THE UNIVERSITY OF MANITOBA

EFFECT OF RATE AND METHOD OF PLACEMENT OF $CuSO_4$ AND $ZnSO_4$ ON DRY MATTER YIELD AND NUTRIENT UPTAKE OF BARLEY (*HORDEUM VULGARE* L. VAR CONQUEST)

by

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ABSTRACT

Copper sulphate ($CuSO_4.5H_2O$) at rates varying from 0 to 1000 ppm Cu and $ZnSO_4.7H_2O$ at rates varying from 0 to 2000 ppm Zn were incubated for 7 days with Pine Ridge sand (Degraded Eutric Brunisol) and Lakeland clay loam (Gleyed Carbonated Rego Black), respectively. The higher rates were to simulate band application, whereas the lower rates were to simulate thorough mixing with the soil. The proportions of applied Cu and Zn extracted with water were very small (0.22-5.0%), were not appreciably affected by time of incubation, and decreased with increasing concentration of applied Cu or Zn. The proportions of applied Cu and Zn extracted with DTPA were considerably more (50 - 95%) than the proportions extracted with water, were not appreciably affected by rate and decreased slightly with time. The high proportions of applied Cu and Zn which were DTPA extractable suggested that much of the Cu and Zn which was not H_2O soluble was absorbed or complexed and therefore potentially plant available. Since the porportions of applied Cu and Zn which were H_2O or DTPA extractable, did not increase with increasing Cu and Zn, there was no evidence that banding Cu and Zn sulphates would increase their chemical availabilities.

The effect of rate and method of placement of $CuSO_4$ and $ZnSO_4$ into Pine Ridge sand and Lakeland clay loam, respectively, upon the growth and nutrient content of barley (Hordeum vulgare L.) were investigated in growth chamber studies. Concentration and total uptake of Cu and Zn into six week old barley shoots indicated that the most effective method of application of both $CuSO_4$ and $ZnSO_4$ was mixing throughout the soil, followed by banding with the seed which was more effective than banding

below the seed. Applying $CuSO_4$ or $ZnSO_4$ in a point below the seed was not effective in increasing Cu or Zn uptake. Plant Cu and Zn concentrations increased more than dry matter yield as rates of Cu and Zn sulphates were increased. In addition, mixing $CuSO_4$ or $ZnSO_4$ with the soil was not more effective than banding with the seed in increasing dry matter yield. The failure of dry matter yield to respond to micronutrient fertilization as much as Cu and Zn uptake resulted at least partially from Zn deficiency in the Cu experiment and Fe deficiency in the Zn experiment. Application of $CuSO_4$ decreased total Zn uptake from Pine Ridge sand to the extent that most plants did not contain enough Zn for their nutritional needs. Pine Ridge sand was not only deficient in Cu but also marginal in its ability to supply Zn to barley. Application of $ZnSO_4$ to Lakeland clay loam decreased total Fe to the extent that most plants were Fe deficient. Lakeland clay loam was therefore marginally deficient in Fe in addition to being deficient in Zn. Those additional Zn and Fe deficiencies made it impossible to determine optimal application rates for $CuSO_4$ and $ZnSO_4$ or to accurately determine plant Cu and Zn critical levels. Nevertheless, the critical Cu concentration in six week old barley shoots was estimated at 5.2 ppm and the critical Zn concentration at 12.5 ppm.

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I. PREFACE

Micronutrients are just as essential for plant growth as macroelements. Notwithstanding the fact that micronutrients are required for plant growth in amounts considerably lower than that of macronutrients required, the metabolism of plants is still strongly affected by the nutritional levels of microelements. Copper and Zn have been established as two micronutrients which constitute potential nutrient deficiency problems in Manitoba soils. Previous field and greenhouse research workers have established that Cu deficiencies occur mainly on acidic, leached, sandy Podzolic and Gray Luvisolic mineral soils as well as organic soils of south-eastern Manitoba, whereas Zn deficiencies are prevalent on soils with high carbonate contents.

Previous researchers have also diagnosed soil environmental factors, such as the levels of micronutrients and/or macronutrients, carbonates, organic matter, hydrous oxides of Al, Fe and Mn, etc., which are capable of accentuating Cu and Zn deficiencies. Apart from delving extensively into chemistry of Cu and Zn in soils, these workers also investigated with useful results, appropriate diagnostic extraction methods for assessing the levels of plant available soil Cu and Zn. They recommended suitable organic and inorganic Cu and Zn fertilizer carriers which, when properly applied to soils, can supply adequate Cu and Zn to plants. However, most of these previous investigations left some questions unanswered in that they did not delve deeply enough into which methods or rates of application of their recommended Cu and Zn fertilizer carriers would be most appropriate. Moreover, investigations were concentrated on crops such as corn or

field beans which are particularly susceptible to micronutrient deficiencies, thus neglecting important cereal crops such as barley and oats probably because of general fear that these crops might not bring about fruitful and conclusive research findings. This fear probably arose from the general assumption that these cereal crops are not as sensitive to micronutrient deficiencies.

Experiments were conducted, therefore, to:

(1) Assess the effect of time and method of placement of $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ on their chemical availabilities;

(2) Evaluate the influence of rates and methods of placement of $CuSO_4$ and $ZnSO_4$ on the yield and nutrient uptake of barley plants;

(3) Establish the critical levels of Cu and Zn in barley plants below which deficiencies of these micronutrients become inevitable.

II. REVIEW OF THE LITERATURE

A. IMPORTANCE OF Cu AND Zn IN HIGHER PLANTS

Copper is very much involved in the metabolism of higher plants and is therefore essential for normal plant growth. Copper is an essential constituent of several important enzymes (113). In addition, enzymes such as phenolases (121), cytochrome oxidase and probably poly-phenol oxidase (142) are strongly affected by the nutritional levels of Cu. Copper is also a metal activator for several other enzymes, including tyrosinase, laccase, ascorbic acid oxidase and butyryl-A-dehydrogenase (76, 177, 187). Copper is essential in photosynthesis and chlorophyll formation (46, 113). Copper deficiency in tungtrees, for example, resulted in decreased CO_2 absorption (96).

Zinc is also essential in plant metabolism. It is a component of several metallo enzymes, including a variety of dehydrogenases, proteinases and peptidases (142, 187). Zinc is also a metal activator for several plant enzymes, such as carbonic anhydrase which catalyses decomposition of H_2CO_3 to CO_2 and H_2O (46). The activity of tryptophan synthetase in Neurospora is decreased by Zn deficiency (122). In higher plants, tryptophan is a precursor for the plant growth substance indole-3-acetic acid which is also known as auxin (46). Considering that biosynthesis of IAA in higher plants is enhanced by Zn (142), and that Zn deficiency in potato decreases the level of IAA (162), Zn is likely necessary for the activity of tryptophan synthetase in higher plants.

Zinc deficiency also results in low RNA (ribo-nucleic acid) and

ribosome levels in a number of plant species (140). Ribosome stability in cytoplasm of Euglena gracilis is decreased by Zn insufficiency (141). In addition, soluble nitrogen components such as amino acids and amides accumulated in Zn deficient potato plants (140). This implies that Zn is involved in protein synthesis in higher plants.

B. COPPER AND Zn DEFICIENCY SYMPTOMS IN HIGHER PLANTS

Copper deficiency symptoms have been observed in many crops and vary considerably among those crops (54, 177). In corn, the younger leaves become yellow and stunted. As Cu deficiency becomes more severe, the older leaves become pale and the younger leaves die, with dead tissues appearing first along the leaftips and edges (177). Cu deficient cereal plants lose colour in the younger leaves. Eventually, leaf midribs break and leaftips become necrotic (177). Severely Cu deficient cereal plants fail to develop heads (33). Severely Cu deficient vegetable crops often fail to flower. The leaves of many Cu deficient vegetables lack turgor and develop a bluish greenish cast leading to chlorosis and curling (177).

Zinc deficiency symptoms have been observed in a number of crops including corn, sorghum, deciduous and citrus fruits, nut trees, tung trees, legumes, cotton, and several vegetable crops (3, 6, 12, 20, 22, 36, 54, 72, 136, 160, 168). Early Zn deficiency symptoms usually involve interveinal chlorosis of the older leaves (6, 177), appearing first at the tips and margins (46). In cotton, interveinal chlorosis is followed quickly by necrotic spotting (34, 113). In corn, chlorosis is followed by bleached tissue on each side of midrib and at the base of the leaf (177). Severe Zn deficiency often results in smaller

leaves, shortened internodes and stunted growth. Seed production in beans (Phaseolus vulgaris) and peas and fruit development in citrus are adversely affected by severe Zn deficiency (46). Zinc deficiency also causes defoliation, loss or absence of flowers (113) and increases in the period required for beans to reach maturity (22).

C. COPPER AND ZN DEFICIENT SOILS

Copper deficiencies were reported in numerous crops on organic (peat and muck) soils (8, 37, 66, 69, 72, 73, 104, 165, 177, 186). Highly weathered coarse-textured sandy mineral soils (8, 9, 66, 67, 72, 73, 137, 186, 187) often did not have sufficient exchangeable Cu for optimum growth of many crops. Examples of such soils are sandy soils of western U.S.A. (73), the sandy soils of Florida (137), podsols in eastern Canada receiving high annual precipitation (mean of 115 cm) (67), and several sandy soils on Prince Edward Island (66).

Manitoba has approximately 15 million hectares of organic soils of which approximately 100,000 hectares are suitable for agricultural development (165). In addition, there are many hectares of acidic sandy soils which one might expect to be Cu deficient. In fact, Cu deficiencies have been reported on some of these soils (37, 104, 144, 163, 166). Campbell and Gusta (37) reported that in field trials, peat deposits near Vivian could not supply sufficient Cu for the optimum growth of carrots (Daucus carota var sativa) and onions (Allium apa). Addition of Cu to carrots increased yield by 5.6 metric tons per hectare and improved the quality of onions. Racz (144) applied Cu in four corn and two sunflower trials on Almasippi sandy loams. In one corn trial on Almasippi sandy loam, there was a trend

towards increased yields but this was not statistically significant. Soper (166) obtained small statistically insignificant responses to Cu in alfalfa on Miniota sand and Pelon loamy fine sand. Greenhouse experiments conducted by McGregor (104) confirmed that Pine Ridge sand contained inadequate Cu for the growth of flax and that Stockton sand contained barely adequate quantities of Cu for the growth of flax.

Zinc deficiencies have been observed under widely varying environmental conditions. Low levels of available Zn have been found in humic gleysols, regosols and organic soils (7, 184). Zinc deficiencies are most common on calcareous soils (19, 48, 73, 83, 84, 97, 107, 120, 136, 146, 154, 177, 186) but also occur on highly leached soils (97, 107, 120) and on soils containing little organic matter (97, 120). Alteration of soil by man can also lead to Zn deficiencies. For example, soils under corrals, barnyards and orchards (97), intensively cropped soils (112), and calcareous subsoils exposed by levelling and furrowing for irrigation (54, 86, 97, 120, 177) sometimes contain low levels of available Zn. High levels of soluble silica in acid soils (152) and excesses of other micronutrients (177) may result in Zn deficiency. Zinc deficiency is often more pronounced when spring weather is particularly wet and cool (7, 42, 48).

Most of the cultivated soils in Manitoba are calcareous and therefore may be deficient in Zn (37, 84, 104, 144, 163, 165). In addition, environmental conditions such as cool, wet springs which may accentuate Zn deficiency are quite common. Racz (144) found that application of Zn to corn and sunflower on Almasippi loamy fine sand

resulted in small statistically insignificant yield increases. McGregor (104) also noted in a greenhouse experiment that a Plum Ridge calcareous soil was moderately Zn deficient while an Almasippi calcareous soil supplied barely adequate quantities of Zn for flax plants.

D. FORMS OF Cu AND Zn IN THE SOIL

The total amount of Cu in soil is often dependent upon the amount in the parent material. The average Cu content of the lithosphere is about 100 ppm whereas that of soil is reported to range between 2 - 100 ppm. The total amount of Cu in the soil, however, is not an indication of its biological availability (177).

The principal Cu containing minerals in the lithosphere are CuS, $Cu_2(OH)_2CO_3$ and $CuSiO_3$ (89). These weather to release Cu^{+2} into soil solution (183). Under slightly acid and oxidizing conditions, Cu combines with common anions in the soil solution to form compounds or complex ions which are water soluble (89). However, under alkaline or reducing conditions, insoluble compounds such as CuS, $Cu(OH)_2$, $CuCl_2$ and Cu_2O are precipitated (89).

Most of the Cu released into solution during weathering or decomposition of organic matter is adsorbed by soil particles (89) because Cu forms strong covalent bonds (129). The Cu^{+2} form is not only adsorbed strongly by clay but also adsorbed appreciably by quartz (11, 89). The Cu adsorptive capacity of clay minerals usually increases with pH (89, 147, 157).

Copper is also adsorbed readily by $Fe(OH)_3$, $Fe_2O_3.3H_2O$ and organic matter fractions (50, 73). Some Cu is also lost in drainage waters (132). Lindsay and Norvell (95) gave the equilibrium reaction

in a Cu-soil system as

$$Cu^{+2} + \text{soil} \rightleftharpoons \text{Cu-soil} + 2H$$

with solubility relationship

$$Cu^{+2} = 10^{3.2}(H^{+})^{2}$$

The level of Cu^{+2} in soil solution as predicted by this equation is far below that expected if complex ions, oxides, and carbonates of Cu were controlling the solubility of Cu (93). The level of Cu^{+2} in the soil solution decreases with increasing pH. However, Cu forms soluble and mobile complexes with organic matter more readily than does Zn. Upnto ,99%pofxCuainlythe9soil Solutionecanibeicomplexed with organic matter (73, 93). Even various copper hydroxide compounds and complex ions formed at pH values greater than 7.3 are strongly complexed by organic matter. Consequently, Cu deficiencies are not as prevalent as Zn deficiencies on calcareous soils even though the concentration of Cu^{+2} is related to soil pH (73,95).

The Zn concentration in the lithosphere is approximately 80 ppm. The total Zn concentration in the soil varies from 10 - 300 ppm but, like Cu, that range is not an indication of its availability to plants (177). Zinc in the lithosphere occurs in shales primarily as ZnS (Sphalerite) (183). Zinc containing minerals weather to release Zn^{+2} into soil solution (167, 183). Unlike Cu^{+2}, Zn^{+2} does not readily form soluble complexes with organic matter and Zn^{+2} remains dominant up to approximately pH 9.0 (183). Under alkaline conditions, Zn^{+2} may react with common anions in the soil solution to form compounds such as $Zn(OH)_2$ and $ZnCO_3$ (41, 120), particularly if the Zn^{+2} concentration is greater than 10^{-4} moles per litre (89). Zinc ions

released into solution may also be adsorbed and/or fixed by clay minerals (12, 147, 157), hydrous oxides of Fe, Al, and Mn (93), carbonates (183), and organic matter (89).

Norvell (95) gave the equilibrium reaction in a Zn-soil system as

$$Zn^{+2} + \text{soil} \rightleftharpoons \text{Zn-soil} + 2H^{+}$$

with the solubility relationship

$$(Zn^{+2}) = 10^{6}(H^{+})^{2}.$$

His equation not only suggests that the solubility of Zn^{+2} is highly pH dependent, but also that compounds such as ZnS, $Zn(OH)_2$, $ZnCO_3$ and complex ions are far too soluble to account for the small concentrations of Zn found in most soil solutions. In fact, $Zn(OH)_2$ and ZnS might very well be good fertilizers (18). Although ZnS is the principal Zn containing mineral in the lithosphere, it is likely that in soils the solubility of Zn is controlled by clay minerals, hydrous oxides, carbonates and organic matter.

Interaction of Cu and Zn with organic matter is very important in the chemistry of soil Cu and Zn. Organic matter can interact with Cu and Zn in many ways. Organically bound Cu and Zn can be mineralized and be made available to plants (89). Consequently, soils low in organic matter may be low in available Cu and Zn (97, 120). Conversely, Cu and Zn can be bound into metallo-organic complexes which are immobile and unavailable to plants (50, 73, 89, 93, 129). Consequently, the addition of organic matter may actually aggravate Cu and Zn deficiencies. Lastly, organic (matter) constituents can form mobile and labile complexes with Cu and Zn (43, 104, 130). In general, the formation of soluble Cu and Zn organic complexes is directly

related to the soluble organic fractions and not to total organic matter content of the soil (73).

Indigenous or applied Cu and Zn can form insoluble complexes with humic acids which are unavailable to plants (171). However, numerous other metallo-organic complexes are soluble and available to plants (130, 165, 171). These include individual biochemical molecules, such as organic acids, amino acids and fulvic acids. These constituents can convert insoluble metal complex ions and compounds which had precipitated at high pH (11, 89) into soluble and available metal complexes (71, 73, 93, 113, 165). Carboxyl groups and amides are ligands particularly involved in formation of complexes with metals by ion exchange, surface adsorption, chelation complex, coagulation and peptization (111).

Some natural chelating agents are produced by micro-organisms or excreted by plants and function in transporting Cu^{+2} and Zn^{+2} to plants' roots (49), or to lower soil horizons (71, 171). Biochemically synthesized chelating compounds include organic acids, peptides, protein molecules, amino acids, aliphatic acids and polysaccharides (60). Up to 99% of soluble Cu and 75% of soluble Zn occurs in soil as metallo-organic complexes (73, 93).

CONCLUSION

It may be summarized that Cu and Zn occur in the soil in at least five forms (183). These are: (a) water soluble Cu and Zn, the levels of which are usually very small; (b) exchangeable Cu and Zn which are also small except in soils very well supplied with these elements; (c) adsorbed, complexed or chelated forms of Cu or Zn, which make up

a far greater proportion than the above two forms because of high affinity with which clay, hydrous oxide and organic materials adsorb Cu and Zn; (d) Cu and Zn occluded in the secondary clay minerals and insoluble metal oxides; (e) Cu and Zn cations in primary minerals. It is thought that the water soluble, exchangeable and adsorbed, complexed or chelated forms of Cu and Zn are the most important pools supplying these metals to plants. The three forms are also thought to be in equilibrium (45), and consequently any change in one of them would result in changes in the other two forms. It is important, therefore, that soil tests for plant available Cu and Zn should extract a portion or all of the three forms.

E. METHODS OF ASSESSING PLANT AVAILABLE Cu AND Zn AND THEIR RESPECTIVE CRITICAL LEVELS

1. SOIL ANALYSIS

Micronutrient soil tests entail many problems which sometimes render the results inevitably questionable: (a) Plant requirements are so small that the prevention of possible contamination, even in the face of the most adequate precautions is often impossible. (b) Environmental conditions such as soil pH, carbonate content, soil texture, water content, soil colloids, temperature, and activities of other micronutrient metals can sometimes correct or induce deficiencies in soils with borderline deficiencies. (c) Errors can be caused by improper sampling and by soil variability. (d) Plants differ in micronutrient requirements and in their susceptibility to micronutrient deficiencies so that the test crop or variety might influence the interpretation of the results (60, 183).

In soil testing, attempt is made to correlate the amounts of micronutrients extracted from the soil with plant micronutrient levels and/or with deficiency symptoms and yield responses of the crops (24, 53, 184). Extractants used to assess the availability of soil Cu and Zn can be placed into six categories (104): (a) extractants which extract total amount of Cu and Zn from the soil; (b) water; (c) biological extractants; (d) salt extractants; (e) acid extractants; and (f) chelating agents.

The various methods for estimating available soil Cu and Zn are summarized in Tables 1 and 2. A good micronutrient soil extractant should extract all or a proportional part of the available forms of the micronutrient such that the amount extracted can be correlated with crop growth and micronutrient uptake. In other words, a good extractant should extract a portion or all of (a) water soluble, (b) exchangeable, and (c) adsorbed, chelated or complexed forms of Cu and Zn, the three pools which are very important in supplying plants with micronutrients.

1. Total Cu and Zn concentrations in soils

Total Cu concentration in soil has been studied as a possible guide for assessing the availability of Cu to plants (40, 76, 104, 123, 135, 169). Neelakantan and Mehta (123) found a positive correlation between carbamate extractable total Cu and neutral 1N NH_4OAc extractable Cu on Western Indian soils. However, total soil Cu content is usually poorly correlated with plant growth, and therefore, is of limited value for predicting availability of Cu to plants (183) except where the total Cu content in soil is low.

TABLE 1. EXTRACTION METHODS AND CRITICAL LEVELS FOR PLANT AVAILABLE SOIL Cu

METHOD	SOIL	LOCATION	CROP	CRITICAL LEVEL (ppm)	RATING	REFERENCE NO.
I. TOTAL						
Improved Carbamate	Acidic mineral	Western India	----	----	Good	(123)
II. WATER	----	----	----	----	Good	(128)
	Podzolic	Eastern Canada	----	----	Fair	(65)
III. BIOLOGICAL						
Aspergillus niger	----	Great Britain	orchard	2.0	Good	(23)
	Pumice-derived	Kenya	wheat	3.0	Fair	(139)
IV. SALT SOLUTIONS						
NH_4OAc	Calcareous	California	----	----	Fair	(128)
NH_4OAc (pH = 4.8)	Leon fine sand	California	citrus	----	Good	(128)
NH_4OAc	Acidic mineral	Western India	----	----	Good	(123)
NH_4OAc	----	----	----	----	----	(64
NH_4OAc	----	----	----	0.2	----	(45)
V. ACIDS 1.0 N HCl	Leon fine sand	California	citrus	----	Poor	(53)
1.0 N HCl	----	----	----	----	Good	(100)
HNO_3	----	----	grasses	----	Good	(87)
HNO_3	----	----	wheat, barley, oats	4.0	Good	(181)
HNO_3	----	----	grasses	3.0 - 4.0	Good	(182)

TABLE 1. (cont'd) EXTRACTION METHODS AND CRITICAL LEVELS FOR PLANT AVAILABLE SOIL Cu

METHOD	SOIL	LOCATION	CROP	CRITICAL LEVEL (ppm)	RATING	REFERENCE NO.
VI. CHELATING AGENTS						
DTPA	Many soils	North Dakota	many crops	0.2	Good	(46)
EDTA	Sandy	Kentucky	corn	----	Good	(13)
0.05 M EDTA	Sandy loam	N. E. Scotland	oats and barley	0.75	Good	(148)
EDTA	Acidic morainic forest	Finland	cereals	----	Good	(156)
0.02 M EDTA	Acidic mineral	Ludhiana (India)	rice	----	Fair	(64)
0.5 M EDTA	Many soils	many areas of the world	----	0.75	----	(45)
Na_2DP	Acidic sandy	Manitoba	barley	1.30	Good	(104)

TABLE 2. EXTRACTION METHODS AND CRITICAL LEVELS FOR PLANT AVAILABLE SOIL Zn

METHOD	SOIL	LOCATION	CRITICAL LEVEL	CROP	RATING	REFERENCE NO.
I. TOTAL	Sandy loam	Wisconsin	----	----	Poor	(65)
	Fine textured	Wisconsin	----	----		
II. WATER	Calcareous	Colorado	----	----	Poor	(73)
	Acidic mineral	New York	----	----	Poor	(73)
	Calcareous	Kansas (greenhouse)	----	Rice	Good	(60)
III. BIOLOGICAL						
Aspergillus niger	Acidic mineral	Florida	0.6 - 2.88 (critical range)	Citrus	Fair	(180)
	----	----	----	Corn	Fair	
IV. SALT SOLUTIONS						
NH_4OAc (pH = 4.8)	Fine sandy loam (alluvial)	Washington	0.2 - 0.72 (critical level range)	Millet, sweet corn	Good	(18, 170)
NH_4OAc (pH = 4.8)	Calcareous	California	----	Citrus	Fair	(128)
NH_4OAc (pH = 4.8)	Calcareous	Jerusalem	----	----	Good	(146)
2 N $MgCl_2$	Calcareous	Washington	0.4	Corn and millet	Good	(100, 170)
1 N KCl	Calcareous	Jerusalem	----	----	Good	(146)
1 N $CaCl_2$	Calcareous	Jerusalem	----	----	Good	(146)
Acidified K_2SO_4	Calcareous	Wisconsin (greenhouse)	----	Rice	Good	(118)
1 N $(NH_4)_2CO_3$	Calcareous	Jerusalem	----	----	Good	(146)

TABLE 2. (cont'd) EXTRACTION METHODS AND CRITICAL LEVELS FOR PLANT AVAILABLE SOIL Zn

	METHOD	SOIL	LOCATION	CRITICAL LEVEL (ppm)	CROP	RATING	REFERENCE NO.
V.	DILUTE ACIDS						
	0.1 N HCl	Calcareous	----	----	Corn	Good	(101)
	0.1 N HCl	Sandy	Maryland	----	Corn	Good	(44)
	0.1 N HCl	Many soils	Many areas	1.0 - 7.5	Many crops	----	(45)
	0.1 N HCl	Latozolic Profiles	Hawaii	----	----	Fair	(86)
	0.1 N HCl	Calcareous	Kansas	1.4	----	Good	(178)
	0.1 N HCl	Sandy clay loam	California	2.7	----	Good	(16)
	0.1 N HCl	Fine sandy loam	Washington	1.6	----	Good	(59, 61)
	0.01 N HCl	Sandy	Maryland	0.2	Corn	Good	(44)
	0.05 N HCl plus 0.05 N H_2SO_4	Sandy	Maryland	0.3	Corn	Good	(44)
VI.	CHELATING AGENTS						
(a)	DTPA	Calcareous	California	0.5	Sweet corn	Good	(30)
	DTPA	Calcareous	Colorado	----	Corn	Good	(90)
	DTPA	Sandy loam and calcareous	Washington	0.5 - 0.8	Zn sensitive crops	Good	(14, 55)
	DTPA (pH = 8.0)	Sandy and/or Calcareous	Manitoba	1.3	Flax	Good	(104)
	DTPA (pH = 7.3)	Calcareous	Many areas	1.0	Many crops	Good	(4 b, 45)
(b)	0.01 M EDTA	----	----	1.4 - 3.0			
	0.01 M EDTA	Acidic morainic	Finland	----	Cereals	Good	(187)

TABLE 2. (cont'd) EXTRACTION METHODS AND CRITICAL LEVELS FOR PLANT AVAILABLE SOIL Zn

	METHOD	SOIL	LOCATION	CRITICAL LEVEL (ppm)	CROP	RATING	REFERENCE NO.
VI.	CHELATING AGENTS (cont'd)						
(b)	0.01 M EDTA	Calcareous	Wisconsin	----	Corn	Good	(47)
	0.2 M Na_2Ca EDTA	Calcareous	Jerusalem	----	----	Good	(147)
	0.01 M EDTA plus 1.0 M $(NH_4)_2CO_3$	humid tropical	Maryland	0.1	Corn	Good	(44)
(c)	DITHIZONE	Calcareous	California	----	Corn	Good	(30)
	"	Calcareous	Wisconsin	----	corn	Good	(101)
	"	Calcareous	California	0.55	----	----	(177)
	"	Many soils	Many areas	------	------	------	(27)
	"	Calcareous	California	0.55	------	Good	(177)
	Dithizone + 1 N $CaO(Ac)_2$	Calcareous	----	------	------	----	(177)
	0.01 M Na_2 EDDHA	Calcareous	Jerusalem	------	------	Fair	(146)
	0.02 M Na_2CDTA	"	"	"	"	"	"
	0.01 ethelene diamine (EN)	"	"	"	"	"	"

Plant species have varying requirements and tolerances for Cu and other micronutrients, and vary in their susceptibility to micronutrient deficiencies (3, 28, 33, 45, 60, 72, 113, 160). Thus, the critical values of micronutrient in soil depend on plant genotypes and method of micronutrient extraction (45, 60, 72, 104, 146). Since total soil Cu is not correlated with plant growth, no total soil Cu critical levels have been reported in the literature. However, total soil Cu varies from 2 to 175 ppm (113, 123, 177).

