Copper and Zinc Nutrition of Cereal and Oilseed Crops in Manitoba

by

David Wayne McAndrew

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ABSTRACT

Copper nutrition of barley, oats, wheat, flax and rapeseed on a severely Cu deficient organic soil was studied in the environmental growth chamber. Copper deficiency symptoms were exhibited by all crops when no Cu was applied. Copper concentrations in plant shoots were considered as low when they ranged from 2.3 to 3.7 ug Cu/g for barley, 1.7 to 2.5 ug Cu/g for oats, 3.0 to 4.9 ug Cu/g for wheat, 2.4 to 3.5 ug Cu/g for flax and 1.7 to 2.7 ug Cu/g for rapeseed at 45, 49, 52, 43 and 43 days after seeding, respectively. Concentrations below those ranges were considered deficient and above those ranges sufficient. The order of tolerance to low Cu was rapeseed > barley > oats > wheat > flax.

Field studies were conducted in 1977 and 1978 to determine severity and extent of Cu and Zn deficiencies in Manitoba and the relative effectiveness of various carriers, placement methods and rates of Cu and Zn. It was also hoped that information concerning DTPA extractable soil Cu and Zn critical levels could be obtained. Cereal and oilseed crops grown on Lakeland clay loam containing as little as 0.8 ug DTPA extractable Zn/g soil did not respond in grain yield to Zn fertilization although shoot Zn concentrations often increased. In addition, plant Zn concentrations in control

treatments were usually above critical levels suggested in the literature. Those results in conjunction with a lack in response to Zn fertilization in other research conducted in 1976 on soil containing 0.4 ug DTPAextractable Zn/g soil suggested that Zn deficiency is not likely in barley, oats, wheat, flax and rapeseed in Manitoba. The results also suggested that the DTPA extractable critical level for cereal and oilseed crops is probably lower than the 0.8 ug Zn/g soil suggested in the literature.

Armyworm damage in 1977 and hail damage in 1978 limited yields in Cu experiments on Pine Ridge and Menisino sands so that it was impossible to determine the extent and severity of Cu deficiency or to estimate DTPA extractable soil Cu critical levels on mineral soils in Manitoba. However, Cu addition to cereal crops on organic soils did increase grain yield. Wheat responded to the addition of fertilizer Cu on three organic soils widely separated geographically. Barley and oat grain yield increases were smaller and not statistically significant. Flax was harvested before maturity in 1977 and was killed by frost in 1978. The results suggest that organic soils are severely deficient in Cu, particularily for very susceptible crops such as wheat. More research is needed to calibrate the DTPA method for organic soils but the critical level is likely above 1 ug Cu/g soil and perhaps close to 2 ug Cu/g soil.

Chelated forms of Cu and Zn were 3 to 5 times as effective as sulfates of Cu and Zn in increasing shoot micronutrient concentrations in barley. Mixing water solutions of chelates or sulfates of Cu and Zn with the surface 10 cm of soil was usually more effective than banding dry materials with the seed. This was particularily true for Cu on organic soils. The differences between the two methods were smaller for Cu on mineral soils. The effectiveness of ZnEDTA was greater when mixed than when drilled. However, placement method did not influence the effectiveness of $ZnSO_4$ for barley in the field. Since mixing $ZnSO_4$ was superior to banding in other research with barley in the growth chamber and blackbeans in both the field and growth chamber, it was concluded that all Cu and Zn carriers should be dissolved in water, sprayed onto the soil surface and mixed thoroughly with the surface 10 cm to maximize efficiency. The commercial products ZnMNS from Cominco and ZincGro from Eagle-Picher were totally ineffective at increasing barley grain yields or shoot Zn concentrations in the year of application, with the methods used. There may be residual effects in subsequent years.

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Chapter I

INTRODUCTION

Copper and Zn are more likely to be deficient than other micronutrients on Manitoba soils. Although plants require only a few grams of Cu and Zn per hectare, some soils in Manitoba are suspected of not being able to supply enough Cu or Zn for normal crop production. Copper deficiencies are suspected in leached, sandy Brunisolic and Gray Luvisolic mineral soils as well as on organic soils. Zinc deficiencies are suspected in soils containing considerable lime.

Most of the responses to Cu and Zn fertilization prior to the initiation of the current research had been obtained in the greenhouse. However, the severity and extent of Cu and Zn deficiencies in the most commonly grown crops in Manitoba, cereal and oilseed crops, had not been studied under field conditions. In addition, little was known about plant and soil critical Cu and Zn concentrations or about the most efficient and economical methods of correcting Cu or Zn deficiencies. Studies were therefore initiated

1. to determine the extent and severity of Cu and Zn deficiencies in Manitoba,

2. to establish plant and soil Cu and Zn critical concentrations such that plant and soil micronutrient diagnostic services could be developed which would assist the farmer in determining when it would be advantageous to apply Cu and Zn fertilizers and

3. to determine the relative efficiencies of various micronutrient fertilizers and placement methods such that efficient and economical methods for correcting Cu and Zn deficiencies could be recommended to farmers.

