Titrateable alkalinity of the samples was determined essentially by the method presented by Nelson et al. (22). Successive 5 ml increments of 0.49006 N HCl were added and after equilibrium was reached the pH was determined and recorded. Smaller additions of 0.0098 N HCl were required for soils exhibiting extremely low buffer capacities. Additions of acid were continued until the soil pH was lowered below pH 5. Graphs of pH vs. ml HCl were prepared and from these the milliequivalents of acid required to lower the soil pH of 100 g of soil to pH 5 was determined by inspection. The titrateable alkalinity values are presented in Table 1.

RESULTS AND DISCUSSION

Soil samples representing four profiles and nine surface samples were collected from northeastern Kansas. Samples representing three of the profiles and six of the surface samples were collected from the Kansas river valley within Shawnee county. All of these samples were taken from areas that had been cut and leveled for irrigation purposes. The Kansas river valley is composed of young alluvial soils having only an A/C profile. Normally zinc is concentrated within the surface or organic horizon but this cannot be expected with profiles on cut areas. However, it is noticed that

the surface 10 inches of the profile represented by sample numbers 30 through 32 does contain a relatively high concentration of available zinc. This area was leveled for irrigation six years ago and the zinc accumulation in the surface is believed to be due to the depositing of zinc in this developing organic horizon by decaying plant tissue. Within each of these three profiles there exists an accumulation of available zinc below the surface horizon. Plants in early vegetative stages of growth when growing on cut areas often exhibit severe zinc deficiency symptoms. Often these plants grow out of the deficiency as they approach maturity. This occurrence has been commonly reported in the Kansas river valley. This is especially evident with respect to the area represented by the profile in section 29, township 10 S. range 13 E. (sample numbers 36, 37, and 38). A tentative explanation may be that prior to cutting and leveling for irrigation purposes there existed below the region of root development a region of normal zinc concentration that had not been used by growing crops. This region, after cutting appears within the root zone of the soil profile. Therefore, young plants growing in the depleted horizon above may show severe zinc deficiencies and then appear to outgrow them as their roots later begin to absorb zinc from this region.

Zinc becomes available at lower pH values and decreases in availability as the soil pH rises. Therefore, a high soil pH or a high titratable alkalinity is usually associated with low zinc availability. This inverse relationship with respect to titratable alkalinity is especially apparent in the profile represented by sample numbers 36 through 38. Only slight differences occur with respect to titratable alkalinity and pH in this profile and the other two profiles sampled in this area.

The six surface samples from Shawnee county were a composite of many surface samples taken at random over the immediate area. These samples were not taken from areas known or suspected of being as zinc deficient as were the profile samples. As could be expected, these samples were found to contain higher concentrations of available zinc.

Two surface samples were collected from a cut and an uncut area in Brown county. These samples correspond to sample numbers 46 and 47, respectively. Available zinc is relatively high in both of these areas with the uncut area being the highest. Also the sample from the uncut area, containing the higher zinc concentration, had a lower soil pH and titratable alkalinity value. However, the difference in pH was very slight.

One surface sample was selected from a cut area in Pottawatomie county. This sample was found to contain a high concentration of available zinc and was accompanied with the highest titratable alkalinity value of any sample from northeast Kansas. No explanation concerning this simultaneous occurrence of high zinc concentration and titratable alkalinity is proposed.

One profile was sampled from an uncut area of the Republican river valley in Geary county. A high available zinc concentration was found in the surface horizon. The available zinc content of the lower horizons decreased uniformly with increase in depth. Usually an increasing free carbonate concentration is associated with decreasing available zinc content and increasing sample depth. This is not evident in this instance, since the free carbonate concentration within this profile, as indicated by the titratable alkalinity value, is relatively constant. Also, soil pH was nearly constant throughout the profile.

Seven profiles were sampled from both cut and uncut areas in north-central Kansas. Six profiles were sampled in Osborne county, and one in Smith county. The profiles from the uncut areas contained appreciable concentrations of available zinc in the surface organic horizons, but the zinc content decreased with increasing depth of sampling. An unusually high available zinc content was found in three of these profiles from the uncut areas below the organic horizon. This included the profiles represented by sample numbers 1 through 4, 5 through 8, and 24 through 26. Generally the inverse relationship between available zinc concentration, and titratable alkalinity and soil pH held with respect to these samples; however, the changes in soil pH were very slight. A direct relation between available zinc concentration and soil organic matter content is evident for these profiles. A high available phosphorus content is also generally related to a high available zinc content within the profiles.