Total soil Zn content has also been studied as a possible indication of Zn availability to plants (76, 101, 104, 118, 146, 170, 177, 179, 183). Total Zn content of the soil is poorly correlated with plant available soil Zn (60, 86, 101, 103, 115, 118, 177, 178, 183), except where total soil Zn is low (183). Most mineral soils contain between 10 and 300 ppm of soil total Zn (86, 113, 177). Total Zn concentration usually decreases with depth as much is associated with organic matter (86). Total soil Zn concentration also varies with clay content. For example, the average total Zn concentrations in fine textured and sandy loam soils were 73.0 and 33.0 ppm, respectively in Wisconsin (170). Since total soil Zn is not correlated with plant growth, no total soil Zn critical levels have been reported in the literature.

2. Water

Water has been used as an extractant to determine the availability of Cu to plants (37, 45, 53, 73, 128, 186). Nishita and Haug (128) found that the amount of H_2O-extractable Cu was greatest when soil was heated to about 200°C prior to extraction. Gupta and MacKay

(65) found that the amount of H_2O-soluble Cu in podzolic soils ranged from 0.09 to 0.46 ppm. However, water usually does not extract sufficient Cu to represent adequately the labile nutrient available to plant roots (45, 65, 186).

Several researchers have attempted to use water as an extractant for plant available soil Zn (45, 58, 60, 73, 83, 118, 128, 186). Hodson, Lindsay and Trierweiler (73) found that the Zn concentration of the soil solution in calcareous Colorado soils was less than 2 ppb, and in acid New York soils, less than 74 ppb. Mortredt and Giordano (60), however, found that deionized H_2O extracted between 1 and 100% of Zn applied as $ZnSO_4.7H_2O$ and ZnO to calcareous soils, and the percentage recovery in each case correlated with agronomic effectiveness of Zn in these inorganic fertilizers. However, several other researchers reported that water did not extract sufficient Zn to represent adequately the labile nutrient available to plant roots (45, 60, 128, 186).

3. Biological extractants (bioassay)

Aspergillus niger has been a common bioassay for assessing the level of Cu available from the H_2O-soluble, exchangeable, and chelated micronutrient pools in the soil (23, 57, 70, 139, 180). Boreld et al. (23) found that the threshold level of Cu in orchard soils of Great Britain was about 2 ppm. In Kenya, Pinkerton (139) delineated 3.0 ppm Aspergillus niger-extractable Cu as the critical level of Cu for wheat in pumice-derived soils of the Rift Valley. Although Aspergillus niger extractable Cu correlated adequately with plant growth (51, 70), the bioassay technique demands purification of chemicals and time for the

growth of organisms (45), and does not always yield a readily reproducible result (70). In addition, it was suggested (180) that its use be limited to acid soils.

Aspergillus niger has also been used as a bioassay to indicate the level of Zn available to plants (101, 179, 180, 187). Martens et al. (101) observed that Aspergillus niger-extractable Zn correlated more highly with Zn uptake by corn than dithizone-0.1 N HCl- and 0.2 M $MgSO_4$- extractable soil Zn, and its use was more convenient and more rapid than acetic acid and EDTA procedures on humid zonal soils. (179). Tucker et al. (180) found that citrus, grown on certain acid soils of Florida, containing 0.6 - 2.88 ppm Aspergillus niger extractable soil Zn, responded to Zn fertilization, but suggested that its use be limited to acid soils.

4. Salt extractants

Neutral or near neutral salt solutions and acidified salt solutions have been used to determine the levels of micronutrients available to plants from the readily exchangeable micronutrient pool in the soil. However, the level of exchangeable micronutrients is too low to be an adequate predictive value (45, 52, 60, 186), even in soils which have received large amounts of micronutrient fertilizers (52). Though some degree of success has been achieved in some instances, determination of readily exchangeable micronutrient cations does not appear to be adequate means of assessing the availability of the micronutrients to the plant roots (45). However, readily exchangeable micronutrient levels better represent plant available levels than either total or H_2O-extractable micronutrient levels.

Nishita and Haug (128) reported that the level of NH_4OAc extractable Cu was highest in calcareous soils of California when these soils were heated prior to extraction. They also reported that exchangeable Cu extracted from Leon fine sand of California with NH_4OAc (acidified to pH 4.8), correlated with citrus root Cu content ($r = 0.807$) more significantly than H_2O extractable Cu ($r = 0.646$) when Cu was applied to this soil as $CuSO_4,5H_2O$ (128). In the soils of Western India, a significant positive correlation was found between NH_4OAc extractable exchangeable Cu and total Cu extracted by the newly improved Carbamate Procedure (123). Grewal et al. (64) also found that responses of maize and wheat to Cu in pot experiments was better estimated using 1 N NH_4OAc than a chelating agent or one normal strength acids. Cox and Kamprath (45) delineated 0.2 ppm NH_4-OAc extractable Cu as the threshold level for most soils in most places.

Salt solutions such as 2 N $MgCl_2$ (58, 60, 100, 115, 116, 170), 0.2 N $MgSO_4$ (101), 1 N KCl, 1 N NH_4NO_3, 1 N $CaCl_2$ (146), acidic K_2SO_4 solution (118) and 1 M $(NH_4)_2CO_3$ buffered with 0.01 M EDTA (pH = 8.6) (189) have all been used as extractants to assess the levels of exchangeable Zn in soils. The uptake of Zn by both millet and corn were more closely related to 2 N $MgCl_2$ extractable soil Zn ($r = 0.663$) than 0.1 N HCl extractable soil Zn ($r = 0.297$) or 1.0 N HCl extractable soil Zn ($r = 0.301$) (100). In most cases, 2 N $MgCl_2$ solution was deemed to be most suitable of all salts for the determination of the readily exchangeable native and applied Zn (115, 116).

The amount of soil Zn extracted using 1 N KCl, 1 N $CaCl_2$ or

1 N $(NH_4)_2CO_3$ correlated as well with plant uptake of Zn as Zn extracted with 1 N NH_4OAc-dithizone procedure (146). The level of Zn, recovered with acidified solution of K_2SO_4 from soils which had received Zn fertilizers, correlated well with agronomic effectiveness of these fertilizers (118). One molar $(NH_4)_2CO_3$ buffered with 0.01 M EDTA was highly successful in separating deficient from non-deficient calcareous soils without destroying soil $CaCO_3$ and releasing occluded Zn (178). In most instances, however, the amount of Zn extracted with neutral salts and acidic salt solutions was too small to represent adequately the labile Zn available to plants (45). In other words, plants are able to extract more than exchangeable Zn from the soil.

Steward and Berger (170) reported that the level of 2 N $MgCl_2$-extractable soil Zn should not fall below 0.4 ppm if the optimum growth of millet is to be ensured. Sweet corn, grown on fine sandy loam alluvial soils containing 0.72 ppm 1 N NH_4OAc-extractable Zn levels, exhibited some Zn deficiency symptoms and subsequently responded to Zn fertilization (27).

5. Dilute acids

Dilute acids are used to determine the amounts of organically bound micronutrients in the soil (100). Full strength acids are not suitable extractants as they extract micronutrients occluded in materials such as $CaCO_3$ and hydrous oxides (178). The most commonly used acids are 1.0 N and 0.1 N HCl. However, the amounts of micronutrients extracted with HCl vary with soil pH, solution-soil ratio, kind of soil, climate, and the length of the extraction period (125, 178). Nevertheless, HCl has been found the most convenient and least time-

consuming (179) of the acid extractants. Generally, dilute acids better assess plant available soil micronutrient levels than water or neutral salts, but are not as desirable as chelating agents.

Martens (100) found that the organically bound Cu level in the soil was best predicted by extraction with 1.0 N HCl (r = 0.637). Yet Fiskell and Leonard (53) found that after application of $CuSO_4$ and CuO, 1.0 N HCl extractable Cu correlated less significantly (r = 0.646) with citrus root Cu concentration than 1.0 N NH_4OAc (acidified to pH 4.8)-extractable Cu (r = 0.807) and H_2O-soluble Cu (r = 0.668). Other workers considered 1.0 N HCl as a suitable Cu extractant but found the procedure laborious (70).

Dilute HNO_3 was also reported by several workers to be suitable extractant of Cu (87, 88, 181, 182). Copper content of grasses correlated well with the level of HNO_3 extractable Cu in the soil (87). The yield of barley, wheat and oats was decreased if the level of HNO_3 extractable Cu was less than 4.0 ppm HNO_3 (181). The critical level of Cu in the soil for grass was 3.0 to 4.0 ppm HNO_3 extractable Cu (182).

Various workers have used 0.1 N HCl to determine plant available Zn in soil (18, 19, 30, 44, 60, 83, 101, 115, 118, 125, 167, 170, 178, 179, 197). Coffman and Miller (44) reported that 0.1 N HCl extractable Zn level correlated more highly (r = 0.822) with Zn concentration in the aerial portion of corn than 0.01 M EDTA + 1.0 N $(NH_4)_2CO_3$ extractable Zn (r = 0.784) but not as highly as 0.05 N HCl + 0.025 N H_2SO_4 (r = 0.916) extractable Zn. Martens et al. (101) found that 0.1 N HCl extractable Zn correlated more highly with Zn uptake by corn

(r = 0.562) than soil total Zn, Aspergillus niger extractable Zn and 0.2 N $MgSO_4$ extractable Zn. In certain Maryland soils, 0.1 N HCl extractable Zn level correlated highly with the Zn content of the aerial portion of corn (r = 0.854) (44). The level of 0.1 N HCl extractable Zn correlated better than total soil Zn with incidence of Zn deficiency in corn (86), and with Zn uptake by corn and sorghum (197). However, although the percentage recovery of Zn with 0.01 N HCl and 0.001 N HCl from soil treated with Zn fertilizers correlated highly with effectiveness of these fertilizers, the level of correlation was not as high as H_2O extractable Zn (118), nor did the 0.01 N HCl and 0.001 N HCl extractable Zn correlate as well as 0.05 N HCl + 0.025 N H_2SO_4 extractable Zn with Zn contents of the aerial portions of corn and sorghum (197).

Cox and Kamprath (45) reported that the critical levels for 0.1 N HCl extractable soil Zn in the literature varied from 1.0 to 7.5 ppm. The amount of Zn extracted with 0.1 N HCl from Hawaiian latozolic soils varied from 0.1 to 17.9 ppm (86). A threshold level of 1.4 ppm HCl extractable Zn separated Zn deficient from non-deficient soils in Kansas (178). In Washington, Ritzville fine sandy loams containing a level 1.6 ppm 0.01 N HCl extractable Zn were suspected to be Zn deficient (16). In Colorado, sandy clay loam calcareous soil was Zn deficient at 2.7 ppm 0.01 N HCl extractable Zn (59, 61). Corn in Maryland responded to Zn fertilization when soils contained 0.2 ppm 0.1 N HCl extractable Zn and 0.3 ppm 0.05 N HCl plus 0.025 N H_2SO_4 extractable Zn (44).

6. Chelating agents

Water soluble, exchangeable, and adsorbed, complexed or chelated micronutrients are available to plants with the adsorbed, complexed or chelated pool being the most important. The level of this pool can be estimated using chelating agents (45) whereas many of the procedures discussed thus far do not extract this pool. Chelating agents have advantages over most acids and neutral salt solutions, because the organically bound soil micronutrients solubilized by chelating agents can be separated more easily from solids of the soil by filtration or by the extraction of the chelated metals into organic solvents (186). Also, the pH of the chelating agents can be maintained more closely to normal pH of the soil (45, 186) and undesirable side reactions, such as attack on carbonates, can be avoided (16, 44, 186). Lastly, the extracting procedures can be made more selective for specific micronutrient cations (186).

Ethylene diamine tetra acetic acid (EDTA) has been the most commonly used extractant to assess the level of the plant available Cu in soil (13, 70, 148, 186, 187). Henriksen (70) recommended the use of 0.02 M EDTA as the least laborious and the least time consuming. Other investigators recommended both EDTA and DTPA (diethylene triamine penta acetic acid) as good extractants of soil Cu (186). On the other hand, McGregor (104) considered Na_2DP as the most suitable extractant of Cu in Manitoba soils. Cheng and Bray (40) recommended citrate, EDTA and 1.0% (0.027 M) versanate solution for assessing the level of plant available soil Cu. Massey (13) found a high correlation between EDTA extractable Cu and Cu uptake by corn on 34 Kentucky soils. In

north-east Scotland, Reith (148) reported significant correlations between 0.05 M EDTA extractable Cu and yield response in both field and pot experiments. Viro (187) found that the level of EDTA extractable Cu in acidic glacial till soils of Finland could be used to predict the level of plant available Cu for wheat. Grewal et al. (64) reported that 0.02 M EDTA, though not as good as 1 N $NH_4C_2H_3O_2$, was a better Cu extractant than 1 N HCl and 1 N HNO_3.

Cox and Kamprath (45) delineated 0.2 ppm $NH_4C_2H_3O_2$ (pH 4.8) extractable Cu, and 0.75 ppm 0.5 M EDTA extractable Cu as threshold levels of Cu in soils. Reith (148) reported 0.75 ppm 0.05 M EDTA extractable Cu as the critical level of Cu in north-east Scotland for the growth of oats and barley. The level of 1.3 ppm Na_2DP extractable Cu in certain Manitoba soils may imply Cu deficiency (104). Several soil testing laboratories in the United States use the DTPA method of Lindsay and Norwell (94) for estimating the plant available levels of soil Cu, Zn, Fe and Mn. The North Dakota Soil Testing Laboratory assumes that the critical level for DTPA extractable Cu is 0.2 ppm (46).

The most commonly used sequestering agents to assess the level of plant available soil Zn are DTPA (14, 16, 30, 47, 55, 90, 95, 104, 186), EDTA (30, 47, 178, 179, 186, 187), dithizone (17, 18, 19, 30, 83, 100, 103, 128, 138, 148, 158, 179) and NH_4OAc-dithizone (6, 154, 158, 161, 170, 186). However, of all these chelating agents, DTPA is most often recommended as the best Zn extractant (14, 16, 30, 55, 90, 95, 104) because it can be used to assess the level of available Zn in fertilized and unfertilized soils (55), the pH is most easily

controlled (186) and it can be used to extract Zn simultaneously with Cu, Fe, and Mn (95, 186). Brown et al. (30) found that DTPA extractable level of Zn predicted 83% of Zn responses in sweet corn on 92 Californian soils whereas, on the same soils, the Na_2EDTA extractable Zn level predicted 72% of the responses. The figures for 0.1 N HCl and dithizone were 73% and 79% respectively. The level of DTPA extractable Zn correlated highly with the Zn uptake by corn grown on certain soils of Colorado ($r^2 = 0.97$) (90). Recovery of Zn with DTPA from soil fertilized with Zn and cropped consecutively with corn and oats suggested that DTPA soil Zn test may be useful for monitoring the residual effects of Zn fertilizers (14, 55). More recently, McGregor (104) found DTPA (pH 8.0) to be the best extractant for predicting the available level of Zn in Manitoba soils, and Brown et al. (16) reported that 0.005 M DTPA extractable Zn best predicted the amount of Zn available to sweet corn from Zn fertilizers. Ethylene diamine tetra acetic acid (EDTA) has been recommended as a promising alternative to DTPA.

Viro (187) found that the level of EDTA extractable soil Zn of acidic till soils of Finland could be used to determine the level of Zn available to wheat. Dolar et al. (47) reported that 0.01 M EDTA was very useful for assessing available Zn in Wisconsin soils. Trieweiler and Lindsay (178) found that EDTA extractable soil Zn correlated very highly with plant uptake of Zn. In certain calcareous soils near Jerusalem, 0.2 M $Na_2CaEDTA$ was very useful in predicting the level of available soil Zn (146). However, Coffman and Miller (44) found that 0.01 M EDTA buffered with 1.0 M $(NH_4)_2CO_3$ was impractical for available Zn test in 12 soils of Maryland treated and

untreated with $ZnSO_4$ because the soil Zn level from this procedure was not highly correlated with Zn concentration in corn shoots. Also, 0.01 N EN (ethylene diamine), 0.01 M Na_2EDDHA, and 0.02 M Na_2CDTA proved to be as suitable as EDTA in calcareous soils near Jerusalem (146). Acetic acid was also found to be as effective as EDTA, but less rapid and not as convenient as the EDTA procedure (187).

Dithizone was found in some instances to be more convenient than both the EDTA and acetic acid procedures (179). Brown et al. (30) found that dithizone extractable Zn predicted 79% of the Zn responses in sweet corn on a number of soils in California whereas on the same soils, 72% and 73% of the Zn responses were predicted by Na_2EDTA extractable Zn and 0.01 N HCl extractable Zn, respectively. Martens et al. (101) found that in Wisconsin soils dithizone extractable Zn correlated more highly with Zn uptake by maize ($r = 0.696$) than Zn extracted by the 0.01 N HCl, Aspergillus niger, total, and 0.2 M $MgSO_4$ procedures. Massey (103) also reported a high correlation between dithizone extractable level of soil Zn and Zn uptake by corn whereas no positive correlations were noticed with other extractants. Extracting solutions containing dithizone buffered with 1.0 N $Ca(OAc)_2$, 1.0 N NH_4OAc, 1.0 N NaOAc and deionized H_2O were found to be equally suitable extractants for soil Zn (138). The level of 1.0 N NH_4OAc-dithizone extractable Zn predicted best the level of Zn uptake by plants and available level of Zn on certain calcareous soils near Jerusalem (146).

A host of critical levels have been delineated for the various chelating agents. Boawn (14) has proposed 0.8 ppm DTPA extractable

soil Zn as the critical level for Zn sensitive crops grown in Washington soils. After reviewing the results of many researchers, Cox and Kamprath (45) proposed a critical level of 1.0 ppm DTPA + $CaCl_2$ (pH = 7.3) extractable Zn for calcareous soils. In a research involving 92 soils in California, sweet corn responded to Zn fertilization in 80% of these cases in which the DTPA extractable Zn was less than 0.5 ppm (30), however, sweet corn did not respond to applied Zn in soils containing more than 1.35 ppm DTPA extractable Zn. In Manitoba, soils containing less than 1.3 ppm DTPA extractable Zn were suspected of being deficient in Zn for flax and soils containing less than 0.8 ppm DTPA extractable Zn were Zn deficient (104). The North Dakota Soil Testing Laboratory delineated 1.0 ppm DTPA extractable Zn as the critical level for Zn sensitive crops such as corn, potatoes and field beans (46). The reported critical levels for Zn extracted with EDTA buffered with $(NH_4)_2CO_3$ varied between 1.4 to 3.0 ppm. Coffman and Miller (44) found yield increases with corn grown on Maryland soils containing 0.1 ppm extracted with 0.01 M EDTA buffered with 1.0 M $(NH_4)_2CO_3$. Sweet corn responded to added Zn in 71% of the instances in which soils contained less than 1.25 Na_2EDTA extractable Zn. Responses to added Zn occurred in 86% of those instances in which the dithizone extractable Zn level was less than 0.55 ppm in experiments involving 53 Californian soils. In the same experiments, there were no responses to Zn in 76% of those instances in which the dithizone extractable Zn level was greater than 0.55 ppm (177). Brown et al. (28) reported that sweet corn responded to Zn on Californian soils containing less than 0.55 ppm dithizone extractable Zn; but sweet corn

did not respond to Zn on soils containing more than 1.3 ppm dithizone extractable soil Zn (30). After reviewing the results of many researchers, Cox and Kamprath (45) found that the critical level of Zn usually varied between 0.3 and 2.3 ppm when extracted with dithizone buffered with $NH_4C_2H_3O_2$. Less than 0.2 ppm 1.0 $\underline{N}$ NH_4OAc-dithizone extractable Zn in fine sandy loam of Washington implied Zn deficiency in those soils (18).

2.) PLANT ANALYSIS

Chemical analysis of plant tissue for micronutrients and calibration with yield response, uptake and deficiency symptoms is often superior to soil testing, particularly for deciduous trees, fruits and citrus (186). Crop nutrition can be controlled by a combination of soil testing and foliar and root analysis (24, 53, 145, 186).

An attempt is made in plant analyses to determine for each crop the micronutrient level in the same plant part and at the same level of maturity, because plant critical levels not only vary among crops and among sets of environmental conditions but also among plants and with age. For cereal crops, the entire aerial portion of the plant just prior to heading is often taken for analyses. In corn, the ear leaf is sampled at silking. For all crops, it is important to sample before the plant begins its reproductive stage of growth and to take only living tissue. Micronutrient concentrations often decrease substantially as the tissue becomes older. It is also important to include numerous subsamples in a sample.

Sufficiency ranges or critical levels for Cu and Zn concentrations in plant material are summarized in Tables 3 and 4.

TABLE 3

TYPICAL, SUFFICIENCY OR CRITICAL LEVELS OF Cu CONCENTRATION IN PLANTS

CROP PARTS AND GROWTH STAGE	LOCATION	KIND OF SOIL	CONCENTRATION RANGE (ppm)	NATURE OF RANGE	REFERENCE NUMBER
All plant	----	----	5.0-20.0	typical	1, 82
leaf tissues	----	----	4.0	critical	1, 82
trifoliate leaves of soybean harvested prior to podset	Georgia	several major soils	11.0-45.0	typical	4
soybean leaf tissue	----	calcareous	5.0	critical	133
wheat shoots	N. Carolina	sandy soils	3.0-3.8	sufficiency	199, 200
wheat shoots prior to heading	Ohio	several soils	5.0	critical	106
shoots of wheat, barley and oats	----	----	5.0	critical	106
ear leaves of corn at tasseling	----	----	5.0	critical	106
ear leaves of corn	Kansas	peat	4.0-5.0	deficiency	58
ear leaves of corn	Kansas	mineral	4.0-5.0	sufficiency	58
corn leaves at tasseling	----	calcareous	5.0	critical	133
shoots of alfalfa	----	----	1.0-2.0	deficiency	106
	----	----	5.0	critical	106
	----	----	5.0-14.0	sufficiency	106
shoots of alfalfa	New Jersey	sandy soils	5.1-9.6	deficiency	67
shoots of alfalfa	----	----	5.0-12.1	sufficiency	67
roots of young orange	(green house) New York	calcareous	3.0-5.0	critical	53
roots of young orange	Florida	sandy	6.7	sufficiency	24
shoots of eight week old flax	Manitoba	sandy	2.0-3.0	deficiency	104
shoots of clover	Florida	sandy	1.7-12.3	typical	53
legumes	Florida	sandy	1.0-2.0	typical	53
grass tissue	Florida	sandy	2.0-4.3	typical	53

TABLE 4

TYPICAL, SUFFICIENCY OR CRITICAL LEVELS OF Zn CONCENTRATIONS IN PLANTS

CROP PARTS AND GROWTH STAGE	LOCATION	KIND OF SOIL	CONCENTRATION RANGE (ppm)	NATURE OF RANGE	REFERENCE NUMBER
all vegetative plant tissues	----	----	25.0-150.0	typical	82
	----	----	20.0	critical	82
	----	----	400.0	toxic	82
upper fully developed trifoliate leaves of soybean prior to podset	Georgia	major soils	42.0-49.0	typical	4
leaves of soybean at maturity	----	----	45.0	typical	82
stems of soybean at maturity	----	----	19.0	typical	82
pods of soybean at maturity	----	----	40.0	typical	82
wheat vegetative tissue (variety)	India	mineral latozolic	4.2-28.3	deficiency	160
shoots of wheat, barley and oats at heading	Ohio	several soils	10.3-10.5	typical	185
shoots of wheat, barley and oats at heading		sandy loam	15.0	critical	106
upper leaves of Saturn rice at panicle differentiation	Louisiana	mineral soils	22.0-32.0	typical	155
ear leaves of corn	Maryland	calcareous	10.2-26.6	deficiency	44
ear leaves of corn	----	----	15.0	critical	106
corn shoots	Wisconsin	calcareous	15.0	critical	170
alfalfa tissue	California	calcareous	4.0-6.0	critical	17
alfalfa tissue	California	calcareous	7.0-30.0	sufficiency	17
shoots of eight week old flax	Manitoba	calcareous	13.0	critical	104
shoots of millet	Wisconsin	calcareous	28.2	sufficiency	170
vegetative tissue of plants	New York	clay loam	10.0	critical	107

The normal range of Cu concentration in vegetative plant tissue is 5.0 to 20.0 ppm (dry weight basis); and Cu concentrations of less than 4.0 ppm and above 20 ppm imply deficiency and toxicity, respectively, in mature leaves (1, 82). The range of Cu concentration of the upper fully developed trifoliate leaves (without petioles) of soybean, grown on several major soils in Georgia and harvested prior to podset, was 11.0 to 45.0 ppm (4). Oplinger and Ohlrogge (133) considered the soybean leaf tissue containing less than 5.0 ppm Cu to be Cu deficient.