Chapter II

LITERATURE REVIEW

2.1 FUNCTIONS OF MICRONUTRIENTS IN PLANTS

An element is considered as an essential nutrient when it is required for the completion of the normal life cycle of an organism. The requirement must be absolute and not substitutable by another element. The categorization of the various nutrients into macro-, secondary, and micro-nutrients is purely for convenience. A nutrient is placed into a category on the basis of its concentration in the organism.

The hypothesis put forward by Price *et al* [89] that micronutrients function in plants by combining to form stable complexes with natural ligands is too simplistic. The most important functions of micronutrients involve their activation of enzymes essential for the normal metabolism within living cells. The enzyme nitrate reductase, for example, will not function without Mo [89]. Often the activity of an enzyme is so directly affected by the status of a particular micronutrient that the enzyme's activity can be used to detect micronutrient deficiency before the appearance of visual deficiency symptoms. Brown and Clark [17] found that the activity of tyrosinase in sugarbeets decreased considerably when Cu was deficient. Dwivedi and Takkar [32] attempted to follow the activity of ribonuclease, as an early indicator of Zn deficiency. They found that at moderate Zn deficiency, the level of ribonuclease activity increased. Using this as an indicator they could detect Zn deficiencies at between 15 to 20 days after germination in the absence of deficiency symptoms. Dwivedi and Randhawa [31] were able to use the activity of carbonic anhydrase, a Zn-containing enzyme, to determine the Zn status of wheat, maize, and mustard. Edwards and Mohamed [34] also found a decrease in carbonic anhydrase activity in *Phaseolus vulgaris* when Zn was deficient.

Micronutrient deficiencies have also been linked to changes in photoperiod responses. Davies *et al* [25] found that Cu deficiency markedly decreased bud formation in *Chrysanthemum morifolium* when grown in an artifical soil. Graves and Sutcliffe [40] reported that Cu deficiency in *Chrysanthemum morifolium* resulted in a loss of the response to the photoperiod as well as a loss of apical dominance.

Micronutrients also influence the symbiotic association of legumes and rhyzobia. Cartwright and Hallsworth [21] found that the bacteriod content and nodule apex development decreased in subterranean clover when grown in solutions lacking Cu. They also suggested that the Cu enzyme cytochrome c oxidase is important in maintaining the oxygen tension in the root nodule neccesary for nitrogen fixation.

Manganese has been linked directly to the functioning of the photosynthetic system [89] however its exact function has not been delineated. It has been established definitely that Fe functions in the cytochrome system as well as being necessary for the activities of many other enzymes.

2.2 SOIL FACTORS AFFECTING MICRONUTRIENT AVAILABILITY

The complexity of micronutrients in nature results from the many forms that exist simultaneously. They are present in inorganic and organic solids, as well as in soil solution and living matter. Lindsay [60] discussed the nature of micronutrient equilibrium reactions in soils. Uptake by plants depletes the available forms of micronutrients in the soil which in turn upsets the equilibrium and stimulates the dissolution of the solid phases to replenish available micronutrient levels. Plant material may be returned to the soil and the micronutrients may remain in soil organic matter in chelated or complexed forms which may or may not be available for plant uptake. Crop removal for human or animal consumption permanently lowers soil micronutrient levels. Even when plant material is returned to the soil, micronutrients released upon decompostion may be precipitated into inorganic forms unavailable for crop uptake. Thus, a significant portion of each available micronutrient pool consists of plant available organic matter-micronutrient complexes and inorganic micronutrient forms released upon decomposition of organic matter [8,14,27,28,29,49,104,105].

Kinds of rocks which have weathered to form a soil influence micronutrient levels. Kraukopf [55] reported that the average concentration of Fe in basalt is 86,000 ppm whereas in limestone this amount is about 3,800 ppm. Copper also follows the same pattern with basalt containing 100 ppm Cu and limestone 10 ppm Cu on the average. The ranges in soils of total concentrations of Fe, Mn, Cu, and Zn are 10,000-100,000, 20-3,000, 10-80 and 10-300 ppm, respectively. This makes it clear that in most instances the total amount of a micronutrient present in the soil is not the limiting factor. The problem is one of availability.

Micronutrient availability is strongly affected by soil pH [8,60,114]. Martens [66] working with 16 acidic soils in Virgina found that Cu availability was related to soil pH as well as the 1.0N HCl extractable Cu, organic matter and clay content in multiple regression but not individually in simple correlation. He concluded, however, that 1.0N HCl extracted predominantly the organically bound Cu, although plant uptake correlated positively with organic matter and negatively with 1.0N HCl extractable Cu. Martens [66] was not able to relate Zn availabilty to the soil fractions mentioned.