A sharp decrease in available zinc content and organic matter content occurred in the cut areas. This decrease in available zinc content was approximately 50% within the profiles represented by sample numbers 13 through 16 and 21 through 23. It is apparent that a lower soil horizon within these profiles contained a higher available zinc concentration. The presence of this horizon of higher concentration as noted before in cut areas is verified by reports of zinc deficient crops which appear to grow out of the zinc deficiency as the season progresses. The concentration of free carbonates as denoted by the titratable alkalinity decreases with increasing depth within the profile on these cut sites. This is consistent with a horizon of higher available zinc content occurring below the surface.

However, there was no consistent decrease in soil pH corresponding to the decrease in free carbonates. This is due to the insolubility of calcium carbonate. A nearly constant phosphorus content was evident at all depths sampled.

A surface sample was collected from the sandy lands research station in Stafford county. This surface sample from an uncut area contained a low available zinc concentration. This was also accompanied by a relatively low soil pH and titratable alkalinity value. Severe zinc deficiencies could occur on this soil if placed under irrigation and heavy fertilization for maximum yield.

Five profiles were sampled in western Kansas to represent the prevalent calcareous Richfield silt loam. These profiles were selected from Morton, Lane, Hamilton, Wichita, and Haskell counties. Although these profiles were from areas that were uncut for irrigation purposes, varying amounts of surface soil had been removed by wind erosion. It is readily apparent that in general these soils contain appreciable concentrations of available zinc within the surface horizons and decrease in zinc content with increasing depth. Also the inverse relationship between available zinc concentration and titratable alkalinity and soil pH is evident, i.e., high zinc concentration is associated with low soil pH and titratable alkalinity. Organic matter content and in general available phosphorus content are directly related to zinc content on these uncut profiles.

Table 1. Chemical data for soil profiles selected for study of available zinc.

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs/A)	Titrateable alkalinity (me/100g)	ppm Zinc (soil)
1	NW1/4, SE1/4 of NE1/4 Sec. 24, T7S, R12W Osborne	I316 1/20-8	0-8	8.3	30	8.20	5.28
2	"	"	8-15	8.4	15	17.80	4.58
3	"	"	15-24	8.3	5	32.30	1.72
4	"	"	24-32	8.4	6	28.70	2.23
5	NW1/4, NE1/4 of NE1/4 Sec. 21, T7S, R12W Osborne	I2611 1/20-10	0-7	8.1	27	2.70	3.43
6	"	"	7-12	7.8	16	2.10	4.93
7	"	"	20-24	7.9	28	7.40	4.55
8	"	"	30+	8.6	12	81.30	2.37

Table 1. (cont'd.)

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs./A)	Titratable alkalinity (me/100g)	PPM Zinc (soil)
9	SE1/4, SW1/4 of SE1/4 Sec. 33, T6S, R14W Osborne	No de-tailed class. avail.	0-6	8.4	12	14.30	3.10
10	"	"	6-12	8.3	5	26.90	1.53
11	"	"	20-26	8.5	12	9.6	0.70
12	"	"	34-40	8.5	25	8.6	1.70
13	SW1/4, NW1/4 of SE1/4 Sec. 7, T7S, R15W Osborne	No de-tailed class. avail.	0-6	8.6	12	55.9	1.60
14	"	"	6-12	8.8	8	29.4	1.88
15	"	"	18-24	8.6	12	34.0	3.01
16	"	"	30-36	8.9	10	27.4	0.80

Table 1. (cont'd.)

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs/A)	Titratable alkalinity (me/100g)	PPM Zinc (soil)
17	NE1/4, NE1/4 of NW1/4 Sec. 9, T7S, R14W Osborne	T2613 I/2U-14	0-6	8.1	9	36.1	2.63
18	"	"	6-18	8.3	6	66.4	3.34
19	"	"	18-20	8.4	12	100.9	0.20
20	"	"	30-36	8.6	8	90.6	1.55
21	NE1/4, NE1/4 of NE1/4 Sec. 12, T5S, R14W Smith	No de-tailed class. avail.	0-8	8.5	6	58.2	1.40
22	"	"	18-24	8.4	6	33.3	1.44
23	"	"	24-30	8.5	6	53.9	3.00
24	SE1/4, NE1/4 of SW1/4 Sec. 8, T7S, R13W Osborne	2613 1U-12	0-8	8.0	24	1.7	5.37
25	"	"	8-16	7.5	13	1.4	4.18
26	"	"	24-30	7.5	9	1.4	2.19

Table 1. (cont'd.)