A range of 3.0 to 3.8 ppm Cu concentration in the aerial portion of wheat was about sufficient for the nutritional needs of wheat grown in soils of North Carolina (199, 200), as indicated by the analysis of these plants sampled prior to heading. Wheat in Ohio was reported to be Cu deficient when the shoots, analysed just prior to heading, contained less than 5.0 ppm Cu (106). Mosted, Motto and Peck (106) found that wheat, barley and oat shoots containing less than 5.0 ppm Cu were deficient in Cu.

Corn ear leaves containing less than 5.0 ppm Cu at tasselling were Cu deficient (106). Copper deficiency was observed in corn on peat soils when the tissue concentration ranged from 4.0 to 5.0 ppm. On the other hand, corn grown on mineral soils did not exhibit Cu deficiency symptoms when the tissue contained 4.0 to 5.0 ppm Cu (58). Hudson (53) noted that Cu concentration in leaf tissue of corn was as high as 20.0 ppm. Oplinger and Ohlrogge (133) reported that corn, containing less than 5.0 ppm Cu in leaf tissue, was Cu deficient.

Concentrations of 1.0 to 2.0 ppm Cu, 5.0 ppm Cu and 5.0 to

14.0 ppm Cu in alfalfa shoots were regarded as deficient, critical and adequate levels, respectively (106). Gupta and MacKay (67) considered a range of 5.0 to 12.1 ppm in alfalfa tissue as the optimum for plant growth. On the other hand, Viro (135) reported that on certain New Jersey soils, alfalfa containing between 5.1 to 9.6 ppm Cu was Cu deficient.

Young orange trees exhibited severe Cu deficiency when the concentration of Cu in the root was less than 3.0 ppm. Moderate Cu deficiency was noticed in these plants when the Cu concentration in their roots varied between 3.0 to 5.0 ppm (53). Bram and Fiskell (24) felt that a root Cu concentration of 6.7 ppm was sufficient for the nutritional needs of Mandarin orange (citrus reticulata) grown in Florida.

McGregor (104) suggested that eight week old flax plants, grown on sandy soils in Manitoba, were Cu deficient when the Cu concentration in shoots was 2.0 and suspected of being Cu deficient when the Cu concentration was 3.0 ppm.

Fiskell and Leonard (53) reported that Cu concentration in clover from clover-grass mixtures usually varied from 1.7 to 12.3 ppm but was as high as 20.0 ppm. In the grass tissue from clover-grass mixtures, Cu concentrations varied from 2.0 to 4.3 ppm.

Ranges of 8.4 to 13.2 ppm Cu and 2.3 to 2.5 ppm Cu were considered optimal for spinach vegetative tissue and Hudson barley kernels, respectively.

The normal range of Zn concentration in vegetative plant tissue is 25.0 to 150.0 ppm. Concentrations of less than 20.0 ppm or over

400.0 ppm usually imply the plants are deficient or toxic, respectively (82). As with Cu, plant Zn concentrations and threshold levels vary with genotype, plant parts, soil, and stage of growth.

Anderson et al. (4) reported the Zn concentration of the upper fully developed trifoliate leaves of soybeans (petioles removed) just prior to podset on several major soils in Georgia as 42.0 to 49.0 ppm. Jones (82) reported that the Zn concentrations in the leaves, stems and pods of soybeans at maturity were 45.0, 19.0 and 40.0 ppm, respectively. Melton et al. (107) noticed that the growth of pea bean was depressed due to Zn deficiency when the shoot Zn concentration was less than 20.0 ppm.

Skulla and Raj (160) observed that the concentration of Zn in Zn deficient wheat vegetative tissue on soils in India varied from 4.2 to 28.3 ppm among wheat varieties. On the other hand, Viets et al. (185) reported that leaves of wheat, barley and oats at heading stage contained between 10.3 and 10.5 regardless of whether the plants were fertilized with Zn or whether the soil was deficient in Zn (185). Mested et al. (106) reported that a concentration of less than 15.0 ppm Zn in the aerial portion of wheat, barley and oats implied that these crops were deficient in Zn.

Sedberry et al. (155) reported that Zn concentrations in the upper leaves of "Saturn" rice at panicle differentiation were 22.0 and 32.0 ppm, when grown on certain Louisiana soils treated with 0.0 and 35.8 ppm Kg Zn/ha, respectively.

The Zn concentration in the ear leaf of corn on certain Zn deficient soils in Maryland varied from 10.2 to 26.6 ppm. An appli-

cation of 1.25 ppm Zn to these soils nearly doubled the dry matter yield of the corn plants (44). Mested, Motto and Peck (106) reported that a Zn concentration of less than 15.0 ppm Zn in the ear leaf of corn indicated that the plant was Zn deficient (106). On certain Wisconsin soils, corn shoots, containing less than 15.0 ppm Zn, exhibited Zn deficiency symptoms and responded to Zn fertilization (170). However, Massey (103) reported that the Zn concentration in corn plants grown in solution containing low level of Zn was as low as 8.0 ppm, yet the plants never exhibited deficiency symptoms (103).

Boawn et al. (17) proposed that Zn concentration ranges of 4.0 to 6.0 ppm and 7.0 to 30.0 ppm in alfalfa as critical and adequate, respectively. In a green house experiment on several Manitoba soils (104), eight week old flax plants containing less than 9.0 ppm Zn were moderately Zn deficient. Plants were suspected of Zn deficiency when containing less than 13.0 ppm Zn.

Steward and Berger (170) found that the shoots of millet on 42 soils of Wisconsin contained an average of 28.2 ppm Zn and that this level of Zn enabled the millet plants to grow satisfactorily without Zn addition.

Unlike the behavior with Cu, grasses and legumes contained similar levels of Zn which ranged from 15.0 to 40.0 ppm (106).

(F) EFFECT OF TYPE, RATE, AND METHOD OF PLACEMENT OF Cu AND Zn FERTILIZERS ON THEIR EFFECTIVENESS

The numerous research findings presented in this section can perhaps be better understood if we first discuss in some detail the various factors affecting the effectiveness of a micronutrient

fertilizer. These factors include fertilizer solubility and mobility, the solubility of the reaction products formed, fertilizer granule size, method of placement, shape of the root system, ability of the root per unit weight to grow into the soil area containing the fertilizer and ability of the root per unit weight to take up the micronutrient.

Solubility, method of placement and granule size are perhaps the most important factors affecting the effectiveness of micronutrient fertilizers. The order of relative solubility and mobility from the greatest to the least is (a) organic chelates, such as EDTA, (b) organic non chelates, such as polyflavinoid, (c) soluble inorganic compounds, such as $ZnSO_4.7H_2O$ and $CuSO_4.5H_2O$, and (d) sparingly soluble and insoluble inorganic compounds, such as oxides, frits and phosphates. Methods of placement would have little influence on effectiveness of micronutrient fertilizers if micronutrient fertilizers were as mobile as chelates which have about the same availability regardless of method of placement. However, one important element, the cost, militates against universal usage of chelates. Sulphates, although rather soluble, form insoluble reaction products when applied to the soil and therefore behave similarly to the oxides, frits and phosphates. Factors such as method of placement very greatly influence the effectiveness of inorganic micronutrient carriers. This fact and the high cost of chelates makes it necessary to fully understand the effects of factors such as placement or distribution and granule size on the effectiveness of inorganic micronutrient fertilizers.

Micronutrients are applied in small amounts, and placement methods are tailored towards securing the greatest efficiency. In other words, the plant roots must come in contact with applied micronutrient fertilizer in order that its effectiveness be realized. If the fertilizer is not in the form that can move to the roots with soil water, the micronutrients must be placed in the most active root zone area. Distribution is particularly critical at minimal application rates. Generally, micronutrients placed in the soil above the root system are of little value. The materials must be placed where plant roots can make maximum contact.

For sulphates whose reaction products are insoluble, one might expect banding and/or the use of large granules would be the most efficient method of application, since this would cut down the surface area of contact between the fertilizer and the soil such that the reaction products would not form readily. However, particularly for calcareous soils, finely grinding the material and mixing thoroughly throughout the surface soil is often the most efficient. Two opposing factors are very important in this instance. Although banding would cut down the formation of insoluble reaction products and increase chemical availabilities, increasing the surface area of contact between roots and micronutrient fertilizer through finely grinding and thoroughly mixing with the soil appears to be more important. If the root proliferation into micronutrient band were very pronounced, then sulphates could be most efficiently applied in bands to calcareous soils. But apparently, many crop species are not able to do this.

Good distribution is particularly important with water insoluble or sparingly soluble inorganic micronutrient materials such as oxides, frits and phosphates. With these materials, particle size is likewise critical. These materials must be finely ground in order to increase the surface area of contact between plant roots and the micronutrient fertilizer. The best results are achieved with water insoluble or sparingly soluble inorganic fertilizers on both acid and calcareous soils when they are applied in powdered form or in very fine granules and mixed thoroughly with soil of the root zone. This is more important on calcareous than on acid soils.

Some research findings indicated that H_2O-insoluble inorganic materials were most effective on both calcareous and acid soils when granulated and/or banded. However, some other more recent experimental evidence indicated that H_2O-soluble inorganic micronutrient fertilizers are most effective when pulverized and thoroughly mixed with the soil. Fertilizer carriers of Mn and Fe, of course should not be applied directly to the soil but as foliar sprays because they form extremely insoluble reaction products.

1.)(A) ORGANIC Cu AND Zn FERTILIZERS

Metal organic chelate complexes are quite soluble even at high pH's, and can be taken up by plant roots. In addition to the high solubility of such complexes, they are very stable (do not ionize) so that they retain Cu and Zn in soluble form permitting their absorption by the roots yet preventing their conversion to insoluble compounds such as hydroxides (92, 104, 177). Method of placement and the macronutrients or micronutrients fertilizers with which Cu and Zn chelates

are applied have much less influence on their effectiveness than those factors have on inorganic Cu and Zn sources.

Chelating agents without the metals are usually not effective in correcting micronutrient deficiencies because they often compete with roots and soils for micronutrients (190). For example, addition of barnyard manure to Brookston soil produced chelating agents which immobilized Cu^{+2} ions and decreased biological availability of Cu to corn and soybean (109, 110). On the other hand, Wallace and Mueller (194) found that Na_2EDTA added to the soil without the metal Zn increased the specific activities of Zn in corn, cotton and beans. Chelating agents are sometimes susceptible to microbiological attack, thus affecting their usefulness in the soils. Wallace et al. (193) suggested, therefore, that Cu and Zn polyamino-polyacetates which are resistant to microbiological decay might be useful as fertilizers.

Tisdale (177) recommended the use of CuDTPA, CuCDTA, CuEDDHA, Cu sulfonates and Cu polyflavinoids as soil applied fertilizers at rates of 1.0 to 6.0 kg Cu per ha, or as foliar sprays at considerably lower rates. McGregor (104) reported that Na_2EDTA was the best source of H_2O soluble Cu and that it was more soluble in calcareous soils than in non-calcareous soils. Wallace and Mueller (195) found that 5.0 ppm Cu applied as CuEDTA to loamy soils near Los Angeles resulted in higher levels of Cu in bush beans than 25.0 to 50.0 ppm Cu applied as $CuSO_4.5H_2O$.

The most commonly used Zn organic chelate is ZnEDTA. Numerous workers have found it and other Zn chelates far more effective than

inorganic sources. Tisdale (177) recommended ZnDTPA, ZnEDDHA, Na_2ZnEDTA, ZnCDTA, NaZnNTA (Zn = 13.0%), NaZnHEDTA (Zn = 90%) either as foliar or soil applied fertilizers. However, treating the seeds with these compounds was not very successful. Kalbasi and Racz (84) recommended ZnEDTA over $ZnSO_4$. After 32 weeks of laboratory incubation, the H_2O soluble Zn concentration in soils treated with ZnEDTA was much higher than those treated with $ZnSO_4$. McGregor (104) recommended Na_2ZnEDTA as the best Zn fertilizer because it was found more soluble than inorganic sources particularly on calcareous soils. Boawn (15) found that ZnEDTA broadcast and ploughed down was more effective in correcting Zn deficiency in bean plants than $ZnSO_4.7H_2O$ applied in the same manner. Zinc EDTA, banded prior to planting, was more effective than $ZnSO_4.7H_2O$ applied in the same manner. Banding ZnEDTA prior to planting of beans and leaching the soil with sprinkler irrigation was highly effective source of Zn (15) for beans whereas $ZnSO_4.7H_2O$ applied in the same manner had no effect. Holden and Brown (75) found in the green house research that ZnEDTA increased Zn concentration in alfalfa twice as much as $ZnSO_4$ in neutral soil and up to six times as much in calcareous soil. Judy (83) observed in the field and in greenhouse studies that the dry matter yield and Zn uptake of beans were higher on calcareous soils treated with ZnEDTA than when treated with $ZnSO_4$. MacGregor et al. (98) found in the greenhouse experiments that dusting corn seeds with Na_2ZnEDTA had no significant effect on leaf Zn level or on annual grain yield but increased total corn grain yield over a five year period. Wallace and Romney (191) noticed that ZnEDTA was more efficient than ZnNTA

which in turn was more efficient than $ZnSO_4$ in increasing Zn uptake by Golden Cross bantam corn in pot culture studies with Dinuba fine sandy loam. Moreover, ZnEDTA was found to be 3 x 10^5 times more stable than ZnNTA. However, ZnNTA increased corn yield more than did ZnEDTA. In field studies with six forest and savannah incepisols of Western Nigeria, Osiname et al. (134) reported that Na_2ZnEDTA broadcast and incorporated in N-P-K fertilizers, at the rates of 0.0, 1.0, 2.0, 4.0, and 8.0 kg Zn/ha before planting, increased yield response to Zn on savannah grassland soils but no response was observed in forest soils. Sequestrine, (NA_2Zn 15% Zn), incorporated into Ritzville fine sandy loam in Washington with N-P-K fertilizers, was more readily utilized by Red Mexican beans than $ZnSO_4$ applied in the same manner.

Usually, the method of placement and method of incorporation into other micronutrient or macronutrient fertilizer have little effect upon the availability of micronutrient chelates. For example, Richards (149) reported that Na_2ZnEDTA, NaZnHEETA and ZnNTA incorporated into granular mixed fertilizers, remained H_2O soluble in soils whether mixing was prior to ammoniation or after; or whether the Zn chelates were coated on these fertilizers, whereas all inorganic Zn sources remained soluble in the soil only when they were incorporated into N-P-K fertilizer carriers after ammoniation or when coated onto these fertilizers. Schnapinger (152) found that ZnEDTA, broadcast on Norfolk loamy fine sand at the rates of 1.12 kg Zn/ha gave corn the highest grain yield whereas neither ZnDTPA nor $ZnSO_4$ applied to the soil surface nor ZnEDTA sprayed on the leaves increased corn grain

yield. This implied that $ZnSO_4$ and ZnDTPA applied to soil surface was not mobile. Boawn et al. (18) found that 2.0 ppm Zn incorporated into fine sandy loam as ZnEDTA together with 20.0 ppm P as K_2HPO_4 was more readily utilized by Red Mexican beans than Zn added as $ZnSO_4.7H_2O$ in the same manner. Jackson et al. (80) found that ZnEDTA remained H_2O soluble in N-P-K carriers which otherwise have a large capacity to immobilize free Zn ions. In one greenhouse pot experiment (112), 2.0% Zn as ZnEDTA, incorporated into the soil with ammoniated macronutrient fertilizer carriers, increased forage yield and Zn uptake whereas $ZnSO_4$ and ZnO applied in the same manner did not. In other greenhouse studies, Morvedt and Giordano (117) found ZnEDTA the most efficient Zn source when granulated with N-P-K fertilizer carrier or when applied to the soil alone. The effectiveness of ZnEDTA was significantly higher than that of Rayplex Zn whether applied alone or with $(NH_4)_2HPO_4$. However, the solubility of ZnEDTA was 100% in soil when coated on granulated micronutrient fertilizer together with $MnSO_4$ but the solubility decreased to only 40% when coated on the macronutrient carriers together with MnO (51). Finally, the solubility decreased to only 10% when the ZnEDTA was incorporated into granular N-P-K fertilizers before addition to the soil.

Rasmussen and Boawn (145) found Zn polyflavinoid superior to ZnEDTA and $ZnSO_4$ as seed treatment for beans. However, both ZnEDTA and Zn polyflavinoid did not supply enough Zn to meet Zn requirements of beans. More uniform maturity resulted when seed treatment was used in conjunction with soil and foliar application with $ZnSO_4.7H_2O$. Brown and Krantz (26) in several greenhouse experiments, reported that

Rayplex Zn, an organic complex, was as effective as ZnEDTA and reagent grade $ZnSO_4.7H_2O$ for correcting Zn deficiency in sweet corn when thoroughly mixed with soil, however, its effectiveness decreased considerably relative to the ZnEDTA when banded under the seeds or when applied in granulated form.

2.) (B) Cu AND Zn SULPHATES

Chelates are approximately five times more effective than sulphates. Nevertheless, sulphates are far more commonly used because of their cost. Chelates would have to be 10 times as effective as inorganic sources (113) to compete with them on an economic basis.

The use of $CuSO_4.5H_2O$ (25.5% Cu, 12.8% S) has been recommended (177) for either foliar or soil application because of its high solubility. Incorporation of Cu with the soil at rates of 7.0 to 14.0 kg Cu per ha as $CuSO_4$ should provide adequate Cu for several years on most soils. However, when banded with the seed, these rates should be decreased to prevent possible plant injury. Fiskell (53) indicated that Cu concentration in the roots of citrus trees grown on Leon fine sand increased proportionally with the amount of $CuSO_4.5H_2O$, whether placed in the planting hole, broadcast around trees, or foliar applied. Cauliflower, spinach, barley, timothy and alfalfa in greenhouse studies on some podzolic soils of Prince Edward Island did not respond significantly to $CuSO_4.5H_2O$. However, plant tissue Cu content of barley straw and spinach increased by about 400% and 50%, respectively (67). Mixing $CuSO_4.5H_2O$ with a silty clay loam at the rates of 22.4 to 44.8 kg Cu/ha increased both leaf Cu concentrations and dry matter yields of corn and soybean by up to 12.0% and 14.0%, respectively, at five locations on

calcareous soils (133). Pack et al. (135) found that application of $CuSO_4.5H_2O$ increased yields and Cu concentrations of red clover and wheat shoots on certain New Jersey mineral soils but depressed the yields of clover on peat soils.

Smith et al. (135) observed that $CuSO_4.5H_2O$ was highly mobile in the subsoil of the highly leached Lakeland fine sand in Manitoba, whereas retention of Cu broadcast as $CuSO_4.5H_2O$ was high particularly when pH and organic matter levels of the surface soils were high. This implies that the loss of Cu on acid sandy soils may be greater when $CuSO_4.5H_2O$ is mixed with soil than when Cu is broadcast on the surface. On the other hand, both field and greenhouse studies have indicated considerable residual effects of $CuSO_4.5H_2O$ on yield (169).

One must avoid adding too much Cu. Plant Cu concentrations need not be very high before toxic effects result. For example, tobacco seedlings exhibited external chlorotic symptoms and internal toxic effects when grown on quartz sands treated with 0.32 and 0.64 ppm Cu applied as $CuSO_4.5H_2O$. Dry matter yields of the entire tobacco seedlings were highest at 0.04 and 0.08 ppm and lowest at 0.32 and 0.64 ppm Cu (172).

Younts (199) found that $CuSO_4.5H_2O$, $CuSO_4.3Cu(OH)_2$ and CuEDTA were equally effective for wheat on mineral soils of varying organic matter levels. In field trials, Gniliskaya (63) found that dusting of corn seeds with $CuSO_4.5H_2O$ at concentration of 300 mg Cu/ha of grain increased grain yields, grain protein and grain starch contents. Application of $CuSO_4.5H_2O$ with N-P-K fertilizer was also reported suitable.

Mineral soils are usually not as Cu deficient as organic soils but occasionally sandy acidic mineral soils respond to Cu. Heavier mineral soils such as clay loam have also occasionally responded to Cu application. Organic soils are often very deficient in Cu. For instance, Campbell and Gusta (37) reported that an addition of $CuSO_4.5H_2O$ to Vivian peat deposits in Manitoba increased the yield of carrots by about 6.2 tons/acre and improved the quality of onions. Carrots, onions, spinach, cauliflower and lettuce grown successfully in pails of virgin sphagnum peaty soils, limed slightly to pH of 5.0, responded significantly to Cu applied as $CuSO_4.5H_2O$ (99).

Soil and foliar applications of $ZnSO_4.7H_2O$ have been recommended for vegetable, field and fruit crops (177). A newly developed Zn fertilizer Zn-Fe-$(NH_4)_2SO_4$, $ZnSO_4.H_2O$, $ZnSO_4.7H_2O$ and $ZnSO_4.4Zn(OH)_2$ are also recommended for both foliar and soil application (113, 177) because of the relative solubilities. Usually sulphates are more plant available than other inorganic sources. For example, the uptake of Zn by various grasses in the greenhouse was in the order $ZnSO_4$ > ZnO > ZnS (175). In a similar field trial (201), the order was $ZnSO_4$ > ZnO = ZnS.

It was mentioned at the beginning of the section on relative effectiveness of Cu and Zn fertilizers that placement method influences greatly the efficiency of some micronutrient fertilizers. Usually those fertilizers which are sparingly soluble or quickly form sparingly soluble reaction products are more effective if finely ground and mixed throughout the surface soil than if banded. Thus, Barrow (6) observed that the growth of one year old tung tree was

better when 28.0 kg $ZnSO_4$/ha were mixed with the soil whereas the tung tree absorbed very little Zn when 56.0 and 112.0 kg $ZnSO_4$/ha were applied to the surface. Yet in another trial, Zn mobility was so high that 28.0 kg $ZnSO_4$/ha broadcast onto the soil was toxic to the tree. The powdery form of $ZnSO_4.7H_2O$, thoroughly mixed with soil, was found to be as effective as ZnEDTA or Rayplex Zn, a chelated Zn form, for correction of Zn deficiency in sweet corn (26). However, $ZnSO_4.7H_2O$ was not as effective as ZnEDTA or Rayplex Zn when it was banded below the seed, applied in granular form or placed in a point in the soil. Dry matter yields of 6 week old sweet corn increased (28) when 4.0 kg Zn/ha as $ZnSO_4.7H_2O$ were thoroughly mixed with the soil. That amount of Zn was adequate for six successive crops while 10.0 kg Zn/ha as $ZnSO_4.7H_2O$ were adequate for 10 successive sweet corn crops. Corn plants responded to $ZnSO_4.7H_2O$ thoroughly mixed with the soil. No further significant yield increase was observed when the Zn concentration in the corn tissue was above 12.0 ppm (44). MacGregor et al. (98) found in the greenhouse studies that $ZnSO_4.7H_2O$, mixed with Zn deficient calcareous silty clay loam soils, increased Zn concentrations in leaves of corn whereas row-banded $ZnSO_4.7H_2O$ had little or no effect on leaf Zn concentrations. Corn forage yield and Zn uptake were much higher when $ZnSO_4$ was mixed with soil, whereas $ZnSO_4$ placed in a specific spot in the soil was much less effective (115). In four greenhouse experiments, forage yields and Zn uptake of corn were higher when Zn as finely ground $ZnSO_4$ was mixed with soil than when the granular form of $ZnSO_4$ was banded or mixed with

soil (117). Pumprey et al. (143) found that 6.0 kg Zn/ha as $ZnSO_4$ broadcast and ploughed down before planting increased the early grain yield of corn on soils of western Nebraska whereas banding the sulphate under the seeds or placing it in a specific spot in the soil were less effective. Rasmussen and Boawn (145) noticed that seed treatment with $ZnSO_4$ did not supply enough Zn to meet Zn requirements of soybean although more uniform maturity resulted when seed treatment was supplemented with foliar or soil application.

Macronutrient fertilizers applied with micronutrient can influence considerably the effectiveness of the micronutrient carriers. The effects of macronutrient fertilizers on the efficiency of micronutrients are dependent upon the properties of the macronutrient fertilizer; whether the micronutrient and macronutrient fertilizers are applied separately, mixed together or the micronutrient incorporated into the macronutrient fertilizer; and the method of placement in the soil. Kalbasi and Racz (84) suggested that phosphates applied with Zn fertilizers such as $ZnSO_4$ might decrease the solubility and availability of Zn to plants. In field experiments, Boawn et al. (17) observed an increase in the yield of navy beans when Zn as $ZnSO_4.7H_2O$ was applied as a foliar spray whereas Zn as $ZnSO_4$ banded at the planting of navy beans together with 200 ppm P as K_2HPO_4 depressed the yield of the plants. Boawn et al. (18) reported that Zn uptake by red Mexican beans from $ZnSO_4.7H_2O$, incorporated into N-P-K fertilizers on a sandy loam soil, was considerably less than Zn uptake from ZnEDTA applied in the same manner. Concentration and uptake of Zn by corn were highest when $ZnSO_4$ was broadcast

with $(NH_4)_2SO_4$ and least when $ZnSO_4$ was broadcast with $Ca(NO_3)_2$ (19). Ellis et al. (50) reported that incorporation of $ZnSO_4.7H_2O$ into basal N-P-K fertilizer carriers decreased the H_2O solubility of Zn, Zn total uptake in pea beans and their dry matter yield relative to the same level of $ZnSO_4$ hand mixed with basal fertilizers at planting time. Mixing $ZnSO_4$ alone with a sandy clay loam soil was more effective in correcting Zn deficiency in two successive crops than when $ZnSO_4.7H_2O$ was incorporated into granules of NH_4NO_3, NH_4 polyphosphate or concentrated super phosphate and subsequently banded with the seeds or mixed with the soil (59). Nevertheless, $ZnSO_4$ was more effective than ZnS regardless of method of placement.