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs/A)	Titrateable alkalinity (me/100g)	ppm Zinc (soil)
27	NE1/4, NE1/4 of SE1/4 Sec. 12, T11S, R4E Geary	Cass fine sandy loam	0-8	7.4	110	1.0	3.31
28	"	"	8-17	7.4	55	1.2	2.55
29	"	"	17+	7.5	48	0.8	1.28
30	SE1/4, SW1/4 of SE1/4 Sec. 13, T11S, R14E Shawnee	T332 1/20-12	0-10	6.5	8	0.8	3.70
31	"	"	12-24	6.7	5	0.9	2.23
32	"	"	24-30	7.1	8	0.8	4.00
33	NE1/4, NE1/4 of SW1/4 Sec. 35, T10S, R13E Shawnee	C02 IX-12	0-10	6.9	24	1.0	1.98
34	"	"	10-24	6.9	15	0.8	5.25
35	"	"	24-30	6.7	26	1.1	2.60

Table 1. (cont'd.)

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs/A)	Titratable alkalinity (me/100g)	PPM Zinc (soil)
36	SW1/4, NW1/4 of NE1/4 Sec. 29, T10S, R13E Shawnee	T43 I/2U-12	0-10	7.2	9	0.6	1.1
37	"	"	10-24	6.9	10	0.5	3.46
38	"	"	24-30	6.9	13	0.4	4.58
39	SW1/4, NW1/4 of SE1/4 Sec. 8, T11S, R14E Shawnee	T312 I/2U-12	0-6	6.2	70	1.4	5.16
40	SE1/4, SW1/4 of SW1/4 Sec. 30, T10S, R13E Shawnee	IH823 I/2U-10	0-6	6.8	70	1.1	4.15
41	SW1/4, NW1/4 of SE1/4 Sec. 8, T11S, R14E Shawnee	T312 I/2U-12	0-6	6.3	70	1.4	6.92
42	SE1/4, SW1/4 of SW1/4 Sec. 30, T10S, R13E Shawnee	IH823 I/2U-10	0-6	6.7	75	0.9	4.0
43	NE1/4, NE1/4 of SW1/4 Sec. 35, T10S, R13E Shawnee	002 IX-12	0-6	5.6	80	1.0	2.75

Table 1. (cont'd.)

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs/A)	Titrateable alkalinity (me/100g)	PPM Zinc (soil)
44	NE1/4 of NE1/4 of NE1/4 Sec. 11, T10S, R10E Pottawatomie	H62H6 I/2U-8	0-6	7.0	80	3.9	5.15
45	NE1/4, NE1/4 of SE1/4 Sec. 16, T24S, R13W Stafford	No de-tailed class. avail.	0-6	6.1	37	0.3	2.58
46	Sec. 17, T3S, R16E Brown	Grundy silty clay loam	0-6	5.7	55	1.0	4.77
47	NE1/4, NE1/4 of NE1/4 Sec. 10, T2S, R18E Brown	Marshall and Sharpsburg	0-6	5.6	55	0.2	5.70
48	SW1/4, NW1/4 of NE1/4 Sec. 29, T10S, R13E Shawnee	T43 I/2U-12	0-6	6.2	38	0.4	2.40
49	SW1/4, SW1/4 of SW1/4 Sec. 23, T35S, R42W Morton	Richfield silt loam	0-6	7.5	70	2.11	4.17
50	"	"	6-11	7.6	12	2.06	1.57
51	"	"	11-15	8.2	6	12.74	1.90

Table 1. (cont'd.)

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs/A)	Titrateable alkalinity (me/100g)	ppm Zinc (soil)
52	SW1/4, SW1/4 of SW1/4 Sec. 23, T35S, R42W Morton	Richfield silt loam	15-19	8.2	10	44.1	2.65
53	"	"	19-30	8.5	6	145.0	1.91
54	"	"	30-50	8.4	20	145.0	0.83
55	NW1/4, NE1/4 of NE1/4 Sec. 1, T20S, R26W Lane	Richfield silt loam	0-5	7.5	20	2.5	3.40
56	"	"	5-9	7.5	11	2.3	3.12
57	"	"	9-17	8.0	8	4.1	2.86
58	"	"	17-26	8.2	20	196.1	2.56
59	"	"	26-51	8.2	12	84.3	1.07
60	"	"	51-64	8.4	26	58.8	2.86

Table 1. (cont'd.)

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs/A)	Titrateable alkalinity (me/100g)	PPM Zinc (soil)
61	SW1/4, SW1/4 of SW1/4 Sec. 14, T22S, R40W Hamilton	Richfield silt loam	0-4	7.4	70	2.6	3.07
62	"	"	4-8	7.5	47	2.5	3.48
63	"	"	8-13	7.6	12	1.8	1.12
64	"	"	13-25	8.6	13	127.4	1.29
65	"	"	25-37	8.4	21	197.0	0.96
66	"	"	37-62	8.6	14	104.9	1.27
67	SE1/4, SE1/4 of SE1/4 Sec. 20, T18S, R36W Wichita	Richfield silt loam	0-4	7.1	75	2.2	5.4
68	"	"	26-48	7.4	53	2.2	3.55
69	"	"	20-26	8.1	14	2.2	1.08
70	"	"	16-20	8.0	14	49.0	0.40
71	"	"	8-16	8.4	29	196.0	1.11
72	"	"	4-8	8.4	14	122.5	0.41

Table 1. (concluded)

Sample No.	Legal description and county	Soil type	Depth of sample (inches)	pH	Available phosphorus (lbs/A)	Titrateable alkalinity (me/100g)	ppm Zinc (soil)
73	SW1/4, NW1/4 of NW1/4 Sec. 4, T29S, R33W Haskell	Richfield silt loam	0-6	7.8	47	2.0	4.38
74	"	"	6-14	8.4	10	2.5	2.36
75	"	"	14-18	8.7	9	3.9	2.10
76	"	"	18-22	8.5	6	45.1	0.91
77	"	"	22-42	8.4	26	142.1	1.35
78	"	"	42-60	8.3	24	105.8	0.07

SUMMARY

A study was conducted to examine the available zinc content of known or suspected zinc deficient Kansas soils.

Soils from cut areas which had been leveled for irrigation purposes were found to contain low concentrations of available zinc. Crops growing on these soils are often reported to exhibit severe zinc deficiency symptoms. This is explained as the zinc is continually redeposited in the organic horizon by decaying plant material and when this horizon is removed in preparation for irrigation much of the soil's available zinc supply is lost. Also when the surface horizon is removed from calcareous soils either by erosion or in preparation for irrigation a free carbonate concentration is often exposed at the surface. Available zinc readily becomes fixed under these conditions. Mineralization of zinc occurs primarily under slightly acid to acid conditions.

Often zinc deficient crops growing on cut areas under irrigation are reported to grow out of the deficiency. This tendency can be explained by the results of this study since a horizon of high available zinc concentration was found to exist below the surface in most of these cut profiles.

The available zinc content of the profiles from the uncut areas of both the calcareous and noncalcareous areas was found to be concentrated within the organic horizon, thereafter decreasing within the lower horizons. This direct relation between available zinc concentration and organic matter content is to be expected. Also a general direct relationship was evident between available zinc concentration and available

phosphorus concentration. The decrease in available zinc content with depth is consistent with the fixation of zinc under alkaline conditions.

ACKNOWLEDGMENTS

Sincere appreciation is expressed to Dr. Rescoe Ellis, Jr., major professor, for his guidance and assistance during this study and in the preparation of this thesis.

Appreciation is given to members of the supervisory committee for their constructive criticism and suggestions in the preparation of this thesis.

Appreciation is extended to Drs. Jack V. Baird, Orville W. Bidwell, William C. Dahnke, Floyd W. Smith and Mr. Howard W. Wilkins for their assistance in selecting and describing known or suspected zinc deficient profiles in northcentral and northeastern Kansas. Appreciation is extended to Dr. Norman L. Nossaman for his assistance in securing the profile samples from western Kansas.

Partial financial assistance in the support of this project was obtained under Project No. 269, Agricultural Experiment Station, Kansas State University.