Mortvedt (112) found in the greenhouse that increases in forage yields and Zn uptake by corn were lower when Zn as $ZnSO_4$ was incorporated into granular ammoniated fertilizers than when the ammoniated fertilizers contained no Zn. Crop response to Zn also increased with decreases in granule size. The effectiveness of $ZnSO_4$ incorporated into N and P carriers decreased with increasing degree of ammoniation which implied that effectiveness of Zn is low when incorporated with ammoniated fertilizers. The movement of Zn from Zn carriers was retarded in the presence of applied NH_3 whereas $ZnSO_4$ applied to soil without NH_3 was relatively mobile (115). The uptake of Zn by corn grown on a fine sandy loam treated with Zn as $^{65}ZnSO_4$ incorporated into NH_4NO_3 granules was greater than when incorporated into P carriers (116). Better response was obtained when Zn as finely ground $ZnSO_4$ was granulated with N-K carriers than when granulated with P carriers (117). Zinc sulphate and ZnO were equally effective when

granulated with APP (177). On the other hand, $ZnSO_4$ was more effective than ZnO when granulated with CSP or urea before soil application (117). However, banding $ZnSO_4$ with N-P-K fertilizers was superior to incorporation of fine form of $ZnSO_4$ into macronutrient carriers before soil application (117). The highest forage yield and Zn uptake were obtained when $ZnSO_4$ was mixed with the soil separately from macronutrient fertilizers (117). Richards (149) reported that the solubilities of $ZnSO_4.H_2O$, $ZnSO_4.(NH_4)_2SO_4.6H_2O$, $Zn(C_2H_3O_2)_2.2H_2O$, $ZnCl_2$, and Zn polyflavonoids decreased when incorporated into N-P-carriers prior to ammoniation whereas incorporation with N-P carriers after ammoniation or coating the Zn carriers on N-P fertilizers increased the solubility of Zn from the Zn carriers. Terman et al. (175) found that corn yield and Zn uptake from $ZnSO_4$ granules decreased in the following order: $ZnSO_4$ mixed along with the soil > $ZnSO_4$ incorporated into NH_4NO_3 or $(NH_4)_2SO_4$ granules > $ZnSO_4$ incorporated into APP granules > no Zn > $ZnSO_4$ incorporated into CSP granules.

Interactions between Zn and other nutrients may occur. In greenhouse experiments (29) in which $ZnSO_4.7H_2O$ was mixed with clay soil at 4.5 mgZn/2.2 kg soil, growth depression increased as the rate of $CaCO_3$ increased from 0.0 to 40.0%. However, when the same level of $ZnSO_4.7H_2O$ was applied to a fine sandy loam soil, $CaCO_3$ did not depress growth. Application of $CaCO_3$ with 20.0 ppm Zn as $ZnSO_4.7H_2O$ to a fine sandy loam drastically decreased Zn concentration in corn (58). However, when the same rate of Zn was added to APP without $CaCO_3$, Zn concentration increased in corn. Also, Seatz (154) observed that flax and sorghum on loamy soil in Tennessee responded to Zn applied

with 13.0 tons $CaCO_3$/ha. In another greenhouse study (27) in which $ZnSO_4.7H_2O$ was applied at rates of 0.0 ppm, 2.5 ppm, 10.0 ppm, 20.0 ppm and 40.0 ppm Zn, 0.0 ppm, 50.0 ppm, 100.0 ppm, 200.0 ppm and 400.0 ppm P as $Ca(H_2PO_4)_2.H_2O$, KH_2PO_4 and H_3PO_4 concentration of P tended to induce Zn deficiency at a range between 200.0 to 400.0 ppm P.

Temperature also has a great influence on the incidence of Zn deficiency. For example, Wallace et al. (192) found, in a pot experiment with sandy loam on which 11.0 kg Zn/ha as $ZnSO_4$ was uniformly distributed, that cotton responded to Zn only at temperatures below 15°C, bush bean responded to Zn only at temperatures higher than 15°C whereas corn responded to Zn at temperatures below and above 15°C. However, Zn accumulated in the shoots and roots of corn and beans only at temperatures above 15°C.

3.)(C) OXIDES OF Cu AND Zn

Both CuO and Cu_2O are recommended as suitable Cu fertilizers especially if finely ground and mixed well with soil. Their residual effects, like $CuSO_4.5H_2O$ are considerable (169). A granulated mixture of CuO, Cu_2O and elemental Cu, broadcast on sandy loam and on soil high in organic matter, increased leaf Cu concentrations and yields of corn and soybeans in five instances (133). Fiskell (53) found that CuO placed in the planting hole, broadcast around trees and sprayed on the leaves increased the Cu concentration in the roots of young citrus trees on Leon fine sandy soil in California. Since CuO or Cu_2O are not as commonly used as $CuSO_4.5H_2O$, not much literature is available on their effectiveness as fertilizers.

Some studies indicated that ZnO was a good fertilizer although it did not supply as much plant available Zn as $ZnSO_4$ or $Na_2ZnEDTA$ (104, 177). Other studies indicated, however, that ZnO was as good as $ZnSO_4$ in correcting Zn deficiency (183). However, responses in yields and Zn uptake from ZnO depended greatly on the method of placement, the type of macronutrient carrier with which it was applied, and whether it was incorporated into or simply mixed with the macronutrient fertilizer (18, 51, 59, 60, 61, 62, 81, 112, 114, 156).

Boawn et al. (18) found that ZnO, mixed with a fine sandy loam along with N-P-K carriers was as readily utilized by corn, grain and sorghum as Zn applied as $ZnSO_4.7H_2O$ or as stripping acid residue (ZnMNS). Incorporating ZnO into NH_4 polyphosphate was superior to incorporating ZnO into NH_4NO_3 (51). In greenhouse studies, total dry matter yields and uptake of Zn by corn increased when the powdery forms of ZnO or ZnO + $ZnSO_4$ were pressure granulated with NH_4NO_3, $NH_4P_2O_7$ or with NH_4 polyphosphate and thoroughly mixed with soil (60). Jones, Jr. (81) indicated that the use of oil to coat ZnO onto granular 8-32-16 fertilizer had no adverse side effects on the growth of corn and soybeans on a moderately fertile silt loam and on a silty clay loam. Sharpee et al. (156) found that ZnO fused with S resulted in the increase of dry matter yield of corn. However, plant Zn concentrations decreased with increasing size of ZnO-S granules and were much lower when banded than when mixed. Greenhouse studies indicated that ZnO in liquid form containing Zn increased corn shoot yield and Zn uptake more effectively than when granulated and applied

separately or incorporated into granular N carriers (114). The liquid form of ZnO was likely better distributed throughout the soil (112). In greenhouse studies, Giordano et al. (62) found that the dry matter yield and Zn uptake of three week old corn were higher when ZnO and $(NH_4)_2SO_4$ were mixed with the soil or placed in a small spot just prior to planting than when ZnO and NH_3 or ZnO and $CO(NH_2)_2$ were similarly applied. This was likely due to lower pH associated with $(NH_4)_2SO_4$. Yields were, however, lowest when ZnO was spot placed or mixed with soil four weeks prior to planting and when no Zn was applied. Incorporating ZnO into macronutrient fertilizers resulted in lower Zn solubility, Zn uptake and dry matter yield of pea bean than when the same level of ZnO was mixed with macronutrient carriers at planting time (51, 59).

4.7)(D) Cu AND Zn SULPHIDE

Copper sulphide has been used to correct Cu deficiency although it was usually not as efficient as $CuSO_4$ (156, 169, 196). Copper pyrites ($CuFeS_2$), Cu glance (Cu_2S), and bornite (Cu_5FeS_4) were all found to be slightly inferior to $CuSO_4.5H_2O$ in agronomic effectiveness, but further grinding would undoubtedly have increased their efficiencies (169). Copper sulphide has not been used as extensively as CuEDTA or $CuSO_4.5H_2O$ because of its low solubility and low biological availability. Hence, very little literature is available concerning CuS as a fertilizer.

Results to experiments concerning the effectiveness of ZnS as Zn fertilizer have been variable. Often, however, ZnS was less available than ZnO. Kalbasi and Racz (84) found in the laboratory incubation

studies that ZnS dissolved very slowly and persisted for 32 weeks. When ZnS was applied, concentration of H_2O soluble Zn was lower than when $ZnSO_4$ and ZnEDTA were applied. However, H_2O soluble Zn from ZnS increased with time whereas H_2O soluble Zn levels decreased with time when $ZnSO_4$ and ZnEDTA were applied.

Zqureshi and Gammon (201) found that only 15% of Zn applied as ZnS to certain acid Florida soils was 0.05 N HCl + 0.025 N H_2SO_4 extractable compared to 80.0% when ZnEDTA and $ZnSO_4.7H_2O$ were added to the same soil. Other workers have also found little or no response to ZnS. Holden and Brown (75) observed that sphalerite (ZnS) had no effect on the Zn uptake and yield of alfalfa on Florida acid sand whereas willemite ($2ZnO.SiO_2$), a Zn frit, supplied Zn to plants although at a very low level. On a sandy clay loam having pH of 7.3, ZnS was less suitable than either ZnO or $ZnSO_4$ both when mixed thoroughly with the soil and when incorporated into various macronutrient carriers (59). However, McGregor (104) found ZnS to be a good source of water soluble Zn.

57. (E) Cu AND Zn PHOSPHATES AND AMMONIUM PHOSPHATES

Copper ammonium phosphate (30% Cu) is slightly soluble and is slowly available to plants (177). Its use has been recommended for soil application by banding near the seeds and placing the material in the planting hole. It is also suitable for seed treatment. Its availability can be controlled by granulation (25). It can be applied also by foliar spray (25, 177). Bingham and Gabler (12) reported that excess of granulated P carrier mixed with $CuNH_4P_2O_7$ resulted in P induced deficiency in sour orange seedlings. However, strangely

enough, Cu solubility was increased by excess of P fertilization (12). Uptake of fertilizer Cu and Zn is often depressed by liming. However, uptake of Cu from $CuNH_4P_2O_7$ by sorghum was not depressed by liming on both organic and inorganic soils (25).

Zinc ammonium phosphate (35.5% Zn) has been recommended as fertilizer (12, 18, 25, 26, 78, 177). McGregor (104) found $ZnNH_4PO_4$ as a good fertilizer. However, it was less suitable than $Na_2ZnEDTA$ or ZnS. Excess of P material added to the soil with $ZnNH_4PO_4$ reduced the uptake of Zn by sour orange seedlings although the solubility of Zn was found to increase with excess of P fertilization. Such P induced Zn deficiency must be physiological in nature and not caused by formation of $(Zn)_3(PO_4)_2$. Zinc phosphate has been found to be a good fertilizer source of Zn. For example, $(Zn)_3(PO_4)_2$ mixed with a fine silt loam soil along with a N-P-K carrier was as readily utilized by grain sorghum as Zn applied as $ZnSO_4.7H_2O$ or as stripping acid residue (Zn-M-N-S) (19). Granular and pulverulent forms of $ZnNH_4PO_4$ have also been applied to several crops and to different soils. The low solubility usually prevents salt injury when applied to seeds and to plants. Yields and total uptake of corn, sorghum, and soybeans from $ZnNH_4PO_4$ were in all instances as good as those from $ZnSO_4$. It can be applied as seed coating, and placed, near the seed or in planting hole, with seedlings (25). Granulation greatly reduced the effectiveness of $ZnNH_4PO_4$. It is an effective Zn source when finely ground and mixed thoroughly with the soil (26).

6.) (F) SALT FRITS OF Cu AND Zn

One reference indicated that most copper salt frits are suitable

for soil application (177) but no other report was found to corroborate their suitability or agronomic effectiveness.

Zinc silicates have been assessed as fertilizer sources of Zn (18, 74, 75, 117, 149, 177, 183). Application of powdery Zn glasses to soil increased the yield of corn more than fine crystalline forms of $ZnSO_4.7H_2O$ (75), although it had less effect on Zn content of the crop. Hemimorphite ($2ZnO.H_2O.SiO_2$) dissolved at a satisfactory rate in neutral Florida sand but not in a calcareous loam whereas $2ZnO.SiO_2$ supplied very low levels of available Zn. Hoeft and Walsh (74) observed that powdery Zn frits (silicates) mixed with CSP were as effective as $ZnSO_4$ on a neutral soil, but not as effective as $ZnSO_4$ on calcareous soil. Finely ground Zn frits were more effective than the granular form when applied at a rate of 12.0% Zn to calcareous soil. Mixing Zn frits with soil increased the uptake of Zn by corn as compared to banding Zn frits with the seed. To slow down the rapid reversion of Zn from Zn fertilizers to the adsorbed form, Viet, Jr. (183) suggested that Zn fertilizers be placed in bands or incorporated into frits or glasses so that there would be slow release to water soluble form. On the other hand, Boawn et al. (18) found that Zn, in three fritted forms with varying degree of hardness, were not utilized by plants whereas under the same environmental conditions, considerable uptake of Zn from $ZnSO_4.7H_2O$ was noticed. In a greenhouse experiment (117), response of corn to fritted Zn source (Zn silicate FTE 525) was lower than response to ZnEDTA or Rayplex-Zn (6).

Zinc frits are very slowly available. They can serve as effective

Zn fertilizers, however, when finely ground and mixed thoroughly with the soil if the pH of the soil is below 7.0. They may also be effective Zn sources if banded with acidic fertilizer. The poor results obtained by some workers (18, 117) may have been due to alkaline conditions, because research has established that Zn frits are not effective sources of plant available Zn in calcareous soils.

III METHODS AND MATERIALS

A. General Procedures

1A) Cleaning of Apparatus

Prevention of possible contamination is very critical in all micronutrient experimental manipulations. To meet this particular demand, a rigorous washing procedure was meticulously adhered to throughout.

All pieces of apparatus were washed thoroughly with 10.0% soap solution prepared with biodegradable laboratory detergent supplied by Fisher Scientific Company. They were next rinsed four times with tap water, making sure no trace of soap solution remained. This was followed by four rinses with distilled water, brief immersion in 0.1 M EDTA solution, four rinses with distilled water, immersion for 10 minutes in 0.1 N HNO_3, four rinses with distilled water and finally, two rinses with deionized water.

2B) Soil Analyses

1. Description of the soils used

Pine Ridge sand, a degraded eutric brunisol which had been established as Cu deficient (84, 104) and Lakeland clay loam, a gleyed carbonated rego black, which had been established as deficient in Zn (84, 104) were used in both the incubation and the growth chamber studies.

A sample of each of the two soils was air dried and thoroughly mixed to ensure against possible variability during field sampling. This was followed by grinding a portion with a porcelain pestle and mortar until it passed through a 2 mm sieve. This sieved portion

was stored for subsequent incubation experiments and laboratory analyses. The unsieved portion was stored for growth chamber experiments.

2. pH

Soil pH was determined electrometrically following the procedure outlined by Schofield and Taylor (153). 25.0 Grams of soil were suspended in 25.0 ml 0.01 N $CaCl_2$ rather than in water. A calomel electrode pH meter was used.

3. Organic matter

The organic carbon was determined using the modified method of Walkley and Black (189), fully described by Allison (2). The organic carbon content of 0.5 g of the soil was digested in 10.0 ml 1.0 N $K_2Cr_2O_7$ and 20.0 ml concentrated H_2SO_4 for 30 minutes. The volume was subsequently brought to 300 ml with distilled water. The unreacted $K_2Cr_2O_7$ was back titrated with 0.5 N $FeSO_4$ using an automatic titrator (radiometer). The end point was set at 750 millivolts.

4. NO_3-N

The soil NO_3-N was determined using a method similar to that described by Kamphake and Hannah (85). Ten g of soil was added to 50.0 ml of an extracting solution containing 0.02 N $CuSO_4$ and 0.06% Ag_2SO_4. The mixture was shaken for 15 minutes. This was followed by an addition of 1 cc of $Ca(OH)_2$ which was previously heated in muffle furnace at 750°C for two hours. This was followed by an addition of 0.7 cc of solid $MgCO_3$. The shaking continued for 15 minutes. The filtrate was collected using Whatman no. 42 paper. Twenty-five ml of the filtrate were pipetted into a 50.0 ml beaker and evaporated

to dryness. The dried material was dissolved with 2.0 ml phenol disulphonic acid and 25.0 ml distilled water. The dissolved residue was later washed into a 100 ml flask and rotated for 15 minutes. This was followed by slow addition of dilute NH_4OH until a yellow colour developed. The mixture was finally brought to 100 ml with distilled water. The NO_3-N concentration was determined colorimetrically at 415 mμ.

5. Plant available P

Phosphorus was extracted from the soil with $NaHCO_3$ and the P level in the extract determined using the acid molybdate method of Murphy and Riley (119). Five g of soil were shaken for 30 minutes in 100 ml of 0.5 M $NaHCO_3$ solution containing 1.0 g of activated charcoal. The mixture was filtered through no. 42 paper. One drop of 2,4-dinitrophenol was added to 25.0 ml of the filtrate which was followed by slow addition of concentrated H_2SO_4 until the solution changed from yellow to clear. Acid molybdate reagent was prepared by mixing four parts of a solution containing 7.5 g of $(NH_4)_6Mo_7O_{24}.4H_2O$, 14.0 g of antimony potassium tartrate and 88.0 ml of concentrated H_2SO_4 in 1000 ml with one part of a solution containing 2.5 g of L-ascorbic acid in 100 ml of H_2O. Five ml of the acid molybdate reagent were added to the 25 ml of filtrate. The intensity of the blue colour was measured after 5 minutes at 885 mμ with a Cecil model 202 ultraviolet spectrophotometer.

6. Plant available K

Five g 2 mm soil were shaken with 100.0 ml of 1.0 N NH_4OAc containing 250.0 ppm of lithium for one hour. The filtrate was

collected through Whatman's no. 42 paper. The K concentration of the filtrate was determined using Perkin-Elmer model 303 atomic absorption spectro photometer.

7. DTPA extractable Cu, Zn, Fe and Mn

Plant available Cu, Zn, Fe, and Mn were determined by the DTPA (diethylene triamine penta acetic acid) method of Lindsay and Norvell (94, 95) as modified by the Kansas State University Soil Testing Laboratory. The extracting solution contained 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M triethanolamine (TEA) as a buffer. The quantities of micronutrients extracted vary considerably with the pH of the DTPA solution. For determination of indigenous micronutrients, the pH of DTPA solution was carefully adjusted with 1.0 N HCl to 7.3, the value recommended by Lindsay and Norvell. For determination of micronutrient levels in the incubation experiment, however, the pH of DTPA was adjusted to 8.0, the value recommended by McGregor (104) for Manitoba soils. Lindsay and Norwell recommended a soil-extracting solution ratio of 1:2. For determination of indigenous micronutrient levels, 25.0 g of soil were shaken for 3 hours with 50 ml of DTPA solution. In the incubation study, 5 g of soil were shaken with 25 ml of extracting solution in order to minimize overloading the DTPA solution. For all determinations, the DTPA solution-soil suspensions were filtered through Whatman's no. 42 paper, and micronutrient concentrations in the filtrates determined with Perkin-Elmer model 303 atomic absorption spectrophotometer.

8. Water extractable Cu and Zn

Five g of soil and 25 ml deionized water were shaken together

for 3 hours. The mixture was filtered through Whatman no. 42 paper and the Cu and Zn concentrations in the filtrate determined with a Perkin-Elmer model 303 atomic absorption spectrophotometer.

9. Cation exchange capacity

The cation exchange capacity of the soil was determined using an ammonium saturation method fashioned after Chapman (39). The exchange sites of 10 g of 2 mm clay loam and 25 g of sandy soil were saturated with NH_4^+ by shaking in 50.0 ml of neutral 1.0 N NH_4OAc for one hour. The adsorbed NH_4^+ ions were subsequently displaced with 225.0 ml of acidified 0.005 N NaCl. This was followed by addition of 25.0 ml of 1.0 N NaOH into the filtrate in an 800 ml Kjeldahl flask. Sixty ml of the solution were then distilled into 50 ml of 2.0% boric acid. The absorbed NH_3 was titrated with 0.1 N H_2SO_4 using 10 drops of bromocresol green-methyl red as the indicator. The end point was taken as that point at which the solution changed from bluish green through bluish purple to pink.

10. Inorganic C

The inorganic C (carbonate) content was determined using the procedure described by Ridley (150). One g of soil was digested with 0.1 N HCl for 20 minutes. The CO_2 evolved was sucked through an absorption train which included a Nesbitt tube containing asbestos saturated with NaOH (ascarite). The percentage CO_3 of the soil was calculated from the weight of CO_2 absorbed on the ascarite.

11. Field capacity

The top half of soil in a 4.5 by 10.2 cm plastic cylinder was saturated with water. The sample was allowed to equilibrate for

48 hours in a desiccator containing water to maintain a humid environment. Following equilibration, soil from above the wetting front in the cylinder was placed in a 600 ml beaker and dried at 105°C for 24 hours. The weight of the water lost was determined and the moisture content expressed as percent of oven dry soil.

3.) Plant Analyses

1. Plant total Cu, Zn, Fe, Mn and K

Barley shoots were dried to constant weight at 70°C and the dry matter yields determined. The shoots were sectioned into 0.5 cm lengths with stainless steel scissors. It was felt that this procedure would result in less contamination with Fe than if the plant material were ground in a Wiley mill. After thorough mixing, a one gram subsample was digested in 5.0 ml of 1.0 N HNO_3 and 2.0 ml of 1.0 N $HClO_4$ until the mixture was clear and the volume had decreased to approximately 2.0 ml (approximately after 3 hours). The digest was cooled and diluted to 20.0 ml, filtered through Whatman no. 42 filter paper, and brought to volume in a 25.0 ml volumetric flask with deionized water.

Each sample was sealed and stored at 4°C to prevent evaporation and spoilage while awaiting nutrient analysis. Copper, Zn, Fe, Mn and K concentrations in the filtrate were determined with a Perkin-Elmer 303 atomic absorption spectrophotometer.

2. Total P

The filtrates were assayed for P by acid molybdate method of Murphy and Riley (119). Acid molybdate reagent was prepared as for the available soil P analyses. After the necessary dilution of the

HNO_3-$HClO_4$ plant digest, 25.0 ml of the diluted digest was mixed with 5.0 ml of the mixed acid-molybdate reagent. The blue colour was allowed to develop for five minutes after which absorbency was measured at 885 mμ using a Cecil 202 ultraviolet spectrophotometer.

3. Total N

The total N concentration of the plant material was determined using the modified Kjeldahl-Gunning method described by Jackson (79). One g of oven dried, sectioned barley shoots was placed in an 800 ml Kjeldahl flask. One Kelpak no. 1, containing 9.9 g K_2SO_4, 0.41 g of HgO and 0.08 g of $CuSO_4$, was dropped into the flask as a digestion accelerator, followed by 25.0 ml of 0.1 N H_2SO_4. The mixture was digested for approximately one hour on a Labonco Kjeldahl N apparatus. After cooling, 60.0 ml of a 50% NaOH solution was added to the plant digest and the NH_3 distilled into 70.0 ml of 2.0% boric acid solution which was subsequently titrated to neutrality with 0.1 N H_2SO_4.

B. Experimental Design

1. Incubation Study

The laboratory incubation study was a brief prelude to the growth chamber experiments. The primary objective of this study was to determine the effect of time and method of placement on the chemical availability of soil applied $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$. Two extractants, H_2O and DTPA, were used to estimate the chemical availabilities.

Air dry Pine Ridge loamy sand was mixed with finely ground $CuSO_4.5H_2O$ at rates of 0.0, 1.0, 5.0, 10.0, 25.0, 50.0, 100.0, 250.0, 500.0, and 1000.0 ppm Cu. Air dry Lakeland clay loam was mixed with finely ground $ZnSO_4.7H_2O$ at rates of 0.0, 2.0, 10.0, 20.0, 50.0, 100.0,

200.0, 500.0, 1000.0, and 2000.0 ppm Zn. Three subsamples from each Cu and Zn level were placed in 3.0 by 5.0 cm plastic cylinders, wetted to field capacity by adding 3.78 g of H_2O to the sandy soil and 5.88 g of H_2O to the clay loam and incubated for 7 days at 20°C in a sealed water-humidified dessicator. At the end of the incubation period, the subsamples were air dried for 48 hours at room temperature. Water and DTPA extractable Cu and Zn concentrations in those subsamples and in triplicated subsamples taken just prior to wetting (time = 0) were determined according to the procedures already outlined. The extractable native Cu and Zn value was subtracted from the Cu and Zn value for each treatment receiving fertilizer Cu and Zn in order to arrive at a value reflecting the availability of only the added micronutrient.

It was felt that the lower levels of applied Cu and Zn would simulate mixing the micronutrients with soil whereas the higher levels of Cu and Zn would simulate band placement.

2) Growth Chamber Studies

Growth chamber studies were initiated to assess the effects of rate and method of application of $CuSO_4$ and $ZnSO_4$ upon the dry matter yield and the nutrient uptake of barley shoots and to determine the critical levels of Cu and Zn in barley shoots.