LITERATURE CITED

- (1) Alben, A. O. and Boggs, Hugh M.
Zinc content of soils in relation to pecan rosette. *Soil Sci.* 41:329-332. 1936.
- (2) Anomalous.
The Need for Zinc. American Zinc Institute, 292 Madison Avenue, New York 17, New York.
- (3) Barnette, R. M., Camp, J. P., Warner, J. D., and Gall, O. E.
The use of zinc sulphate under corn and other field crops. *Florida Agr. Exp. Sta. Bull.* 292. 1936.
- (4) Barrows, Harold L. and Drosdoff, Matthew
A rapid polarographic method for determining extractable zinc in mineral soils. *Soil Sci. Soc. Am. Proc.* 24:169-171. 1960.
- (5) Bingham, Frank T. and Garber, M. J.
Solubility and availability of micronutrients in relation to phosphorus fertilization. *Soil Sci. Soc. Am. Proc.* 24:209-213. 1960.
- (6) Boawn, Louis C. and Viets, Frank G., Jr.
Zinc deficiency of alfalfa in Washington. *Agron. J.* 44:276. 1952.
- (7) Boawn, Louis C., Viets, Frank, Jr., and Crawford, Carl L.
Plant utilization of zinc from various types of zinc compounds and fertilizer materials. *Soil Sci.* 83:219-227. 1957.
- (8) Brown, A. L., Krantz, B. A., and Martin, P. E.
Plant uptake and fates of soil-applied zinc. *Soil Sci. Soc. Am. Proc.* 26:167-170. 1962.
- (9) Brown, J. C. and Tiffin, L. O.
Zinc deficiency and iron chlorosis dependent on the plant species and nutrient-element balance in Tulare clay. *Agron. J.* 54:356-358. 1962.
- (10) Brown, Lamar C. and Wilson, Charles C.
Some effects of zinc on several species of Gossypium L. *Plant Phy.* 27:812-817. 1952.
- (11) Burleson, C. A., Dacus, A. D., and Gerard, G. J.
The effect of phosphorus fertilization on the zinc nutrition of several irrigated crops. *Soil Sci. Soc. Am. Proc.* 25:365-368. 1961.

- (12) Camp, A. F.
Zinc as a nutrient in plant growth. *Soil Sci.* 60:157-164. 1945.
- (13) Ellis, Roscoe, Jr., Davis, J. F., and Thurlow, D. L.
Zinc availability in calcareous Michigan soils as influenced by phosphorus level and temperature. *Soil Sci. Soc. Am. Proc.* 28:83-86. 1964.
- (14) Gall, O. E. and Barnette, R. M.
Toxic limits of replaceable zinc to corn and cowpeas grown on three Florida soils. *Agron. J.* 32:23-32. 1940.
- (15) Hiatt, A. J. and Massey, H. F.
Zinc levels in relation to zinc content and growth of corn. *Agron. J.* 50:22-24. 1958.
- (16) Johnson, C. M., and Ulrich, A. II.
Analytical methods for plant analysis. *California Agr. Exp. Sta. Bull.* 766. 1959.
- (17) Jurinak, J. J. and Inouye, T. S.
Some aspects of zinc and copper phosphate formation in aqueous systems. *Soil Sci. Soc. Am. Proc.* 26:144-147. 1962.
- (18) Loneragan, J. F.
The effect of applied phosphate on the uptake of zinc by flax. *Aus. J. of Sci. Res.* B4:108-114. 1951.
- (19) Lyman, Clarence and Dean, L. A.
Zinc deficiency of pineapples in relation to soil and plant composition. *Soil Sci.* 54:315-324. 1942.
- (20) Massey, H. F.
Relation between dithizone-extractable zinc in the soil and zinc uptake by corn plants. *Soil Sci.* 83:123-129. 1947.
- (21) Nearpass, D. C.
Estimation of available zinc in soils from yield-of-zinc curves. *Soil Sci. Soc. Am. Proc.* 20:482-488. 1956.
- (22) Nelson, J. L., Boawn, L. C., and Viets, F. G., Jr.
A method for assessing zinc status of soils using acid-extractable zinc and titratable alkalinity values. *Soil Sci.* 88:275-283. 1959.
- (23) Quinlan-Watson, T. A. F.
Aldolase activity of zinc-deficient plants. *Nature* 167:1033-1034. 1951.

- (24) Reed, Howard S.
Effects of zinc deficiency on phosphate metabolism of the tomato plant. *Am. J. of Bot.* 33:778-784. 1946.
- (25) Reed, Howard S.
Effects of zinc deficiency on cells of vegetative buds. *Am. J. of Plant Phy.* 28:10-17. 1941.
- (26) Riceman, D. S. and Jones, G. B.
Distribution of zinc and copper in seedlings of Subterranean clover (*Trifolium subterraneum* L.) in solution culture. *Aust. J. of Agr. Res.* 7:495-503. 1956.
- (27) Rogers, L. H. and Wu, chih-hwa
Zinc uptake by oats as influenced by application of lime and phosphate. *Agron. J.* 40:563-566. 1948.
- (28) Shaw, E., and Dean, L. A.
Use of dithizone as an extractant to estimate the zinc nutrient status of the soil. *Soil Sci.* 73:341-348. 1952.
- (29) Skoog, Folke
Relationships between zinc and auxin in the growth of higher plants. *Am. J. of Bot.* 27:939-951. 1940.
- (30) Thorne, D. W.
Zinc deficiency and its control. In A. G. Norman, ed. *Advan. Agron.* Academic Press, Inc., New York. IX:31-65. 1957.
- (31) Thorne, D. W. and Wann, F. B.
Nutrient deficiencies in Utah Orchards. *Utah Agr. Exp. Sta. Bull.* 338. 1950.
- (32) Tsui, Cheng
The effect of zinc on water relations and osmotic pressure of the tomato plant. *Am. J. of Bot.* 35:309-311.
- (33) Tsui, Cheng
The role of zinc in auxin synthesis in the tomato plant. *Am. J. of Bot.* 35:172-179.
- (34) Viets, F. G., Jr., Boswn, L. C., and Crawford, C. L.
Zinc contents and deficiency symptoms of 26 crops grown on a zinc-deficient soil. *Soil Sci.* 78:305-316. 1954.
- (35) Viets, F. G., Jr., Boswn, L. C., and Crawford, C. L.
Zinc content of bean plants in relation to deficiency symptoms and yield. *Plant Phy.* 29:76-79. 1954.

- (36) Viets, Frank G., Jr., Poawn, Louis C., and Crawford, Carl L.
The effect of N and types of N carrier on plant uptake of
indigenous and applied zinc. Soil Sci. Soc. Am. Proc.
21:197-201. 1957.
- (37) Viets, F. G., Jr., Poawn, L. C., Crawford, C. L., and Nelson, C. E.
Zinc deficiency in corn in central Washington. Agron. J.
45:559-565. 1953.
- (38) Woltz, S., Toth, S. J., and Bear, F. E.
Zinc status of New Jersey soils. Soil Sci. 76:115-122.
1953.
- (39) Wood, J. G. and Sibly, Pamela M.
The distribution of zinc in oat plants. Aust. J. of Sci. Res.
E3:14-27. 1950.

APPENDIX I

A general soil fertility laboratory analysis was conducted on the 78 selected profile samples. These results are presented in Table 2.

Table 2. Percent organic matter and exchangeable potassium contents of the selected profile samples.

Sample No.	Depth of sample (inches)	Organic matter content (%)	Exchangeable potassium (lbs/A)
1	0-8	2.0	500+
2	8-15	1.7	500+
3	15-24	1.4	500+
4	24-32	1.0	452
5	0-7	1.6	500+
6	7-12	1.3	352
7	20-24	0.6	464
8	30+	0.6	500+
9	0-6	0.9	500+
10	6-12	0.6	349
11	20-26	1.3	357
12	34-40	1.1	487
13	0-6	0.5	500+
14	6-12	0.3	500+
15	18-24	0.4	500+
16	30-36	0.4	500+
17	0-6	1.4	500+
18	6-18	1.0	340
19	18-20	0.7	267
20	30-36	0.6	276
21	0-8	0.0	460
22	18-24	0.0	460
23	24-30	0.0	500+
24	0-8	1.2	500+
25	8-16	0.9	500+
26	24-30	0.5	500+
27	0-8	0.4	500+
28	8-17	0.9	387
29	17+	0.1	382

Table 2. (cont'd.)

Sample No.	Depth of sample (inches)	Organic matter content (%)	Exchangesble potassium (lbs/λ)
30	0-10	1.4	379
31	12-24	0.6	236
32	24-30	0.5	267
33	0-10	0.6	291
34	10-24	0.5	251
35	24-30	1.5	257
36	0-10	0.4	145
37	10-24	0.0	129
38	24-30	0.1	111
39	0-6	1.4	500+
40	0-6	0.9	365
41	0-6	1.6	500+
42	0-6	0.7	344
43	0-6	1.0	261
44	0-6	1.2	500+
45	0-6	0.8	205
46	0-6	2.2	310
47	0-6	2.6	500+
48	0-6	0.9	205
49	0-6	0.7	500+
50	6-11	0.7	500+
51	11-15	0.5	500+
52	15-19	0.5	500+
53	19-30	0.4	500+
54	30-50	0.2	500+
55	0-5	0.2	500+
56	5-9	1.0	500+
57	9-17	0.7	500+
58	17-26	0.4	500+
59	26-51	0.2	500+
60	51-64	0.0	500+
61	0-4	1.3	500+
62	4-8	0.8	500+
63	8-13	0.5	500+
64	13-25	0.4	500+
65	25-37	0.6	500+
66	37-62	0.0	500+