1. Cu Experiment

Copper was applied as $CuSO_4$ to Pine Ridge sand at rates of 0.5, 1.0, 2.0, 4.0, and 8.0 ppm in four methods of placement which included mixed throughout the soil, banded with the seed, banded below the seed and placed in a point below the seed. The 20 treatments were arranged factorially. A control treatment which received no Cu was also

included. The 21 treatments were replicated three times in a randomized complete block design.

Each pot consisted of 12 barley (Hordeum vulgare L. var conquest) seeds at a depth of 2 cm in 4120 grams of soil in an 18.5 cm by 16.8 cm plastic pot. Twelve days after planting each plot was thinned to 6 plants. All macronutrients and $CuSO_4$ were sprayed in solution onto soil. Before planting, all of the soil from every plot was thoroughly mixed with 66 ppm N as NH_4NO_3 and 200 ppm K and 80 ppm S as K_2SO_4. Every plot also received 66 ppm N and 100 ppm P as $NH_4H_2PO_4$ applied in a band 2 cm in width. At the centre of the band were the barley seeds. The top of this band was therefore 1 cm below the soil surface. Copper sulphate was also added to the 2 cm $NH_4H_2PO_4$ band for the banded with the seed treatment. Copper sulphate was mixed with a 2 cm band of soil directly below the $NH_4H_2PO_4$ band for the banded below the seed treatment. For the point placed treatment, $CuSO_4$ was mixed with 5 g of soil which was placed in the centre of the pot, 2 cm below the barley seeds.

The soil was wetted to 70% of field capacity for the first week after planting in order to avoid seed rotting. The soil was then moistened to field capacity and maintained at that level by as many as two waterings per day. Additional 50 ppm N as NH_4NO_3 were added to each pot four weeks after emergence of the seeds. The barley was grown in a controlled environmental chamber at $20^{o}C$ - $15^{o}C$ day-night temperatures with a 15 hour photo period. Lighting was provided with Sylvania "Grow-Lux" fluorescent lamps and incandescent bulbs which together resulted in a light intensity of approximately 30,000 lux at the tops of the plants. The relative humidity was 65% at night and 45% during

the day. Pots within each of the three blocks and the blocks themselves were rotated periodically to minimize non-treatment variation. Plants were harvested when at heading six weeks after emergence. They were washed with deionized water, dried at 70°C for three days, weighed and assayed for nutrient content according to the methods already described.

2. Zn Experiment

Zinc was applied as $ZnSO_4$ to Lakeland clay loam at rates of 1.0, 2.0, 4.0, 8.0 and 16.0 ppm in the same four methods of placement employed in the Cu experiment. As in the Cu experiment, a control treatment receiving no Zn was also included. Each plot consisted of 20 barley seeds in 5000 g of soil in a 21.3 cm by 19.7 cm plastic pot. Twelve days after planting, each plot was thinned to 12 plants. Although plot size in the Zn experiment was larger than that in the Cu experiment, width and depth of the fertilizer bands as well as all other procedures were identical to those in the Cu experiment.

3. Statistical Analysis of Data

It was not possible to conduct "standard" factorial analyses of variance of all treatments in the growth chambers studies because only one (triplicated) zero treatment was included in each experiment. A zero treatment for each method of placement would have been required in order to employ such statistical analyses. It was therefore necessary to conduct "combined" analyses of variance which were combinations of simple analyses of variance of all treatments and factorial analyses of variance of all except the zero treatments.

An abbreviated example of the simple analyses of variance conducted on all 21 treatments including the zero is illustrated in Table 5.

Table 5

Simple Analysis of Variance
of 21 Treatments

Source of variation	Degrees of freedom (df)	Sum of squares (ss)	Mean square (ms)	F value
Treatments	20	A	$\frac{A}{20}$	$\frac{2A}{C}$
Block	2	B	$\frac{B}{2}$	$\frac{20B}{C}$
Error	40	C	$\frac{C}{40}$	---
Total	62	---	---	---

When the F test indicated that there were significant treatment differences at the 5% level, Duncan's Multiple Range Test was used to determine which of the differences among the 21 treatment means were significant. In order to more accurately assess the effects of micronutrient rate and placement method and to compare the zero treatment with the average of all other treatments, a factorial analysis of variance excluding the zero treatment (Table 6), and the simple analysis of variance (Table 5) were combined (Table 7). In the factorial analysis, it was only necessary to calculate the sums of squares (ss) for placement (D), rate (E) and interactions (F) (Table 6) for inclusion in the "combined" analyses of variance (Table 7). The error sum of squares (C) in the "combined" analysis was taken directly from the simple analysis of variance. The sum of squares for zero versus the average of other treatments was calculated by subtracting the sum of the placement (D) rate (E) and interaction (F) sums of squares from the treatment sum of squares (A) in the simple analysis of variance. When the F test indicated that there were significant differences at the 5% level due to placement method or rate, Duncan's Multiple Range Test was employed to determine which of the differences among the four placement methods or among the four micronutrient rates (excluding the zero) were significant. When the F test indicated that the zero treatment was significantly different from all others, the value for the zero treatment was compared to values for each of the four rates using the LSD test. The least significant difference was calculated in the following manner:

$$LSD_{.05} = \sqrt{\frac{\frac{C}{40}}{3} + \frac{\frac{C}{40}}{12}}$$

Table 6

Factorial Analysis of Variance
of 20 Treatments

Source of variation	Degrees of freedom (df)	Sum of squares (ss)	Mean square (ms)	F value
Placement	3	D	not necessary	not necessary
Rate	4	E		
Interaction	12	F		
Block	2	not necessary		
Error	38	not necessary		
Total	59	---	---	---

Table 7

"Combined" Analysis of Variance
of 21 Treatments

Source of variation	Degrees of freedom (df)	Sum of squares (ss)	Mean square (ms)	F value
Block	2	B	already calculated	already calculated
Placement	3	D	$\frac{D}{3}$	$\frac{40D}{3C}$
Rate	4	E	$\frac{E}{4}$	$\frac{10E}{C}$
Interaction	12	F	$\frac{F}{12}$	$\frac{10F}{3C}$
Zero vs. remainder	1	A-(D+E+F)	A-(D+E+F)	$\frac{40(A-(D+E+F))}{C}$
Error	40	C	$\frac{C}{40}$	——
Total	62	---	---	---

CHAPTER IV

RESULTS AND DISCUSSION

A. Soil Characteristics

The physical and chemical characteristics of soils used in the incubation and growth chamber studies are given in Table 8. Lakeland clay loam contained a rather low level of plant available P but high levels of exchangeable K and NO_3-N. It contained far more DTPA extractable Cu than the 0.2 ppm critical level suggested by Lindsay and Norvell (4b). The DTPA extractable Zn level in Lakeland clay loam was exactly the same as the critical level suggested by Lindsay and Norvell (4b) whereas the DTPA extractable Fe and Mn levels were well above the suggested critical levels of 4.5 ppm Fe and 1.0 ppm Mn (4b). The high inorganic C level of Lakeland clay loam indicated that the soil likely contained finely divided limestone. That may have partially caused the lower plant available P, Zn and Fe levels in Lakeland clay loam as compared to Pine Ridge sand.

Pine Ridge sand contained a rather high level of plant available P but low levels of exchangeable K and NO_3-N. Although the DTPA extractable Cu level was considerably lower than that for Lakeland clay loam, it was still above the suggested critical level of 0.2 ppm. Both Fe and Mn were well above the suggested critical levels.

B. Incubation Study

The amounts of Cu and Zn extracted with water were not appreciably affected by duration of incubation, were very small and were similar to values obtained by Gupta and MacKay (65), Hodson et al. (73) and McGregor (104) (Tables 9 - 12). The proportions of applied Cu and Zn

TABLE 8

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE SOILS

Soil Name	Particle Size Class	Genetic Sub-group	P (ppm)	K (ppm)	NO_3-N (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)	Mn (ppm)	O.M (%)	C.E.C. (meq/ 100 g)	pH	Inorg. C (%)
Lakeland	Clay Loam	Gley carbonated Rego Black	3.8	502.0	95.0	1.36	1.0	11.0	5.6	3.26	24.1	8.2	25.6
Pine Ridge	Sand	Degraded Eutric Brunisol	8.6	22.0	7.2	0.56	1.2	22.0	2.6	1.36	7.3	6.3	0.06

TABLE 9

COPPER EXTRACTED WITH H_2O AND DTPA
AT TIME 0 FROM PINE RIDGE SAND
TREATED WITH $CuSO_4.5H_2O$

Cu applied to soil ppm	H_2O extractable Cu ppm	DTPA extractable Cu ppm	% of applied extracted with H_2O	% of applied extracted with DTPA
0.0	0.035	0.37	----	----
1.0	0.05	0.89	5.00	89.0
5.0	0.316	4.51	6.32	90.2
10.0	0.330	9.27	3.30	92.7
25.0	0.51	23.3	2.04	93.1
50.0	0.91	49.1	1.82	98.2
100.0	1.07	91.6	1.07	91.6
250.0	1.48	187	0.59	74.7
500.0	1.86	403	0.39	80.6
1000.0	3.48	897	0.35	89.7

TABLE 10

COPPER EXTRACTED FROM PINE RIDGE SAND TREATED WITH $CuSO_4.5H_2O$ AND INCUBATED FOR A PERIOD OF 7 DAYS

Cu applied to soil ppm	H_2O extractable Cu ppm	DTPA extractable Cu ppm	% of applied extracted with H_2O	% of applied extracted with DTPA
0.0	0.026	0.56	----	----
1.0	0.031	0.83	3.10	83.0
5.0	0.22	3.30	4.40	66.0
10.0	0.25	6.64	2.50	66.4
25.0	0.30	16.3	1.20	65.2
50.0	0.81	32.5	1.62	64.9
100.0	0.96	86.9	0.96	86.9
250.0	1.03	145	0.41	59.9
500.0	1.35	316	0.27	63.3
1000.0	3.45	757	0.35	75.7

TABLE 11

ZINC EXTRACTED WITH H_2O AND DTPA
AT TIME 0 FROM LAKELAND CLAY
LOAM TREATED WITH $ZnSO_4.7H_2O$

Zn applied ppm	H_2O extractable Zn ppm	DTPA extractable Zn ppm	% of applied extracted with H_2O	% of applied extracted with DTPA
0.0	0.04	0.39	----	----
2.0	0.11	1.63	5.50	81.5
10.0	0.29	6.92	2.90	69.2
20.0	0.47	16.6	2.35	83.3
50.0	1.08	45.4	2.16	90.8
100.0	1.22	81.8	1.22	81.8
200.0	1.69	176	0.85	67.8
500.0	2.07	473	0.41	94.3
1000.0	2.47	812	0.25	81.2
2000.0	18.59	1790	0.93	89.6

TABLE 12

ZINC EXTRACTED FROM LAKELAND CLAY LOAM TREATED WITH $ZnSO_4.7H_2O$ AND INCUBATED FOR 7 DAYS

Zn applied ppm	H_2O extractable Zn ppm	DTPA extractable Zn ppm	% of applied extracted with H_2O	% of applied extracted with DTPA
0.0	0.03	0.32	----	----
2.0	0.096	1.23	4.8	61.5
10.0	0.15	5.8	1.5	58.3
20.0	0.44	15.6	2.2	78.2
50.0	0.62	39.1	1.24	78.3
100.0	0.92	73.8	0.92	73.8
200.0	1.05	135	0.53	67.6
500.0	1.43	461	0.29	92.2
1000.0	1.73	712	0.17	71.2
2000.0	2.47	1610	0.12	80.4

which were extracted with H_2O decreased with increasing levels of applied Cu and Zn. The proportions of applied Cu and Zn which were extracted with DTPA were much higher than the proportions extracted with water. They decreased slightly with duration of incubation but were not appreciably affected by rates of Cu and Zn application.

The low porportions of applied Cu and Zn which were H_2O extractable even at time 0, indicated that Cu and Zn were very quickly adsorbed and/or precipitated as water-insoluble reaction products by soil materials such as clay minerals, organic matter, and hydrous oxides of Al, Fe and Mn. This result tends to agree with previous research workers that water did not extract sufficient Cu (45, 65, 186) and Zn (45, 60, 128, 186) to represent adequately labile nutrients available to plants.

The proportions of applied Cu and Zn extracted with DTPA at both incubation times suggested that most of H_2O insoluble portions of applied Cu and Zn were adsorbed, chelated, complexed or exchangeable and therefore were potentially available. Very little of the applied Cu and Zn was present in insoluble precipitates and unavailable to plants.

After seven days of incubation, however, a bit more of the plant available Cu and Zn had been converted to insoluble precipitates as indicated by the decrease in DTPA and H_2O extractable Cu and Zn levels. This finding tends to coincide with earlier research findings (45, 73, 93) that up to 99% of the Cu and 75% of the Zn in the soil could be chemically adsorbed or form metallo-organic complexes.

This study provided no evidence that banding of Cu and Zn sulphates would decrease the amount of fixation as the proportion of applied Cu

and Zn extracted with H_2O or DTPA did not increase with application rates. Conversely, the result did not invalidate the assertion that banding of inorganic micronutrient fertilizers improves their chemical availability. Although the DTPA to soil extraction ratio was much higher than that recommended by Lindsay and Norvell (94, 95), the extraction capacities of DTPA and particularly H_2O may have been exceeded at the higher rates of Cu and Zn application. In order to have used the high micronutrient rates to simulate banding and the lower rates to simulate mixing throughout the extraction solution to soil ratios should have been increased proportionally with rates of Cu and Zn.

C. Growth Chamber Cu Experiment

1. Dry matter yield of barley shoots

Application of Cu did not result in higher dry matter yields when all placement methods were considered as indicated by the combined analysis of variance (see footnote 3 to Tables 13(a) and (b)). This likely resulted from the low effectiveness of banding below the seeds and placing the Cu fertilizer carrier in a point in the soil (Tables 13(b) and (c)). Banding $CuSO_4$ with the seed was the most effective in increasing the yield, followed by mixing with the soil and finally placing the Cu carrier in a point (Table 13(a) and Fig. 1). There were definite responses to Cu when $CuSO_4$ was either banded with the seeds or mixed throughout with the soil (Table 13(c) and Fig. 1). Dry matter yield was increased significantly by 0.5 ppm Cu when banded with the seeds. However, when mixed with the soil, 1.0 ppm Cu was required in order to significantly increase yields. The optimum application rate

TABLE 13(a)

EFFECT OF RATE OF $CuSO_4$ ON DRY MATTER YIELD OF BARLEY SHOOTS

Cu Rate[4]	Dry matter yield per 6 plants
(ppm)	(g)
0.0	15.353[3]
0.5	16.677[2]
1.0	16.736
2.0	16.588
4.0	17.136
8.0	16.080

TABLE 13(b)

EFFECT OF METHOD OF PLACEMENT OF $CuSO_4$ ON DRY MATTER YIELD OF BARLEY SHOOTS

Placement[4]	Dry matter yield per 6 plants	
	(g)	
Banded with seeds	17.961[1]	d
Banded 2 cm below seeds	16.335	b
Point source	14.933	a
Mixed with soil	17.345	c

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from combined analysis of variance).
2. Values for rates 0.5 to 8.0 ppm are not significantly different from one another (from combined analysis of variance).
3. 0.0 treatment was not significantly different from the average of all other treatments (from the combined analysis of variance).
4. Interaction between rate and placement was not significant.

TABLE 13(c)

EFFECT OF RATE AND METHOD OF PLACEMENT OF $CuSO_4$ ON DRY MATTER YIELD OF BARLEY SHOOTS

Treatment		Dry matter yield	
Cu level	Placement	per 6 plants	
(ppm)		(g)	
0.0	Banded	15.353	b[1]
0.5	Banded with seeds	17.320	c d e f
0.5	Banded 2 cm below seeds	16.920	b c d e f
0.5	Point source	15.357	b
0.5	Mixed with soil	17.110	b c d e f
1.0	Banded with seeds	18.030	c d e f
1.0	Banded 2 cm below seeds	15.843	b c d
1.0	Point source	15.387	b
1.0	Mixed with soil	17.683	c d e f
2.0	Banded with seeds	16.470	b c d e
2.0	Banded 2 cm below seeds	16.680	b c d e f
2.0	Point source	15.323	b
2.0	Mixed with soil	17.880	c d e f
4.0	Banded with seeds	18.123	d e f
4.0	Banded 2 cm below seeds	16.087	b c d e
4.0	Point source	15.950	b c d e
4.0	Mixed with soil	18.383	e f
8.0	Banded with seeds	19.860	f
8.0	Banded 2 cm below seeds	16.143	b c d e
8.0	Point source	12.650	a
8.0	Mixed with soil	15.667	b c

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

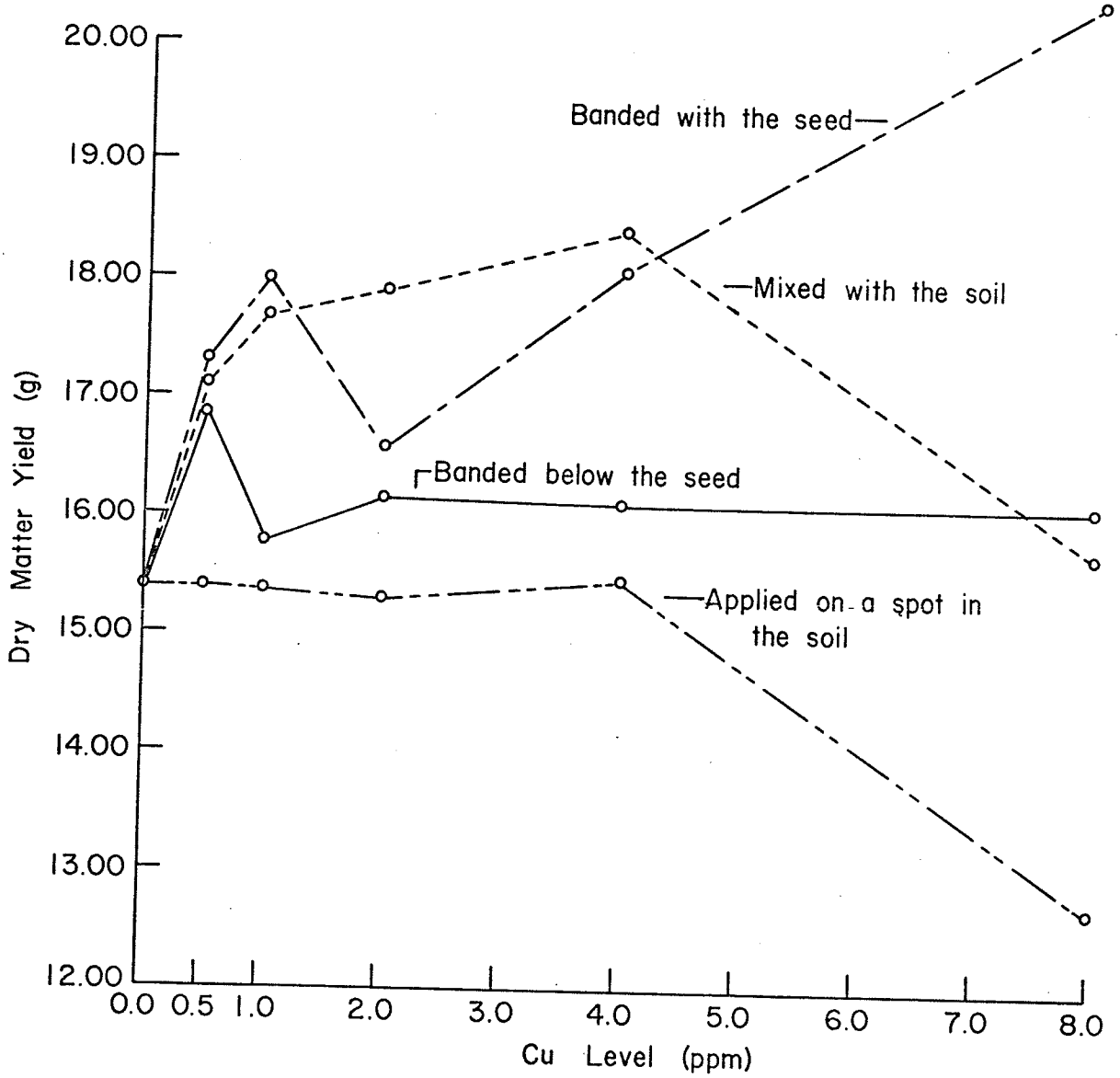

Figure I Influence of rate and method of application of $CuSO_4$ on the dry matter yield of barley shoots.

when $CuSO_4$ was banded with the seeds was 8.0 ppm Cu. However, when mixed with the soil, the optimum rate appeared to be 4.0 ppm. Mixing $CuSO_4$ with the soil at the rate of 8.0 ppm Cu did not significantly increase dry matter yield; the apparent lack of response may have been related to Cu-Zn antagonism which is discussed under Zn uptake. Banding $CuSO_4$ below the seeds or placing it in a point did not result in yields greater than the check.

2. Concentration and uptake of Cu

Application of $CuSO_4$ generally increased Cu concentration in barley shoots (see footnote 3 to Tables 14(a) and (b)). In contrast to dry matter yield, mixing $CuSO_4$ with the soil was the most effective in increasing plant Cu concentration, followed by banding with the seeds, banding below the seeds and finally, placing the Cu carrier in a point (Table 14(b)). A rate of 0.5 ppm Cu, when mixed with the soil, was sufficient to increase plant Cu concentrations (Table 14(c) and Fig. 2) whereas, when banded with the seeds or banded below the seeds, a rate of 1.0 ppm was required to increase the plant Cu concentration. The optimum application rate when $CuSO_4$ was mixed with the soil was 2.0 ppm Cu. When banded with the seeds, the optimum rate was 4.0 ppm and when banded below the seeds, it was 8.0 ppm. However, placing $CuSO_4$ in a point did not increase plant Cu concentration at any rate of application. This likely caused the significant interactions between rate and placement method in Cu concentration and uptake (see footnote 2 to Tables 14(a) and (b)). Copper uptake into barley shoots followed the same trend as Cu concentration.

Mixing $CuSO_4$ with the soil was the best method of placement

TABLE 14(a)

COPPER UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $CuSO_4$

Rate[2]	Cu concentration in the barley shoots		Cu uptake into 6 barley shoots	
(ppm Cu)	(ppm)		(mg)	
0.0	2.80[3]	a	0.043[3]	a
0.5	4.03	b[3]	0.062	b
1.0	4.33	b	0.073	c
2.0	5.48	b	0.092	d
4.0	5.14	b	0.089	d
8.0	5.68	b	0.092	d

TABLE 14(b)

COPPER UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $CuSO_4$

Placement	Cu concentration in barley shoots		Cu uptake into 6 barley shoots	
	(ppm)		(mg)	
Banded with seeds	5.02	c[1]	0.086	c
Banded 2 cm below seeds	4.46	b	0.073	b
Point source	3.37	a	0.050	a
Mixed with soil	6.87	d	0.119	d

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from combined analysis of variance).
2. Interaction between rate and placement for uptake of Cu was significant (at the 5% level)(from combined analysis of variance).
3. 0.0 treatment was not significantly different from average of all other treatments (from combined analysis of variance).

TABLE 14(c)

UPTAKE OF Cu INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $CuSO_4$

Treatment		Cu concentration in barley shoots	Cu uptake into 6 barley shoots
Cu level	Placement		
(ppm)	----	(ppm)	(mg)
0.0	----	2.80 a[1]	0.043 a
0.5	Banded with seeds	3.43 a b c	0.060 a b c d
0.5	Banded 2 cm below seeds	3.37 a b	0.058 a b
0.5	Point source	2.83 a	0.043 a
0.5	Mixed with soil	5.20 d e	0.089 e f
1.0	Banded with seeds	4.73 b c d e	0.085 d e f
1.0	Banded 2 cm below seeds	4.47 b c d e	0.071 b c d e
1.0	Point source	3.23 a	0.050 a b
1.0	Mixed with soil	4.90 c d e	0.087 d e f
2.0	Banded with seeds	4.73 b c d e	0.078 c d e f
2.0	Banded 2 cm below seeds	4.87 c d e	0.081 c d e f
2.0	Point source	3.80 a b c d	0.058 a b c
2.0	Mixed with soil	8.50 g	0.152 h
4.0	Banded with seeds	5.73 f	0.104 f g
4.0	Banded 2 cm below seeds	4.10 b c d	0.066 a b c d e
4.0	Point source	3.53 a b c	0.056 a b
4.0	Mixed with soil	7.20 g	0.132 g h
8.0	Banded with seeds	5.20 d e	0.103 f g
8.0	Banded 2 cm below seeds	5.50 e f	0.088 e f
8.0	Point source	3.47 a b c	0.043 a
8.0	Mixed with soil	8.33 g	0.133 h

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

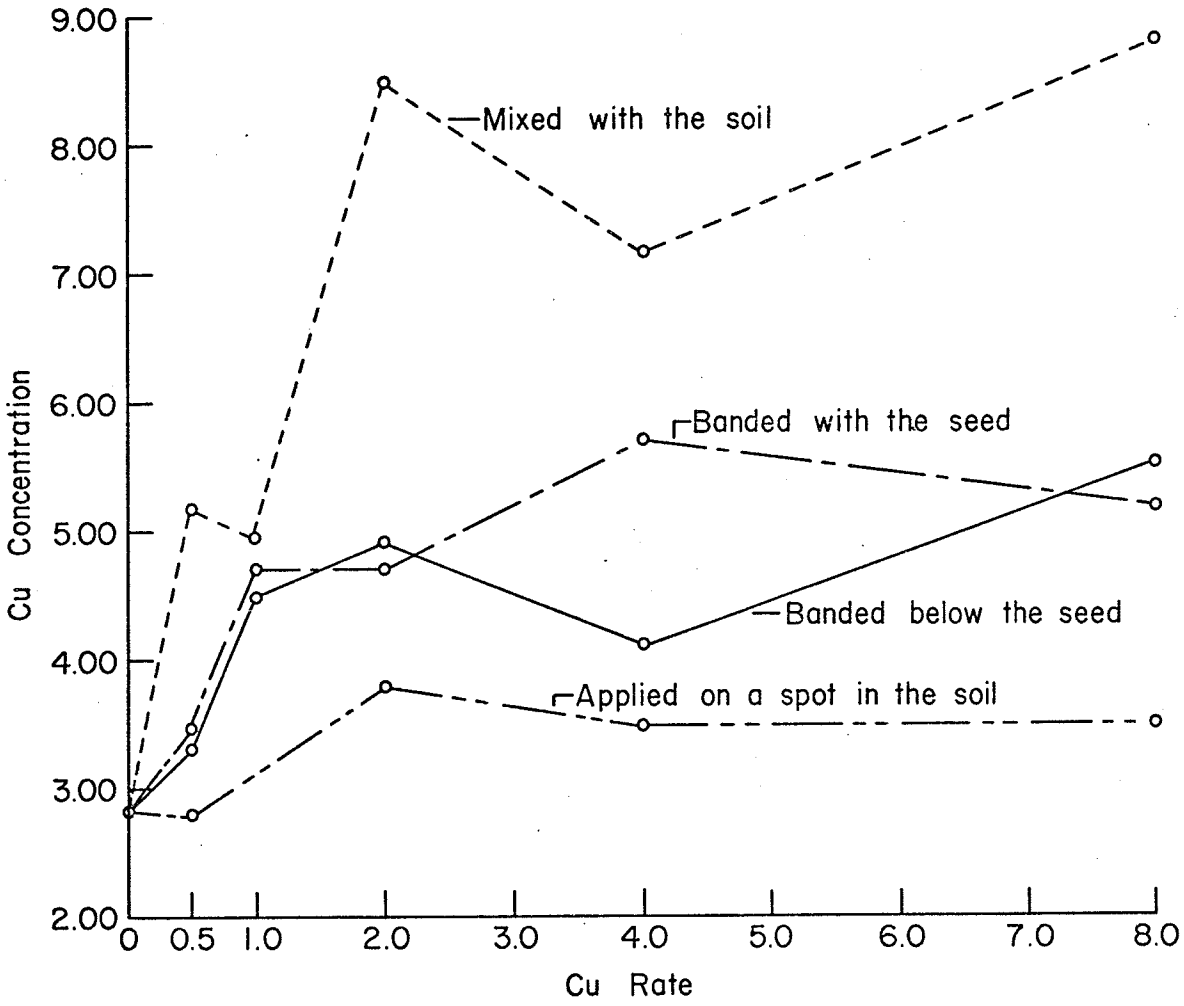

Figure II The effect of rate and method of placement of $CuSO_4$ on the Cu concentration of barley shoots.

according to uptake data. However, the dry matter yield data indicated that banding with the seed was the best method. Both methods were far better than banding below the seeds according to both dry matter yield and uptake data. Both the yield and uptake data indicated undoubtedly that placing the Cu carrier in a point in the soil was never an effective method of application. This result tends to be in line with previous research findings (133, 135, 177) that mixing $CuSO_4$ with the soil or banding with the seeds in lesser amounts provided the optimum nutritional Cu level in plants, resulting in better growth and higher yields.

3. Critical level of Cu in barley shoots

The critical level of Cu concentration in the barley tissue was determined using the modified method proposed by Cate and Nelson (38) and elucidated in Cox and Kamprath (45). The method, designed for determination of the critical levels of micronutrients in soil, was applied to plants. Yields were plotted against respective Cu concentrations (Fig. 3). Two perpendicular lines were drawn, one parallel with the X axis and the other with the Y axis, so that there was minimum number of observations in the upper left-hand and lower right-hand quadrants. The intersection with the X axis was taken as the critical level. In effect, this mechanism separated the plants with larger yield responses from those with lower or no yield responses. On this basis, the critical level of Cu concentration in barley shoots was found to be 5.3 ppm. This same critical level of Cu concentration was proposed by Melsted, Motto and Peck (106) for wheat, barley and oats. However, it must be conceded that this estimated critical level

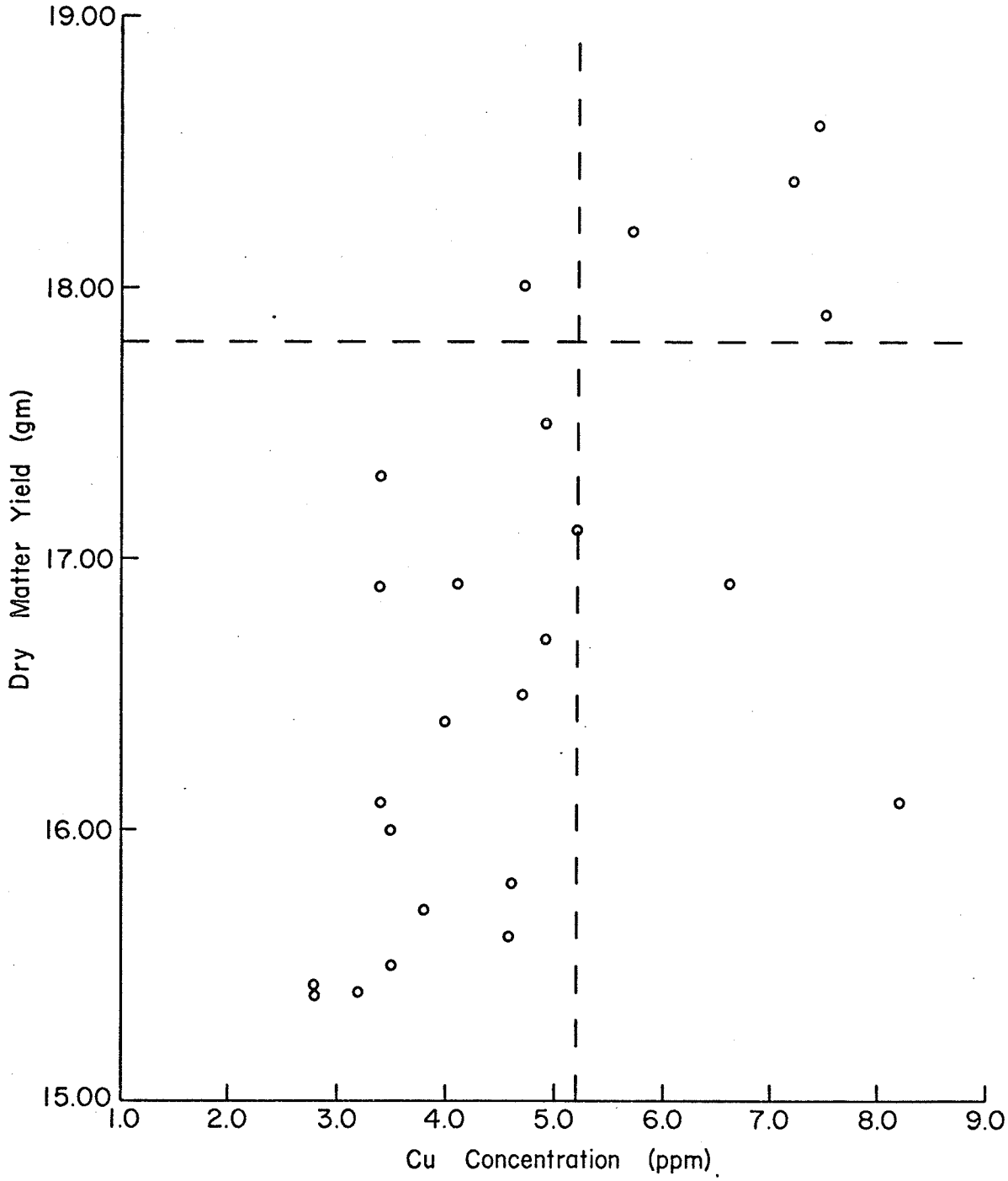

Figure III The critical level of Cu in barley shoots.

may be lower than the actual critical level as the Zn nutritional status of these plants may have been limiting yields.

4. Concentration and uptake of Zn

Zn concentration in the barley shoots and Zn uptake into barley shoots decreased as the rate of applied Cu increased (Table 15(a)). However, method of $CuSO_4$ placement had no significant effect upon Zn concentration or uptake (Table 15(b)). In general, Zn concentrations tended to be low when Cu concentrations were high (Tables 14(c) and 15(c)). The low Zn concentrations associated with high Cu concentrations may have resulted from something more than dilution since Zn uptake decreased in the same pattern as Zn concentration when Cu concentration increased. High Cu may have in some way inhibited Zn uptake or the translocation of Zn from the roots to the shoots. The critical level of Zn concentration in the Zn experiment was 12.5 ppm. This implies that all barley plants in the Cu experiment were Zn deficient with the exception of those receiving no Cu, those receiving 0.5 ppm Cu banded below the seeds or placed in a point, and those receiving 1.0 or 2.0 ppm Cu banded below the seeds. It is also interesting to note that the DTPA extractable Zn level of this soil was only 1.2 ppm (Table 8), just slightly above the critical level of 1.0 suggested by Lindsay and Norvell (4b). According to the uptake data, the optimum Cu level was 8.0 ppm when mixed throughout. The failure of dry matter yield to behave similarly may have resulted from Zn deficiency. Had Zn been applied in the Cu experiment, the highest yield would perhaps have been obtained, provided other factors are not limiting growth, when $CuSO_4$ was mixed with the soil.

TABLE 15(a)

ZINC UPTAKE INTO BARLEY SHOOTS
AS AFFECTED BY RATE OF $CuSO_4$

Rate[3]	Zn concentration in barley shoots	Zn uptake into 6 barley shoots
(ppm Cu)	(ppm)	(mg)
0.0	16.2[2] d[4]	0.248[2] d[4]
0.5	13.9 c	0.230 c
1.0	12.2 b	0.204 b
2.0	11.5 a b	0.191 b
4.0	10.9 a	0.187 a b
8.0	10.8 a	0.173 a

TABLE 15(b)

ZINC UPTAKE INTO BARLEY SHOOTS AS AFFECTED
BY METHOD OF PLACEMENT OF $CuSO_4$

Placement	Zn concentration in barley shoots	Zn uptake into 6 barley shoots
----	(ppm)	(mg)
Banded with seeds	11.3[1]	0.203[1]
Banded 2 cm below seeds	12.3	0.201
Point source	12.6	0.189
Mixed with soil	11.2	0.194

1. Values for placement are not significantly different.
2. 0.0 treatment is significantly higher (at 5% level) than average of all other treatments (from combined analysis of variance).
3. Interaction between rate and placement was not significant.
4. Values followed by different letters are significantly different at the 5% level (from combined analysis of variance).

TABLE 15(c)

UPTAKE OF Zn INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $CuSO_4$

Treatment			
Cu level	Placement	Zn concentration in barley shoots	Zn uptake into 6 barley shoots
(ppm)	----	(ppm)	(mg)
0.0	----	16.2[1] c d	0.248 c d
0.5	Banded with seeds	11.9 a b c	0.204 b c
0.5	Banded 2 cm below seeds	13.6 b c	0.230 b c d
0.5	Point source	18.4 d	0.284 d
0.5	Mixed with soil	11.8 a b c	0.201 b c
1.0	Banded with seeds	12.0 a b c	0.216 b c d
1.0	Banded 2 cm below seeds	13.0 a b c	0.203 b c
1.0	Point source	11.7 a b c	0.181 b c
1.0	Mixed with soil	12.2 a b c	0.215 b c d
2.0	Banded with seeds	10.2 a b	0.168 b
2.0	Banded 2 cm below seeds	13.3 a b c	0.221 b c d
2.0	Point source	10.4 a b	0.169 b
2.0	Mixed with soil	12.0 a b c	0.213 b c d
4.0	Banded with seeds	11.5 a b c	0.209 b c
4.0	Banded 2 cm below seeds	10.5 a b	0.209 b c d
4.0	Point source	11.1 a b	0.177 b c
4.0	Mixed with soil	10.5 a b	0.193 b c
8.0	Banded with seeds	11.0 a b	0.219 b c d
8.0	Banded 2 cm below seeds	11.3 a b	0.181 b c
8.0	Point source	11.5 a b	0.146 a
8.0	Mixed with soil	9.4 a	0.147 a

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

It has been reported in the literature (177) that excesses of other micronutrients can induce Zn deficiency. In this experiment, Cu may have induced Zn deficiency. McGregor's (104) finding was similar to this work. He observed that increasing the level of Cu decreased both Zn concentration and Zn uptake in flax. The effect, in other words, was not likely due to dilution alone. He concluded, however, that Zn was not deficient at the higher levels of Cu because plant Zn concentrations were all above any critical levels reported in the literature. Although dry matter yields were often higher when both Cu and Zn were applied than when Cu was applied alone, he attributed this to Zn increasing the effectiveness of Cu rather than to Zn deficiency. In this experiment, Cu was applied alone and excess of Cu depressed Zn concentration and uptake to the extent that nearly all the plants were Zn deficient, and this Cu-Zn antagonism was reflected in the yields.

5. Concentration and uptake of Fe

Iron concentration and uptake followed the same trend as Zn concentrations and uptake, decreasing as the level of applied Cu was increased (Table 16(a)). Method of placement of $CuSO_4$ had no effect on Fe concentration (Table 16 (b)). However, Fe uptake decreased in the order banded with the seeds, banded below the seeds, mixed with the soil, and point source. (Table 16(b)). The effect of placement of $CuSO_4$ on Fe uptake likely resulted from placement's influence upon dry matter yield. As with Zn, both Fe concentration and uptake tended to be low when Cu concentration and uptake were high (Tables 16(c) and 14(c)). Notable exceptions to that trend were the point source appli-

TABLE 16 (a)

IRON UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $CuSO_4$

Rate	Fe concentration in barley shoots		Fe uptake into 6 barley shoots	
(ppm Cu)	(ppm)		(mg)	
0.0	132.5	d[2]	2.03	d[2]
0.5	101.5	c	1.68	c
1.0	90.4	b	1.53	b
2.0	82.3	a	1.36	a
4.0	89.0	b	1.52	b
8.0	77.1	a	1.25	a

TABLE 16(b)

IRON UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $CuSO_4$

Placement	Fe concentration in barley shoots	Fe uptake into 6 barley shoots	
----	(ppm)	(mg)	
Banded with seeds	93.5[1]	1.68	d
Banded 2 cm below seeds	91.8	1.50	c
Point source	84.7	1.27	a
Mixed with soil	82.2	1.42	b

1. Values for placement are not significantly different.
2. 0.0 treatment was significantly different (at the 5% level) from the average of all other treatments (from combined analysis of variance).

TABLE 16(c)

UPTAKE OF Fe INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $CuSO_4$

Treatment			
Cu level	Placement	Fe concentration in barley shoots	Fe uptake into 12 barley shoots
(ppm)	----	(ppm)	(mg)
0.0	----	132.5[1] f	2.03 e f
0.5	Banded with seeds	98.3 c d e f	1.71 c d e f
0.5	Banded 2 cm below seeds	86.7 a b c d e	1.47 b c d e f
0.5	Point source	122.5 e f	1.88 d e f
0.5	Mixed with soil	98.3 c d e f	1.68 b c d e f
1.0	Banded with seeds	116.7 d e f	2.11 e f
1.0	Banded 2 cm below seeds	93.3 b c d e f	1.49 b c d e f
1.0	Point source	60.0 a	1.08 a b
1.0	Mixed with soil	81.7 a b c d e	1.44 b c d e f
2.0	Banded with seeds	83.3 a b c d e	1.37 b c d e
2.0	Banded 2 cm below seeds	93.3 b c d e f	1.55 b c d e f
2.0	Point source	85.0 a b c d e	1.30 a b c d
2.0	Mixed with soil	67.5 a b c	1.21 a b c
4.0	Banded with seeds	88.3 a b c d e	1.60 b c d e f
4.0	Banded 2 cm below seeds	103.3 c d e f	1.66 b c d e f
4.0	Point source	84.2 a b c d e	1.34 a b c d
4.0	Mixed with soil	80.0 a b c d	1.46 b c d e f
8.0	Banded with seeds	80.8 a b c d	1.61 b c d e f
8.0	Banded 2 cm below seeds	82.5 a b c d e	1.33 a b c d
8.0	Point source	61.7 a b	0.74 a
8.0	Mixed with soil	83.3 a b c d e	1.32 a b c d

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

cation at 1.0 and 8.0 ppm. Since both the concentration and uptake of Fe were low when Cu concentration and uptake were high, the low Fe concentrations may not have been caused by dilution alone. However, the low Fe uptake associated with high Cu uptake may have resulted partially from Zn limiting growth. The critical level of Fe in cereal vegetative tissue was reported by Jones (82) to be 50.0 ppm. Consequently, regardless of whether the low Fe concentrations were caused by dilution or Cu-Fe antagonism, it is unlikely that low Fe status was limiting the response to applied Cu.

6. Concentration and uptake of Mn, N, P and K

Concentrations of Mn, N, P and K in barley shoots and uptake of Mn, N and K into barley shoots were not affected by rate or method of placement of $CuSO_4$ (Tables 17 to 20, (a), (b) and (c)). However, P uptake was influenced by method of placement of $CuSO_4$ (Tables 19 (b) and (c)). This probably resulted from the effect of Cu nutritional status upon dry matter yield rather than a Cu-P antagonism.

The critical level for Mn, N, P and K in cereal plants have been established at 20.0 ppm, 1.25%, 0.15% and 1.25%, respectively (82, 106). The barley plants in this experiment were not deficient in Mn, N or P. However, some plants may have been deficient in K. This deficiency probably was not serious enough to erroneously affect any conclusions concerning Cu nutrition of the barley.

D. Growth Chamber Zn Experiment

1. Dry Matter Yield

Application of $ZnSO_4$ significantly increased the yield of barley shoots as indicated by the combined analysis of variance (see footnote

TABLE 17(a)

MANGANESE UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $CuSO_4$

Rate	Mn concentration in barley shoots	Mn uptake into 6 barley shoots
(ppm Cu)	(ppm)	(mg)
0.0	27.0[1]	0.415[1]
0.5	24.4	0.421
1.0	25.1	0.415
2.0	29.9	0.496
4.0	23.8	0.500
8.0	31.2	0.486

TABLE 17(b)

MANGANESE UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $CuSO_4$

Placement	Mn concentration in barley shoots	Mn uptake into 6 barley shoots
----	(ppm)	(mg)
Banded with seeds	25.2[1]	0.450[1]
Banded 2 cm below seeds	24.6	0.398
Point source	28.0	0.411
Mixed with soil	29.8	0.523

1. There were no significant differences.

TABLE 17(c)

UPTAKE OF Mn INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $CuSO_4$

Cu level	Treatment Placement	Mn concentration in barley shoots	Mn uptake into 12 barley shoots
(ppm)	----	(ppm)	(mg)
0.0	----	27.0[1]	0.415[1]
0.5	Banded with seeds	21.7	0.374
0.5	Banded 2 cm below seeds	26.3	0.443
0.5	Point source	27.1	0.417
0.5	Mixed with soil	22.5	0.386
1.0	Banded with seeds	16.7	0.299
1.0	Banded 2 cm below seeds	25.5	0.404
1.0	Point source	32.2	0.492
1.0	Mixed with soil	26.1	0.465
2.0	Banded with seeds	32.9	0.542
2.0	Banded 2 cm below seeds	19.6	0.326
2.0	Point source	29.3	0.446
2.0	Mixed with soil	37.8	0.671
4.0	Banded with seeds	30.0	0.543
4.0	Banded 2 cm below seeds	16.7	0.269
4.0	Point source	24.6	0.392
4.0	Mixed with soil	23.8	0.434
8.0	Banded with seeds	24.6	0.492
8.0	Banded 2 cm below seeds	35.0	0.548
8.0	Point source	26.8	0.308
8.0	Mixed with soil	38.6	0.597

1. Values were not significantly different.

TABLE 18(a)

NITROGEN UPTAKE INTO BARLEY SHOOTS
AS AFFECTED BY RATE OF $CuSO_4$

Rate	N concentration in barley shoots	N uptake into 6 barley shoots
(ppm Cu)	(%)	(mg)
0.0	2.59[1]	369[1]
0.5	2.14	356
1.0	2.40	399
2.0	2.60	431
4.0	2.48	424
8.0	2.56	400

TABLE 18(b)

NITROGEN UPTAKE INTO BARLEY SHOOTS AS AFFECTED
BY METHOD OF PLACEMENT OF $CuSO_4$

Placement	N concentration in barley shoots	N uptake into 6 barley shoots
----	(%)	(mg)
Banded with seeds	2.31[1]	414[1]
Banded 2 cm below seeds	2.23	364
Point source	2.55	372
Mixed with soil	2.65	458

1. There were no significant differences.

TABLE 18(c)

UPTAKE OF N INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $CuSO_4$

Cu level	Treatment Placement	N concentration in barley shoots	N uptake into 12 barley shoots
(ppm)	----	(%)	(mg)
0.0	----	2.59[1]	396[1]
0.5	Banded with seeds	2.05	369
0.5	Banded 2 cm below seeds	2.19	365
0.5	Point source	2.26	346
0.5	Mixed with soil	2.07	354
1.0	Banded with seeds	2.07	372
1.0	Banded 2 cm below seeds	2.30	365
1.0	Point source	2.54	384
1.0	Mixed with soil	2.69	474
2.0	Banded with seeds	2.19	362
2.0	Banded 2 cm below seeds	2.19	364
2.0	Point source	2.76	423
2.0	Mixed with soil	3.26	577
4.0	Banded with seeds	2.67	483
4.0	Banded 2 cm below seeds	2.36	378
4.0	Point source	2.27	362
4.0	Mixed with soil	2.61	473
8.0	Banded with seeds	2.54	501
8.0	Banded 2 cm below seeds	2.14	345
8.0	Point source	2.92	343
8.0	Mixed with soil	2.64	409

1. Values are not significantly different from each other.

TABLE 19(a)

PHOSPHORUS UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $CuSO_4$

RATE	P concentration in barley shoots	P uptake into 6 barley shoots
(ppm Cu)	(%)	(mg)
0.0	0.503[1]	77.2[1]
0.5	0.477	79.3
1.0	0.456	72.7
2.0	0.485	80.7
4.0	0.514	91.5
8.0	0.498	78.7

TABLE 19(b)

PHOSPHORUS UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $CuSO_4$

Placement	P concentration in barley shoots	P uptake into 6 barley shoots
----	(%)	(mg)
Banded with seeds	0.440[1]	79.4[2] b
Banded 2 cm below seeds	0.519	84.5 b
Point source	0.476	70.3 a
Mixed with soil	0.509	88.2 c

1. Values are not significantly different.
2. Placement values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from combined analysis of variance).

TABLE 19(c)

UPTAKE OF P INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $CuSO_4$

Cu level	Treatment Placement	P concentration in barley shoots	P uptake into 12 barley shoots
(ppm)	----	(%)	(mg)
0.0	----	0.503[1]	77.2[2] a b c d e f
0.5	Banded with seeds	0.437	75.2 a b c d e f
0.5	Banded 2 cm below seeds	0.587	99.0 e f
0.5	Point source	0.447	68.3 a b c d
0.5	Mixed with soil	0.437	74.7 a b c d e f
1.0	Banded with seeds	0.373	67.1 a b c
1.0	Banded 2 cm below seeds	0.410	65.0 a b
1.0	Point source	0.463	71.5 a b c d e f
1.0	Mixed with soil	0.497	87.3 b c d e f
2.0	Banded with seeds	0.403	66.4 a b c
2.0	Banded 2 cm below seeds	0.533	88.8 b c d e f
2.0	Point source	0.450	68.8 a b c d e
2.0	Mixed with soil	0.553	98.7 d e f
4.0	Banded with seeds	0.517	94.6 c d e f
4.0	Banded 2 cm below seeds	0.430	81.0 b c d e f
4.0	Point source	0.563	89.8 b c d e f
4.0	Mixed with soil	0.547	101 f
8.0	Banded with seeds	0.470	93.5 c d e f
8.0	Banded 2 cm below seeds	0.557	88.5 b c d e f
8.0	Point source	0.457	53.2 a
8.0	Mixed with soil	0.510	79.7 a b c d e f

1. Values are not significantly different.
2. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

TABLE 20(a)

POTASSIUM UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $CuSO_4$

Rate	K concentration in barley shoots	K uptake into 6 barley shoots
(ppm Cu)	(%)	(mg)
0.0	1.88[1]	288[1]
0.5	1.56	261
1.0	1.41	235
2.0	1.13	188
4.0	0.98	166
8.0	1.44	232

TABLE 20(b)

POTASSIUM UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $CuSO_4$

Placement	K concentration in barley shoots	K uptake into 6 barley shoots
----	(%)	(mg)
Banded with seeds	1.35[1]	245[1]
Banded 2 cm below seeds	1.29	208
Point source	1.39	209
Mixed with soil	1.18	202

1. There are no significant differences.

TABLE 20(c)

UPTAKE OF K INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $CuSO_4$

Cu level	Treatment Placement	K concentration in barley shoots	K uptake into 12 barley shoots
(ppm)	----	(%)	(mg)
0.0	----	1.88[1]	288[1]
0.5	Banded with seeds	1.79	312
0.5	Banded 2 cm below seeds	1.40	236
0.5	Point source	1.89	295
0.5	Mixed with soil	1.17	199
1.0	Banded with seeds	1.57	282
1.0	Banded 2 cm below seeds	1.68	264
1.0	Point source	1.12	170
1.0	Mixed with soil	1.27	223
2.0	Banded with seeds	1.04	171
2.0	Banded 2 cm below seeds	1.02	169
2.0	Point source	1.18	179
2.0	Mixed with soil	1.29	231
4.0	Banded with seeds	0.93	168
4.0	Banded 2 cm below seeds	0.90	144
4.0	Point source	1.31	208
4.0	Mixed with soil	0.79	144
8.0	Banded with seeds	1.44	293
8.0	Banded 2 cm below seeds	1.46	228
8.0	Point source	1.45	192
8.0	Mixed with soil	1.39	215

1. Values are not significantly different.

to Tables 21(a) and (b)). Dry matter yield of barley shoots was significantly increased by 0.5 ppm Zn when all placements were taken together (Table 21(a)) but 2.0 ppm or more of Zn did not increase yields over that for 1.0 ppm. Banding $ZnSO_4$ with the seeds and mixing the Zn carrier with the soil were the most effective in increasing the yields, followed by banding the Zn carrier below the seeds. Placing $ZnSO_4$ in a point was the least effective (Table 21(b)). Only 1.0 ppm Zn banded with the seeds or mixed throughout the soil was needed to significantly increase the yields over that for check (Table 21(c) and Fig. 4). In addition for those two methods, no further increases in yield were obtained above 1.0 ppm Zn. A rate of 4.0 ppm Zn when banded below the seed was required to significantly increase yield over check. When banded below seed, there were no further yield increases above 4.0 ppm Zn. Regardless of rate, point source application was not effective in increasing yield.