Table 2. (concluded)

Sample No.	Depth of sample (inches)	Organic matter content (%)	Exchangeable potassium (lbs/A)
67	0-4	1.7	500+
68	4-8	1.6	500+
69	8-16	0.8	500+
70	16-20	0.5	500+
71	20-26	0.3	500+
72	26-48	0.0	500+
73	0-6	1.3	500+
74	6-14	0.7	500+
75	14-18	0.7	500+
76	18-22	0.5	500+
77	22-42	0.5	500+
78	42-60	0.5	500+

APPENDIX II

Information concerning the preparation of the resin columns, standard curves, zincon-buffer solution, and other solutions and materials necessary for the analysis is presented below.

Preparation of the resin columns:

A small plug of Pyrex glass wool was placed at the base of each resin column and was held in place by the small constriction as indicated by Fig. 1. A slurry of resin prepared by adding distilled water to Dowex Ix8 20-50 mesh resin was poured into the tube until a 5 to 6 cm resin column was obtained. Air bubbles were prevented from forming within the resin columns by making repeated applications of a dilute slurry. The resin columns were then leached with 20 ml applications of concentrated HCl, 6 N HCl, 2 N HCl, and at last with 50 ml of redistilled water or distilled water that had been passed through a resin column. Before extracting available zinc from a soil sample, 35 ml of 2 N HCl were passed through each column. The above leachates were discarded.

Approximately eight extractions can be obtained from the resin columns before they fail to retain all the available zinc. After this the resin columns must be replaced.

Preparation of Standard Curves:

The standard curve was obtained by plotting optical density against concentration of zinc in the sample obtained from the standard solution. The standard solution was prepared by dissolving 0.1 g of reagent grade zinc metal in one liter of 2 N HCl. This 100 ppm zinc solution was then diluted by a factor of 10 to give a 10 ppm standard zinc solution. All dilutions were made in 2 N HCl. The volumes of the 10 ppm standard zinc

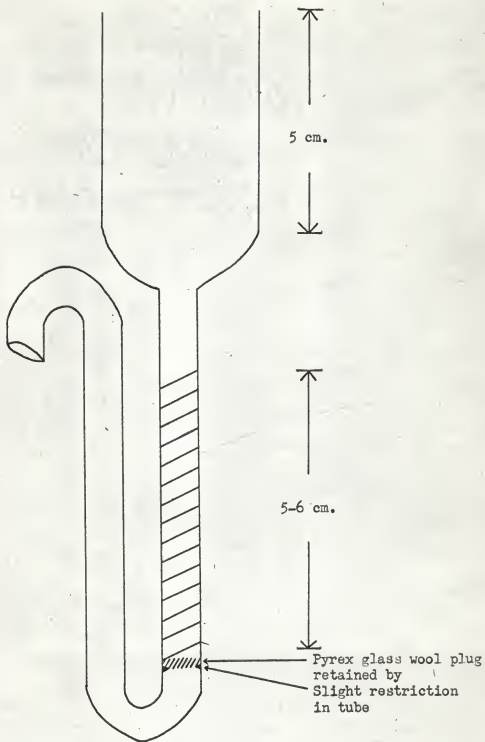


Fig 1. Diagram of resin column (16) for zinc analysis.

solutions chosen to prepare the standard curve for this research study were 0, 1, 2, 3, 4, 5, and 6 ml. When brought to final volume (50 ml) prior to reading, these volumes gave concentrations of 0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 ppm zinc, respectively. Each volume of the standard solution was diluted to 25 ml in 2 N HCl acid before being passed through the resin columns. From this point on the procedure for determining zinc content of the standards is the same as for determining available zinc content of soil samples.

The resulting standard curve is a straight line passing through the origin.

Preparation of the buffer solution:

The buffer solution was prepared by dissolving 31 grams of boric acid and 37 grams of potassium chloride in 800 ml of redistilled water or distilled water that has been passed through a resin column. The solution pH was then adjusted to 9.2 by the addition of approximately 50 ml of 6 N NaOH. The solution was then brought to a final volume of one liter.