2. Concentration and uptake of Zn

Application of $ZnSO_4$ generally increased the Zn concentration and the uptake (footnote 3 to Table 22(a)). In contrast to dry matter yield, however, both Zn concentration and uptake increased as the Zn application level was increased from 1.0 to 16.0 ppm (Table 22(a)). Method of placement also influenced Zn concentration and uptake more than it influenced dry matter yield (Tables 21(b) and 22(b)). Mixing $ZnSO_4$ with the soil was the most effective in increasing the plant concentration and uptake of Zn. This was followed by banded with the seeds > banded below the seeds > point source (Table 22(b)). There was a significant interaction between rate and method of application

TABLE 21(a)

EFFECT OF RATE OF $ZnSO_4$ ON THE DRY MATTER YIELD OF BARLEY SHOOTS

Rate[2]	Dry matter yield per 12 plants	
(ppm Zn)	(g)	
0.0	16.48[4]	a[3]
1.0	19.88	b
2.0	19.69	b
4.0	20.20	b
8.0	21.32	b
16.0	19.80	b

TABLE 21(b)

EFFECT OF METHOD OF PLACEMENT OF $ZnSO_4$ ON THE DRY MATTER YIELD OF BARLEY SHOOTS

Placement[2]	Dry matter yield per 12 plants	
----	(g)	
Banded with seeds	21.04	c[1]
Banded 2 cm below seeds	19.84	b
Point source	18.15	a
Mixed with soil	21.69	c

1. Values followed by different letters are significantly different (at 5% level) using Duncan's Multiple Range Test (from combined analysis of variance).
2. Interaction between rate and placement was not significant at 5% level (from combined analysis of variance).
3. 0.0 treatment was significantly lower (at 5% level) than average of all other treatments (from combined analysis of variance).

TABLE 21(c)

DRY MATTER YIELD OF BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $ZnSO_4$

Treatment			
Zn level	Placement	Dry matter yield per 12 plants	
(ppm)	----	(g)	
0.0	----	16.48	a[1]
1.0	Banded with seeds	21.15	c d e f
1.0	Banded 2 cm below seeds	19.66	a b c d e f
1.0	Point source	18.53	a b c
1.0	Mixed with soil	20.16	b c d e f
2.0	Banded with seeds	20.99	c d e f
2.0	Banded 2 cm below seeds	19.43	a b c d e f
2.0	Point source	17.56	a b
2.0	Mixed with soil	20.76	b c d e f
4.0	Banded with seeds	19.36	a b c d e f
4.0	Banded 2 cm below seeds	19.74	b c d e f
4.0	Point source	19.22	a b c d e
4.0	Mixed with soil	22.50	d e f
8.0	Banded with seeds	22.70	e f
8.0	Banded 2 cm below seeds	20.51	b c d e f
8.0	Point source	18.99	a b c d
8.0	Mixed with soil	23.10	f
16.0	Banded with seeds	20.98	b c d e f
16.0	Banded 2 cm below seeds	19.86	b c d e f
16.0	Point source	16.44	a
16.0	Mixed with soil	21.93	c d e f

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

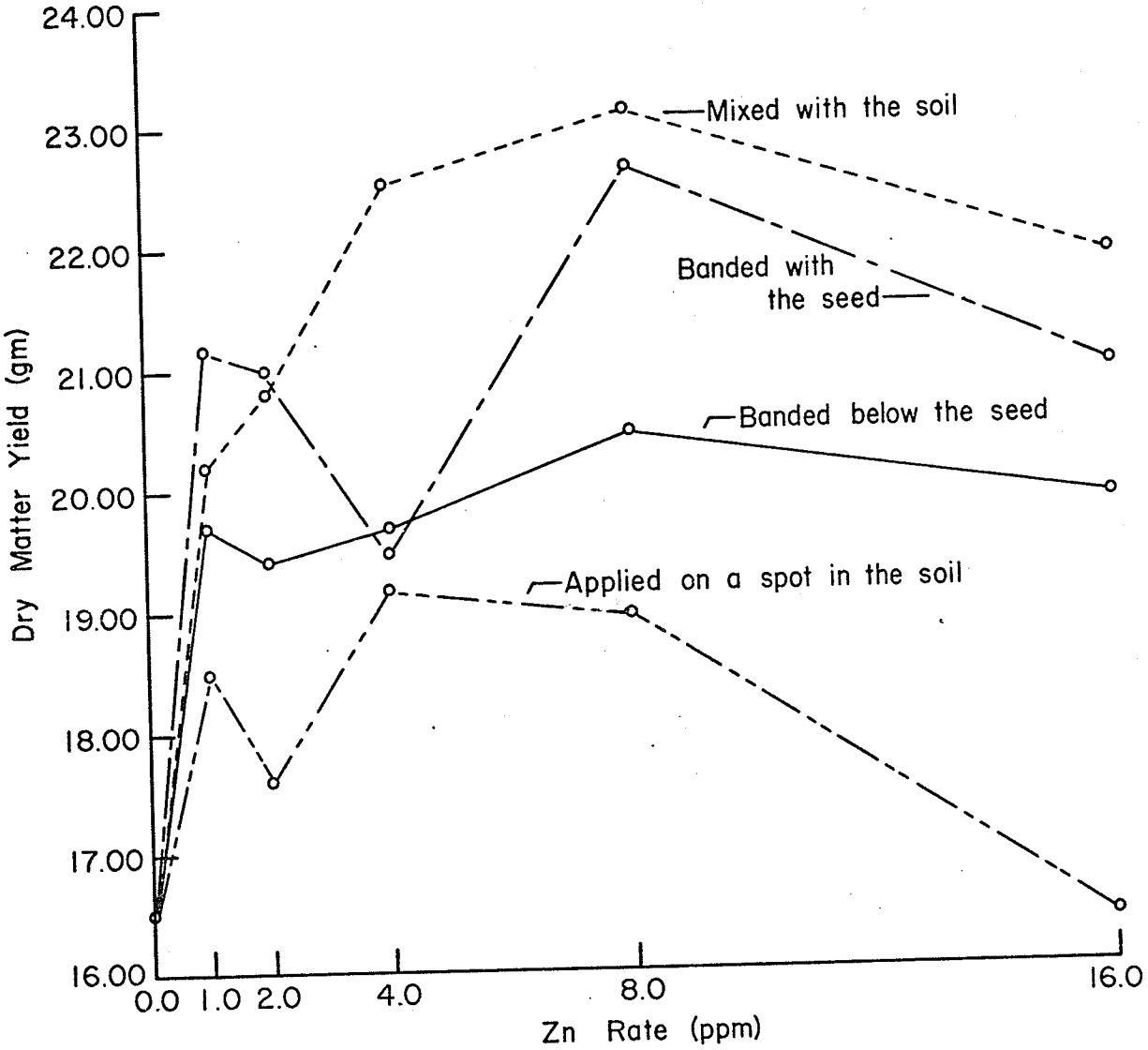

Figure IV The effect of rate and method of placement of $ZnSO_4$ on the dry matter yield of barley shoots.

TABLE 22(a)

ZINC UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $ZnSO_4$

Rate[2]	Zn concentration in barley shoots		Zn uptake into 12 barley shoots	
(ppm Zn)	(ppm)		(mg)	
0.0	9.07[3]	a	0.150[3]	a
1.0	14.1	c	0.296	c
2.0	12.6	b	0.243	b
4.0	16.4	d	0.340	d
8.0	21.6	e	0.475	e
16.0	29.7	f	0.620	f

TABLE 22(b)

ZINC UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $ZnSO_4$

Placement2	Zn concentration in barley shoots		Zn uptake into 12 barley shoots	
----	(ppm)		(mg)	
Banded with seeds	19.5[1]	c	0.412	c
Banded 2 cm below seeds	16.1	b	0.321	b
Point source	9.8	a	0.173	a
Mixed with soil	30.2	d	0.674	d

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from the combined analysis of variance).
2. Interaction between rate and placement was significant at the 5% level (from combined analysis of variance).
3. 0.0 treatment was significantly lower (at 5% level) than average of all other treatments (from the combined analysis of variance).

for both concentration and uptake of Zn indicating that rate behaved differently depending upon method of application (footnote 2 to Table 22(a) and Fig. 5). When mixed with soil, only 1.0 ppm Zn was required to significantly increase Zn concentration, but when banded with the seeds, 4.0 ppm was required. However, when banded below the seeds, 8.0 ppm was required (Table 22(c) and Fig. 5). Regardless of Zn level, applying $ZnSO_4$ in a point did not increase plant Zn concentration. This explains the failure of applying Zn fertilizer in a point to increase the dry matter yield. In addition, it explains why there was significant interaction between rate and method. The optimum Zn concentration level for all methods except point source was 16.0 ppm. The failure of application of $ZnSO_4$ to influence growth as much as Zn concentration may have been caused by a relatively low critical level or some other factor other than Zn supply limiting growth.

With a few minor exceptions, Zn uptake behaved similarly to Zn concentration (Table 22(c)). The critical level of Zn concentration in barley shoots as estimated in the same manner as Cu critical level was found to be 12.5 ppm (Fig. 6). This value is somewhat lower than the critical level of 15.0 ppm reported by Melsted et al. (106) for wheat, barley and oats. As discussed later under Fe uptake, it is possible that the Fe nutritional status of the barley shoots may have limited the yield. That may at least partially account for the rather low Zn critical level obtained in this experiment.

The findings in this experiment were similar to certain previous research findings (6, 26, 28, 98) that mixing $ZnSO_4$ with soil at

TABLE 22(c)

UPTAKE OF Zn INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $ZnSO_4$

Treatment			
Zn level	Placement	Zn concentration in barley shoots	Zn uptake into 12 barley shoots
(ppm)	----	(ppm)	(mg)
0.0	----	9.07 a[1]	0.153 a
1.0	Banded with seeds	15.1 a b c	0.322 c d e f
1.0	Banded 2 cm below seeds	13.1 a b	0.261 a b c d
1.0	Point source	9.37 a	0.181 a b
1.0	Mixed with soil	18.9 c d	0.434 e f
2.0	Banded with seeds	13.7 a b	0.292 b c d e
2.0	Banded 2 cm below seeds	12.8 a	0.244 a b c d
2.0	Point source	9.77 a	0.156 a
2.0	Mixed with soil	13.9 a b	0.293 b c d e
4.0	Banded with seeds	17.9 b c d	0.353 d e f
4.0	Banded 2 cm below seeds	13.7 a b	0.281 a b c d e
4.0	Point source	9.83 a	0.197 a b c
4.0	Mixed with soil	24.1 e	0.549 g h
8.0	Banded with seeds	20.2 d e	0.467 f g
8.0	Banded 2 cm below seeds	17.9 b c d	0.377 d e f
8.0	Point source	9.00 a	0.178 a b
8.0	Mixed with soil	39.2 g	0.909 i
16.0	Banded with seeds	30.4 f	0.648 h
16.0	Banded 2 cm below seeds	22.6 d e	0.455 f g
16.0	Point source	10.9 a	0.187 a b
16.0	Mixed with soil	54.9 h	1.21 j

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

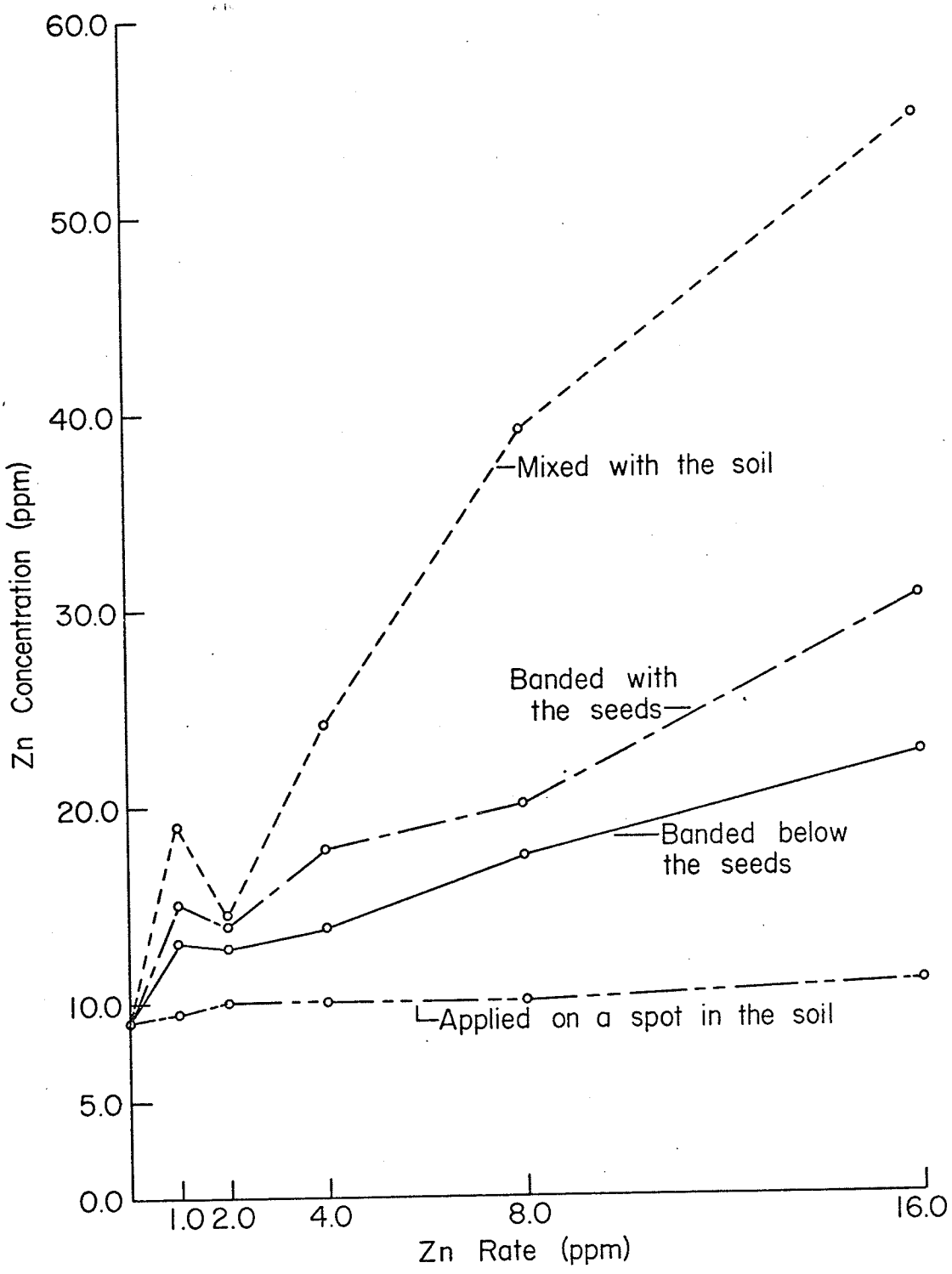

Figure V The effect of rate and method of placement of $ZnSO_4$ on Zn concentration of barley shoots.

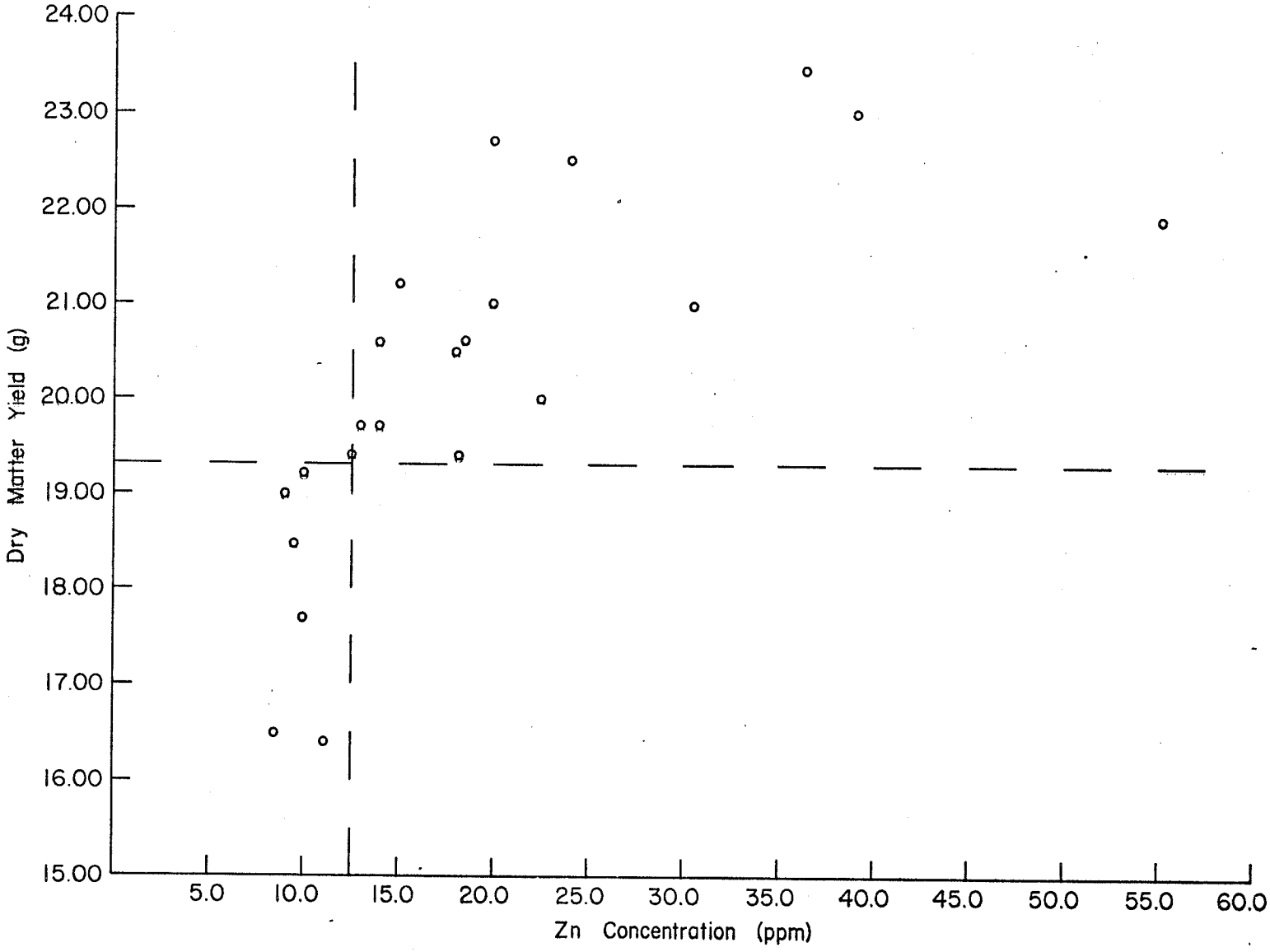

Figure VI The critical level of Zn in barley shoots.

various rates was more effective than banding with the seeds or placing in a point in the soil and that mixing the Zn carrier with the soil was sometimes as effective as ZnEDTA in increasing the yield and uptake of Zn for the crops. The observation of Terman et al. (175) is particularly relevant in this work. They found that the yield and uptake of Zn by corn from $ZnSO_4$ applied to certain calcareous soils in Tennessee increased in order $ZnSO_4$ mixed alone with soil > $ZnSO_4$ incorporated into NH_4NO_3 or $(NH_4)_2SO_4$ > $ZnSO_4$ incorporated into APP > no Zn. The corresponding similar treatments in this work would then be mixing $ZnSO_4$ with the soil > $ZnSO_4$ banded together with $NH_4H_2PO_4$ with the seeds > no Zn. In other words, mixing $ZnSO_4$ alone with soil is probably the best method of application.

3. Concentration and uptake of Cu

Both Cu concentration and uptake were unaffected by rate or method of placement of $ZnSO_4$ (Tables 23(a),(b) and (c)). In addition, the level of Cu in the plant tissue was above the critical levels reported in the literature and determined in the Cu experiment. Therefore, Lakeland clay loam probably supplied sufficient Cu for the nutritional needs of barley seedlings.

4. Concentration and uptake of Fe

Barley plants receiving $ZnSO_4$ contained less Fe than barley plants which were not fertilized with the Zn carrier (footnote 3 to Table 24(a)). Both Fe concentration and uptake decreased with increasing level of applied Zn (Table 24(a)). The effect of placement of $ZnSO_4$ on Fe concentration and uptake was the opposite of the effect of the Zn carrier upon Zn concentration and uptake. The Fe concentration and uptake of Fe

TABLE 23(a)

COPPER UPTAKE INTO BARLEY SHOOTS
AS AFFECTED BY RATE OF $ZnSO_4$

Rate[2]	Cu concentration in barley shoots	Cu uptake into 12 barley shoots
(ppm Zn)	(ppm)	(mg)
0.0	6.67[1,3]	0.110[1,3]
1.0	6.16	0.123
2.0	6.27	0.122
4.0	6.62	0.136
8.0	6.51	0.140
16.0	6.00	0.120

TABLE 23(b)

COPPER UPTAKE INTO BARLEY SHOOTS AS AFFECTED
BY METHOD OF PLACEMENT OF $ZnSO_4$

Placement[2]	Cu concentration in barley shoots	Cu uptake into 12 barley shoots
----	(ppm)	(mg)
Banded with seeds	6.11[1]	0.130[1]
Banded 2 cm below seeds	6.39	0.125
Point source	6.55	0.120
Mixed with soil	6.31	0.139

1. Values are not significantly different.
2. Interaction between rate and placement was not significant.
3. 0.0 treatment was not significantly lower (from the combined analysis of variance).

TABLE 23(c)

UPTAKE OF Cu INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $ZnSO_4$

Treatment			
Zn level	Placement	Cu concentration in barley shoots	Cu uptake into 12 barley shoots
(ppm)	----	(ppm)	(mg)
0.0	----	6.67[1]	0.112
1.0	Banded with seeds	6.23	0.137
1.0	Banded 2 cm below seeds	6.50	0.136
1.0	Point source	6.37	0.124
1.0	Mixed with soil	5.53	0.115
2.0	Banded with seeds	5.93	0.126
2.0	Banded 2 cm below seeds	6.50	0.133
2.0	Point source	6.10	0.115
2.0	Mixed with soil	6.53	0.148
4.0	Banded with seeds	6.80	0.143
4.0	Banded 2 cm below seeds	6.40	0.131
4.0	Point source	7.03	0.144
4.0	Mixed with soil	6.23	0.145
8.0	Banded with seeds	5.97	0.142
8.0	Banded 2 cm below seeds	6.17	0.135
8.0	Point source	6.63	0.132
8.0	Mixed with soil	7.40	0.173
16.0	Banded with seeds	5.63	0.127
16.0	Banded 2 cm below seeds	5.90	0.128
16.0	Point source	6.60	0.112
16.0	Mixed with soil	5.87	0.133

1. No significant differences at the 5% level.

TABLE 24(a)

IRON UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $ZnSO_4$

Rate[2]	Fe concentration in barley shoots	Fe uptake into 12 barley shoots
(ppm Zn)	(ppm)	(mg)
0.0	150.0[3] d	2.48[3] e
1.0	69.8 c	1.37 d
2.0	62.7 b	1.21 b c
4.0	64.4 c	1.28 c
8.0	52.0 a	1.15 a b
16.0	58.5 b	1.11 a

TABLE 24(b)

IRON UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $ZnSO_4$

Placement[2]	Fe concentration in barley shoots	Fe uptake into 12 barley shoots
----	(ppm)	(mg)
Banded with seeds	52.9[1] b	1.11[1] b
Banded 2 cm below seeds	56.3 b	1.11 b
Point source	89.7 c	1.68 c
Mixed with soil	46.9 a	1.01 a

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from combined analysis of variance).
2. Interaction between rate and placement was not significant at 5% level (from combined analysis of variance).
3. 0.0 treatment was significantly higher than average of all other treatments (from combined analysis of variance).

decreased in the order point source > banded with the seeds = banded below seeds > mixed with the soil (Table 24(b)). Similarly, it is obvious from Tables 22(c) and 24(c) that Fe concentration and uptake were low when Zn concentration and uptake were high. Decreases in plant Fe concentration with increasing level of applied Zn may not have resulted from dilution alone since total Fe uptake into the barley shoots also decreased. High Zn may have depressed the uptake of Fe or decreased translocation of Fe from the roots to the shoots. The metabolic functioning of Fe in plants is known to be connected in some manner with the supply of Zn. Rossell and Ulrich (150b) reported that as the applied Zn level was increased from 0 to 12 ppm, Fe concentration in leaves of sugar beets decreased from 917 to 94 ppm. Their results were similar to the results in this study. Ambler and Brown (3) also noted that two varieties of navy beans exhibited differential susceptibility to Zn deficiencies because one of the plant varieties contained more Fe and P than the other but less Zn. In other words, the varieties exhibited differentially Zn deficiency symptoms by their control of Fe or P.

The critical level of Fe in cereal (wheat, barley and oats) vegetative tissue according to Jones (82) is estimated at 50.0 ppm. On the basis of this critical level, mixing $ZnSO_4$ with the soil at all rates except 1.0 ppm Zn, banding the Zn carrier at all rates except at 1.0 and 2.0 ppm Zn, and banding the fertilizer below the seeds at 8.0 and 16.0 ppm Zn resulted in Fe deficient barley plants. The Fe deficiency in these plants might have limited response to Zn and resulted in an erroneously low Zn critical level.

TABLE 24(c)

UPTAKE OF Fe INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $ZnSO_4$

Treatment			
Zn level	Placement	Fe concentration in barley shoots	Fe uptake into 12 barley shoots
(ppm)	----	(ppm)	(mg)
0.0	----	150.0[1] h	2.48 h
1.0	Banded with seeds	61.7 b c d	1.30 b c d
1.0	Banded 2 cm below seeds	66.7 c d	1.32 c d e
1.0	Point source	93.3 e f	1.73 e f g
1.0	Mixed with soil	57.3 a b c d	1.15 a b c
2.0	Banded with seeds	67.5 c d	1.42 c d e f
2.0	Banded 2 cm below seeds	65.0 b c d	1.20 a b c d
2.0	Point source	76.7 g c	1.37 c d e
2.0	Mixed with soil	41.7 a	0.84 a
4.0	Banded with seeds	46.7 a b c	0.91 a b
4.0	Banded 2 cm below seeds	59.2 a b c d	1.17 a b c
4.0	Point source	101.7 f g	1.92 g
4.0	Mixed with soil	50.0 a b c	1.13 a b c
8.0	Banded with seeds	44.0 a b	1.01 a b c
8.0	Banded 2 cm below seeds	41.7 a	0.86 a
8.0	Point source	78.3 d e f	1.74 f g
8.0	Mixed with soil	44.2 a b	1.00 a b c
16.0	Banded with seeds	45.0 a b c	0.94 a b
16.0	Banded 2 cm below seeds	49.2 a b c	0.98 a b c
16.0	Point source	98.3 e f	1.61 d e f g
16.0	Mixed with soil	41.7 a	0.91 a b

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

5. Concentration and uptake of Mn

Application of $ZnSO_4$ generally decreased Mn concentration in barley shoots (footnote 4 to Table 25(a)). However, although increasing the applied Zn level from 0.0 to 2.0 ppm decreased plant Mn concentration, no further decreases occurred above 2.0 ppm Zn (Table 25(a)). The effect of placement of $ZnSO_4$ upon Mn concentration was similar to its effect upon Fe concentration. The order of Mn concentration in the plants was point source > banded with the seeds = banded below the seeds > mixed with the soil (Table 25(b)). The inverse relationship between plant Zn and Mn concentrations is also illustrated in Tables 22(c) and 25(c). When banded with seeds, banded below the seeds, or mixed with the soil, increasing applied $ZnSO_4$ from 1.0 to 16.0 ppm either did not affect or decreased slightly plant Mn concentrations. However, when $ZnSO_4$ was placed in a point, increasing the Zn level from 1.0 to 16.0 ppm increased plant Mn concentration. Consequently, in Mn concentration rate interacted significantly with placement (see footnote 3 to Table 25(a)). The inverse relationship between plant Zn and Mn concentration was not as pronounced as the one between plant Zn and Fe concentrations. In addition, total Mn uptake into barley shoots was not affected by rate or method of placement of $ZnSO_4$. Consequently, the lower Mn concentrations associated with higher Zn concentrations likely resulted from dilution.

Jones (82) and allied workers reported that the critical level of Mn concentration in barley plants was 20.0 ppm and the sufficiency level ranged from 25.0 to 100.0 ppm. On the basis of these values, none of the plants in this study were Mn deficient.

TABLE 25(a)

MANGANESE UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $ZnSO_4$

Rate[3]	Mn concentration in barley shoots	Mn uptake into 12 barley shoots
(ppm Zn)	(ppm)	(mg)
0.0	39.0[4] d	0.633[2]
1.0	32.4 b	0.640
2.0	30.7 a	0.601
4.0	34.2 c	0.687
8.0	31.5 a b	0.674
16.0	31.6 a b	0.618

TABLE 25(b)

MANGANESE UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $ZnSO_4$

Placement[3]	Mn concentration in barley shoots	Mn uptake into 12 barley shoots
----	(ppm)	(mg)
Banded with seeds	31.3[1] b	0.661[2]
Banded 2 cm below seeds	31.2 b	0.616
Point source	36.3 c	0.658
Mixed with soil	29.5 a	0.640

1. Values followed by different letters are significantly different at 5% level using Duncan's Multiple Range Test (from the combined analysis of variance).
2. Values are not significantly different.
3. Interaction between rate and placement for concentration was significant at the 5% level (from the combined analysis of variance).
4. 0.0 treatment was significantly higher (at 5% level) than average of all other treatments (from combined analysis of variance).

TABLE 25(c)

UPTAKE OF Mn INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $ZnSO_4$

Treatment			
Zn level	Placement	Mn concentration in barley shoots	Mn uptake into 12 barley shoots
(ppm)	----	(ppm)	(mg)
0.0	----	39.0[1] d	0.631[2]
1.0	Banded with seeds	32.5 a b	0.682
1.0	Banded 2 cm below seeds	32.1 a b	0.631
1.0	Point source	34.6 b	0.643
1.0	Mixed with soil	30.2 a	0.612
2.0	Banded with seeds	33.4 b	0.705
2.0	Banded 2 cm below seeds	29.6 a	0.573
2.0	Point source	30.7 a	0.544
2.0	Mixed with soil	28.9 a	0.601
4.0	Banded with seeds	32.8 b	0.632
4.0	Banded 2 cm below seeds	32.8 b	0.651
4.0	Point source	38.8 c	0.745
4.0	Mixed with soil	32.5 a b	0.736
8.0	Banded with seeds	28.6 a	0.683
8.0	Banded 2 cm below seeds	30.5 a	0.635
8.0	Point source	37.5 c	0.717
8.0	Mixed with soil	29.3 a	0.679
16.0	Banded with seeds	29.0 a	0.614
16.0	Banded 2 cm below seeds	31.0 a	0.622
16.0	Point source	39.6 d	0.664
16.0	Mixed with soil	26.6 a	0.591

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test.
2. Values are not significantly different at the 5% level.

6. Concentration and uptake of N

Nitrogen concentration in the barley shoots was not affected by rate or method of placement of $ZnSO_4$ (Table 26(a) and (b)). But total N uptake into barley shoots was influenced by rate and method of placement of $ZnSO_4$. However, the uptake of N varied in the same order as the dry matter yield (Tables 26(a), (b) and (c)) and therefore was likely caused by variation in dry matter yield. Plant N concentrations in this experiment were higher than those in the Cu experiment. This is not surprising since the level of NO_3-N in Lakeland clay loam was much higher than in Pine Ridge sand (Table 18).

The critical level of N in the cereal vegetative tissue at heading was estimated as 1.25% while the sufficient level ranges from 1.75 to 3.0% (106). On the basis of these values, none of the barley plants were deficient in N; rather, N concentrations were sufficient for optimum growth of barley plants.

7. Concentration and uptake of P

Phosphorus uptake was significantly different in the check treatment than in the other treatments (see footnote 4 to Table 27(a)). Rate of application of $ZnSO_4$ significantly affected P concentration and uptake (Table 27(a)), but placement method of $ZnSO_4$ had no significant effect upon P concentration (Table 27(b)). Also, a number of significant differences in P concentration and uptake appears in Table 27(c). However, none of these differences were consistently related to treatment. For example, 2.0 ppm Zn resulted in the lowest P concentration uptake values whereas 4.0 ppm Zn resulted in the highest (Table 27(a)). The experiment showed no evidence of P-Zn interaction. Plant P

TABLE 26(a)

NITROGEN UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $ZnSO_4$

Rate[3]	N concentration in barley shoots	N uptake into 12 barley shoots	
(ppm Zn)	(%)	(mg)	
0.0	3.08[6]	508.0[5]	a
1.0	3.13[4]	622.0	b
2.0	3.15	619.0	b
4.0	3.04	612.0	b
8.0	3.15	678.0	b
16.0	3.19	636.0	b

TABLE 26(b)

NITROGEN UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $ZnSO_4$

Placement[3]	N concentration in barley shoots	N uptake into 12 barley shoots	
----	(%)	(mg)	
Banded with seeds	3.27[2]	683.4[1]	c
Banded 2 cm below seeds	3.13	622.1	b
Point source	3.10	565.0	a
Mixed with soil	3.03	663.2	c

1. Values followed by different letters are significantly different at 5% level using Duncan's Multiple Range Test (from combined analysis of variance).
2. Values are not significantly different.
3. Interaction between rate and placement was not significant.
4. Rates 1.0 - 16.0 were not significantly different from each other.
5. 0.0 treatment was significantly lower (at 5% level) than average of all other treatments (from combined analysis of variance).
6. 0.0 treatment was not significantly different from the average of all other treatments.

TABLE 26(c)

UPTAKE OF N INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $ZnSO_4$

Zn level	Treatment Placement	N concentration in barley shoots	N uptake into 12 barley shoots
(ppm)	----	(%)	(mg)
0.0	----	3.08[2]	508[1] a b c
1.0	Banded with seeds	3.34	704 f g
1.0	Banded 2 cm below seeds	3.17	622 c d e f g
1.0	Point source	3.05	563 a b c d
1.0	Mixed with soil	2.97	601 b c d e f g
2.0	Banded with seeds	3.20	667 d e f g
2.0	Banded 2 cm below seeds	2.96	480 a
2.0	Point source	3.34	583 a b c d e f
2.0	Mixed with soil	3.10	642 d e f g
4.0	Banded with seeds	3.65	695 e f g
4.0	Banded 2 cm below seeds	2.93	578 a b c d e
4.0	Point source	2.56	491 a b
4.0	Mixed with soil	3.04	683 d e f g
8.0	Banded with seed	3.19	725 g
8.0	Banded 2 cm below seeds	3.37	698 e f g
8.0	Point source	3.20	606 c d e f g
8.0	Mixed with soil	2.84	693 e f g
16.0	Banded with seeds	2.99	627 d e f g
16.0	Banded 2 cm below seeds	3.21	636 d e f g
16.0	Point source	3.38	583 a b c d e f
16.0	Mixed with soil	3.19	697 e f g

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test.

2. Values are not significantly different at 5% level.

TABLE 27(a)

PHOSPHORUS UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $ZnSO_4$

Rate[5]	P concentration in barley shoots	P uptake into 12 barley shoots
(ppm Zn)	(%)	(mg)
0.0	0.481[3]	77.7[4] a
1.0	0.525[2] b	99.8[2] c
2.0	0.308 a	61.1 b
4.0	0.579 c	117.0 d
8.0	0.388 a	82.5 b c
16.0	0.488 b	95.0 c d

TABLE 27(b)

PHOSPHORUS UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $ZnSO_4$

Placement[5]	P concentration in barley shoots	P uptake into 12 barley shoots
----	(%)	(mg)
Banded with seeds	0.433[1]	85.7[1]
Banded 2 cm below seeds	0.420	82.7
Point source	0.510	94.0
Mixed with soil	0.466	102.0

1. Values are not significantly different.
2. Rates 1.0 - 16.0 are significantly different at 5% level using Duncan's Multiple Range Test (from the combined analysis of variance).
3. 0.0 treatment was not significantly different (at 5% level) than average of all other treatments (from the combined analysis of variance).
4. 0.0 treatment was significantly lower (at 5% level) than average of all other treatments.
5. Interaction between rate and placement was not significant at 5% level (from combined analysis of variance).

TABLE 27(c)

UPTAKE OF P INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $ZnSO_4$

Treatment		P concentration	P uptake into
Zn level	Placement	in barley shoots	12 barley shoots
(ppm)	----	(%)	(mg)
0.0	----	0.48[1] c d e f g	77.7 a b c
1.0	Banded with the seeds	0.77 g	140.3 d e
1.0	Banded 2 cm below seeds	0.48 c d e f g	94.7 b c d
1.0	Point source	0.47 b c d e f	87.0 a b c d
1.0	Mixed with soil	0.38 a b c d	77.0 a b c
2.0	Banded with seeds	0.23 a b c	50.0 a b
2.0	Banded 2 cm below seeds	0.40 a b c d e	75.7 a b c
2.0	Point source	0.20 a	35.3 a
2.0	Mixed with soil	0.40 a b c d e	83.3 a b c d
4.0	Banded with seeds	0.72 f g	139.0 d e
4.0	Banded 2 cm below seeds	0.72 f g	141.0 d e
4.0	Point source	0.68 e f g	140.0 d e
4.0	Mixed with soil	0.20 a	45.0 a b
8.0	Banded with seeds	0.22 a b	49.7 a b
8.0	Banded 2 cm below seeds	0.27 a b c	55.3 a b
8.0	Point source	0.50 c d e f g	93.3 b c d
8.0	Mixed with soil	0.57 d e f g	131.7 c d e
16.0	Banded with seeds	0.23 a b c	49.0 a b
16.0	Banded 2 cm below seeds	0.23 a b c	46.0 a b
16.0	Point source	0.70 f g	114.3 c d e
16.0	Mixed with soil	0.78 g	170.7 e

1. Values followed by different letters are significantly different at 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

concentrations in this experiment were somewhat lower than those in the Cu experiment. This is not surprising since Pine Ridge sand contained considerably more plant available P than Lakeland clay loam (Table 8).

The critical level of P in cereal crops was estimated (106) as 0.15% and the sufficient level ranges from 0.2 to 3.0%. On the basis of these values, none of the barley plants were P deficient.

8. Concentration and uptake of K

Both K concentration and uptake in the barley shoots increased as the rate of application of $ZnSO_4$ was increased (Table 28(a)). However, the effect of $ZnSO_4$ upon K uptake into the barley shoots was probably more related to the concentration of the fertilizer Zn in the growing medium than to the concentration of Zn in the plants. Although both K and Zn concentrations increased with increasing fertilizer Zn level, the effect of placement method on K concentration was opposite the effect of placement on Zn concentration (Tables 22(b) and 28(b)). Potassium concentration and uptake were highest when $ZnSO_4$ was banded below the seeds and when placed in a point in the soil (Table 28(b)). The highest K concentrations were often associated with the lowest plant Zn concentration (Table 28(c)). Nevertheless, it is possible that fertilizer Zn in some way facilitated the uptake of K. It is interesting to note that although the exchangeable K level in Pine Ridge sand was much lower than in Lakeland clay loam, the plant K concentrations do not differ greatly between the two experiments.

Melsted et al. (106) estimated 1.25% and 1.5 to 3.0% as the

TABLE 28(a)

POTASSIUM UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY RATE OF $ZnSO_4$

Rate[3]	K concentration in barley shoots	K uptake into 12 barley shoots
(ppm Zn)	(%)	(mg)
0.0	0.97[5] a	162 a
1.0	1.19[4] b	230[4] b
2.0	1.42 c	267 c
4.0	1.85 d	379 d
8.0	1.92 d	406 d
16.0	2.03 e	403 d

TABLE 28(b)

POTASSIUM UPTAKE INTO BARLEY SHOOTS AS AFFECTED BY METHOD OF PLACEMENT OF $ZnSO_4$

Placement[3]	K concentration in barley shoots	K uptake into 12 barley shoots
----	(%)	(mg)
Banded with seeds	1.53 b	328[2]
Banded 2 cm below seeds	1.83 c	368
Point source	1.91 d	343
Mixed with soil	1.47 a	308

1. Values followed by different letters are significantly different at the 5% level using Duncan's Multiple Range Test.
2. Values are not significantly different.
3. Interaction between rate and placement was significantly different at 5% level (from combined analysis of variance).
4. Rates 1.0 - 16.0 are significantly different from each other.
5. 0.0 treatment was significantly lower (at 5% level) than average of all other treatments (from combined analysis of variance).

TABLE 28(c)

UPTAKE OF K INTO BARLEY SHOOTS AS AFFECTED BY RATE AND METHOD OF PLACEMENT OF $ZnSO_4$

Zn level	Treatment Placement	K concentration in barley shoots	K uptake into 12 barley shoots
(ppm)	----	(%)	(mg)
0.0	----	0.987[1] a	161[1] a
1.0	Banded with seeds	0.96 a	192 a b c
1.0	Banded 2 cm below seeds	0.936 a	186 a b
1.0	Point source	1.45 a b c d	264 a b c d e
1.0	Mixed with soil	1.43 a b c	276 a b c d e f
2.0	Banded with seeds	0.95 a	201 a b c
2.0	Banded 2 cm below seeds	1.27 a b	258 a b c d
2.0	Point source	1.94 b c d	338 c d e f g h
2.0	Mixed with soil	1.31 a b	271 a b c d e f
4.0	Banded with seeds	1.85 b c d	359 d e f g h i
4.0	Banded 2 cm below seeds	2.36 d	467 h i
4.0	Point source	2.22 c d	423 f g h i
4.0	Mixed with soil	1.17 a	265 a b c d e f
8.0	Banded with seeds	2.09 c d	476 h i
8.0	Banded 2 cm below seeds	2.42 d	506 i
8.0	Point source	2.02 c d	382 e f g h i
8.0	Mixed with soil	1.13 a	261 a b c d
16.0	Banded with seeds	1.98 b c d	412 e f g h i
16.0	Banded 2 cm below seeds	2.13 c d	423 f g h i
16.0	Point source	1.90 b c d	309 b c d e f g
16.0	Mixed with soil	2.10 c d	466 g h i

1. Values followed by different letters are significantly different at 5% level using Duncan's Multiple Range Test (from simple analysis of variance).

critical level and sufficiency range of K in wheat, barley and oats at heading. This implies that the check plants, and plants, fertilized with 1.0 and 2.0 ppm Zn, banded with the seeds, 1.0 ppm Zn banded below the seeds 4.0 and 8.0 ppm Zn mixed with the soil may have been deficient in K. However, it is unlikely that K deficiency was serious enough to erroneously affect any conclusions concerning Zn nutrition of barley plants.

V. SUMMARY AND CONCLUSIONS

Copper sulphate ($CuSO_4.5H_2O$) at rates varying from 0 to 1000 ppm Cu and $ZnSO_4.7H_2O$ at rates varying from 0 to 2000 ppm Zn were incubated for 7 days with Pine Ridge sand and Lakeland clay loam, respectively, in order to assess the effects of time and placement method upon chemical availabilities of Cu and Zn from $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$. It was felt that the higher micronutrient rates would simulate band application whereas the lower rates would simulate thorough mixing of the micronutrient carriers with the soil.

The proportions of applied Cu extracted with water from Pine Ridge sand and of applied Zn extracted with water from Lakeland clay loam were very small (0.25-5.0%),were not appreciably affected by time of incubation, and decreased slightly with increasing concentrations of applied Cu and Zn. The proportions of applied Cu and Zn extracted with DTPA were considerably more (50 - 95%) than the proportions extracted with water. They were not appreciably affected by rate and decreased slightly with time. Apparently, Cu and Zn were quickly adsorbed, complexed and/or precipitated as indicated by the low levels of H_2O soluble Cu and Zn, even at time = 0. The high proportions of applied Cu and Zn which were DTPA extractable suggested that much of the Cu and Zn which was not water soluble was adsorbed or complexed and probably available to plants. The slight decrease with time in the proportions of applied Cu and Zn which were DTPA extractable suggested that the precipated portions of Cu and Zn increased slightly with time. Since Cu and Zn rates had little effect upon the proportions of Cu and Zn that were H_2O or DTPA soluble, there was no evidence that banding Cu and Zn sulphates would increase their

chemical availabilities.

The effects of rate and method of placement of $CuSO_4$ and $ZnSO_4$ upon growth and nutrient content of barley were investigated in environmental growth chamber studies. From 0.0 to 8.0 ppm, Cu as $CuSO_4$ was mixed with Pine Ridge sand, banded with the barley seed, banded below the seed and applied in a point below the seed. Regardless of rate of application, banding $CuSO_4$ below the seed or applying the Cu carrier in a point below the seed was not effective in increasing dry matter yield of six week old barley shoots. Banding $CuSO_4$ with the seed was most effective in increasing dry matter yield followed by mixing $CuSO_4$ throughout the soil. Only 0.5 ppm Cu when banded with the seed was required to significantly increase the yield over the control. When mixed throughout the soil, 1.0 ppm Cu was required. However, the optimal rate for increasing dry matter yield when banded with the seed was 8.0 ppm Cu whereas the optimal rate when mixed with the soil was only 4.0 ppm Cu.

Placing $CuSO_4$ in a point below the seed did not increase Cu concentration in the barley shoots. Mixing $CuSO_4$ with the soil was most effective in increasing plant Cu concentration followed by banding with the seeds which was greater than banding below the seeds. When mixed with the soil, 0.5 ppm Cu was sufficient to increase plant Cu concentration, but, when banded with the seeds, 1.0 ppm Cu was required. The optimum application rate for plant Cu concentration when $CuSO_4$ was mixed with the soil was 2.0 ppm Cu but when banded with the seeds and banded below the seeds, the corresponding rates were 4.0 and 8.0 ppm Cu, respectively.

Zinc concentrations in the barley shoots were usually low when Cu concentrations were high. This likely resulted from something more than dilution since Zn uptake followed the same trends. Perhaps high Cu decreased Zn uptake or the translocation of Zn from the roots to the shoots. The shoots of all barley, except those receiving no Cu, 0.5, 1.0, and 2.0 ppm Cu banded below the seeds and 0.5 ppm Cu placed in a point, contained less Zn than the critical level of 12.5 ppm Zn established in the Zn growth chamber experiment. Therefore, it is possible that the failure of dry matter yield to increase proportionally with plant Cu concentration resulted at least partially from Zn deficiency. If sufficient Zn had been supplied, it is likely that mixing $CuSO_4$ with the soil would also have been the most effective method of increasing dry matter yield.

The critical level of Cu in barley shoots was estimated at 5.2 ppm. However, that value might have been somewhat higher had not Zn been limiting response of dry matter yield to Cu fertilization.

Concentration and uptake of Fe were also low when plant Cu concentrations were high, suggesting that Cu in some way decreased Fe uptake or translocation of Fe to the barley shoots. Nevertheless, all barley shoots contained enough Fe to meet their nutritional needs.

Concentrations of Mn, N, P and K in the barley shoots were not affected by rate or method of application of $CuSO_4$ and all were sufficiently high to meet nutritional needs of the barley plants.

Zinc sulphate in the Zn growth chamber study was applied to Lakeland clay loam at rates varying from 0.0 to 16.0 ppm Zn. The methods of placement were identical to those in the Cu growth chamber study.

Applying $ZnSO_4$ in a point below the seed was not effective in increasing dry matter yield of six week old barley shoots. Banding $ZnSO_4$ with the seeds and mixing the Zn carrier with the soil were equally effective in increasing barley growth followed by banding $ZnSO_4$ below the seeds. Only 1.0 ppm Zn when banded with the seeds or when mixed with the soil was required to significantly increase yield over the control. However, no further yield increase resulted for those two methods when more than 1.0 ppm Zn was applied. When banded below the seeds, 4.0 ppm Zn was required to increase the yield above the control, but above that rate, no further yield increase occurred.

Zinc concentrations in barley shoots was not increased when $ZnSO_4$ was placed in a point below the seed. Mixing $ZnSO_4$ with the soil was most effective in increasing plant Zn concentrations followed by banding with the seed which was more effective than banding below the seed. When mixed with the soil, only 1.0 ppm Zn was required to significantly increase plant Zn concentration. The corresponding values when banded with the seed or banded below the seeds were 4.0 ppm and 8.0 ppm Zn, respectively. The optimal Zn level for plant Zn concentration was 16.0 ppm Zn for all methods of placement (except the point source).

Concentrations of Fe in the barley shoots were usually low when Zn concentrations were high. That likely resulted from something more than dilution since Fe uptake followed the same trends. Perhaps Zn somehow decreased Fe uptake or the translocation of Fe to the shoots. Much of the barley receiving $ZnSO_4$ contained less Fe than the recommended critical level of 50.0 ppm. Therefore, the failure of dry matter yield to increase proportionally with plant Zn concentration may have resulted

from Fe deficiency.

The critical level of Zn in barley shoots was estimated at 12.5 ppm. However, that value might have been somewhat higher had not Fe been limiting response of dry matter yield to Zn fertilization.

Concentration of Mn in barley shoots decreased with increasing applied Zn. That decrease was likely due to dilution since Mn uptake was not affected by rate of Zn application. Concentrations of Cu and N in barley shoots were not affected by rate or method of placement of Zn. Rate of application of Zn significantly affected both concentration and uptake of P, but that effect was not consistently related to treatment.

Increasing the rate of Zn application increased K concentration and uptake just as Zn concentration and uptake were increased. However, low plant K concentrations were quite often associated with high plant Zn concentration, suggesting that the rate of fertilizer Zn in the soil was more important in influencing K uptake and/or translocation than the concentration of Zn in the plant.

Levels of Mn, Cu, N, P and K were all sufficiently high to meet the nutritional needs of the barley plants.

The research undertaking reported in this manuscript indicated that Pine Ridge sand did not supply sufficient Cu for the growth of barley and was marginal in its ability to supply Zn. Lakeland clay loam was deficient in Zn for barley and may not have contained sufficient plant available Fe. Mixing $CuSO_4$ or $ZnSO_4$ with soil was the best method of application followed by banding with the seed and finally banding below the seeds. Placing $CuSO_4$ or $ZnSO_4$ in a point below the

seed did not increase Cu and Zn uptake. Since Zn deficiency limited response in barley to Cu and Fe deficiency limited response to Zn fertilization, it was not possible to accurately determine plant Cu and Zn critical levels or the optimal application rates of $CuSO_4$ and $ZnSO_4$.

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