Preparation of the zincon-buffer solution:

The zincon-buffer solution was prepared by dissolving 0.125 g of the zincon powder, $\text{o-}\{2\text{-}\sqrt{\text{C}}\text{-}(2\text{-Hydroxy-5-sulfophenylazo)benzylidene}\text{7-hydrazino}\}$ benzoic Acid Sodium Salt, in 250 ml of the buffer solution. The chemical formula of the Zincon powder is $\text{HOC}_6\text{H}_3(\text{SO}_3\text{Na})\text{N}_2\text{NC}(\text{C}_6\text{H}_5)_2$
 $\text{NNHC}_6\text{H}_4\text{COOH}$.

Preparation of hydrochloric acid solutions:

The HCl solutions are prepared by a series of dilutions of concentrated HCl assuming reagent grade concentrated HCl to be 12 N. Six N HCl is prepared by a 1:6 dilution of concentrated HCl, and 0.2 N HCl is prepared by a 1:10 dilution of the already prepared 2 N HCl. Usually no extra purification of reagent grade HCl is necessary but additional purity may be obtained by distillation.

Preparation of normal potassium chloride.

Dissolve 74.5 g of reagent grade potassium chloride in redistilled water or distilled water that has been passed through a resin column and dilute to one liter.

Preparation of 0.1 N sodium nitrate:

Dissolve 8.5 g of reagent grade sodium nitrate in redistilled water or distilled water that has been passed through a resin column and dilute to one liter.

Resins:

Dowex Ix8 20-50 mesh anion exchange resin.

Volumetric flasks:

Twenty-five and 50 ml Pyrex or Kimax volumetric flasks are required.

Funnels:

Sixty degree Pyrex funnels having a 50 mm top diameter are required.

Funnel and resin column supports:

Suitable aligned wooden supports are required to support the funnels and resin columns during the analyses.

ZINC AVAILABILITY IN PROFILES OF SELECTED KANSAS SOILS

by

DAVID ORION TRAVIS

B. S., Oklahoma State University, 1963

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Agronomy

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1965

An investigation of the available zinc supply of selected Kansas soil profiles was conducted. Samples representing four noncalcareous profiles in northeastern Kansas, seven calcareous profiles in northcentral Kansas, and five calcareous profiles in western Kansas were included. In addition nine surface samples were collected from northeastern Kansas. With the exception of samples representing one profile and one surface sample, all of the samples from northeastern Kansas were from areas that had been cut and leveled for irrigation purposes. Profile samples representing both cut and uncut areas were collected from northcentral Kansas while samples of profiles only from uncut areas were collected from western Kansas.

The available zinc content of the soil is normally associated with the surface organic horizon and decreases in concentration within the lower horizons. Fixation of the element occurs at near neutral or higher pH values. Mineralization of zinc occurs primarily at lower pH values. Therefore, an inverse relationship usually exists between available zinc supply and soil pH. A concentration of free carbonates lies at or below the surface of calcareous soils. When the organic horizon of these soils is removed by erosion or in preparation for irrigation the available zinc content of the profile is greatly reduced and often a calcareous horizon is exposed at the surface. The available zinc supply is then largely removed and the remainder is often fixed in an unavailable form. Crops growing under irrigation on these soils often show severe zinc deficiency symptoms. Evidence of this decreased available zinc supply in cut areas is shown by the results of this research study. These marked decreases in available zinc content were evident on newly cut sites of both calcareous

and noncalcareous soils. A near normal available zinc content was found in the surface horizon of a profile that had been cut six years ago. This is believed to be due to the gradual development of an organic horizon. It is also evident from the results that a lower horizon of higher available zinc concentration exists within most of the profiles from the cut areas on both the calcareous and noncalcareous soils. A tentative explanation is suggested that prior to cutting and leveling for irrigation purposes there existed below the region of root development a region of normal zinc concentration that had not been used by growing crops. After cutting this region appears within the rooting zone of the soil profile. Therefore, young plants growing in the depleted horizon above may show severe zinc deficiencies and then appear to outgrow them as their roots later begin to absorb zinc from this region. Field observations of young crops which appear to outgrow the deficiency symptoms tend to verify this explanation.

As could be expected the zinc concentration of the profiles from uncut areas is greatest within the organic horizon and decreases in the lower horizons. The inverse relationship between available zinc content and soil pH as affected by the concentration of free carbonates in the profile was evident. In general a direct relationship was found between available zinc and phosphorus concentrations within the profiles from the uncut areas.