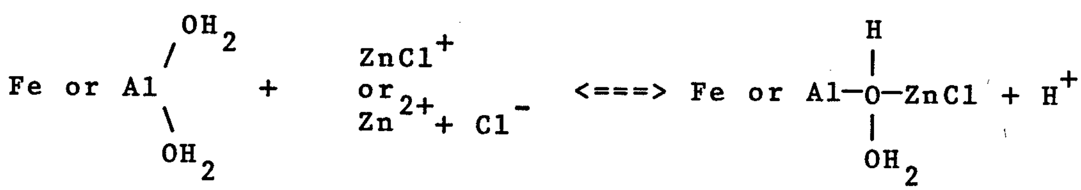
Lindsay and Norvell [61] indicated in one paper that $ZnSiO_3$ and amorphous SiO_2 were controlling the solubility of Zn^{++} in soils. In a later paper [81], however, they indicated that the original conclusion was in error and that $ZnSiO_3$ in fact did not exist in soil under normal conditions. However, they were confident of the empirical formula that they had derived from the study of equilibrium reactions of chelating agents in soil [59,81] which states that soil solution concentration of Zn^{++} decreases 100 times per unit increase in pH. They [61] indicated that if the soil solid controlling soil solution concentration of Fe^{3+} were $Fe_2O_3 \cdot nH_2O$, concentration of iron would decrease 1000 times for each unit increase in soil pH. They also stated that these factors are influenced by $CaCO_3$ and partial pressure of CO_2 in the soil.

Bohn and Aba-Husan [14] working with Sporobulus wrightii, a forage grass adapted to growth in alkaline soils and arid conditions, found that plant Cu and Zn concentrations decreased as pH increased. In contrast to results of most other workers, they found that Mn and Fe concentrations increased as pH increased which they attributed to some unknown physiological effect of pH. Gupta [41] found in both the field and greenhouse that as the pH of a Charlottetown fine sandy loam increased from 4.2 with additions of lime, Mn concentration in barley plants at boot stage decreased. Pailoor et al. [84] found a negative and highly significant relationship between pH and acid soluble soil Mn or Mn concentration in oats shoots. They also reported that application of lime decreased the plant concentrations of Mn and that this was a possible means of correcting Mn toxicity on acid soils.

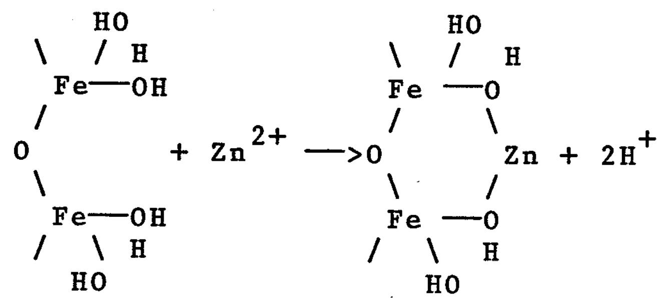
McGregor [68] working with Manitoba soils of varying pH found that Zn uptake by flax and wheat as well as Cu uptake by flax decreased with increasing pH. However, there was no effect of pH on Cu uptake by wheat. He also found that Cu concentrations in flax and wheat increased with increasing clay content.

Bishop and MacEachern [9] found that increasing the pH of highly leached sandy soils by liming increased incidence of Zn deficiency because of the decrease in solubility of Zn-containing compounds. Gupta and Chipman [42] found that as they increased pH of an acid sphagnum peat, Fe and Mn concentrations in the carrot plant decreased while carrot yields increased.

Kalbasi _et al_. [53] in experiments with Al_2O_3 and Fe_2O_3 felt that two forms of Zn^{++} adsorption occurred in the presence of $ZnCl_2$. One type of the adsorption they felt was nonspecific according to the following reaction:



The other type of adsorption was thought to be specific according to the reaction:



which would be in essence an extention of the crystal lattice. Kalbasi _et al._ postulated that both of these types of adsorption may occur in soil and control the solubility of Zn. It is apparent that if Zn solubility were controlled by such mechanisms, that pH would greatly influence Zn availability.

Redox potential in soil also influences availibility of micronutrients such as Fe and Mn which occur in several oxidation states. Olomu and Racz [82] working with flax in a pot experiment established that chlorotic symptoms were due to a Mn-induced Fe deficiency caused by reducing conditions induced by excessive moisture. The high moisture conditions caused reduction of insoluble manganese oxides to more soluble Mn^{++}. Iron was also reduced to the more available Fe^{+2}, but to a lesser extent than Mn so that the increase in Mn uptake was much greater than the increase in Fe uptake. Copper and Zn are not subject to oxidation state changes as readily as Mn and Fe and are thus not affected by reducing conditions in soils.

Soil organic matter also influences micronutrient availability. Elgala et al. [33] in sand culture experiments with barley found that humic acid had a very moderating effect on the availability of micronutrients. In conditions where the nutrients were in relatively low supply, increasing humic acid increased or maintained uptake of Cu, Fe, and Zn. In another experiment they found that humic acid prevented the toxic effects of micronutrients which were present at toxic concentrations.

There is great variation among micronutrients in the method and strength of their binding by organic matter. Bloom and McBride [10] indicated that there was strong evidence that Mn^{++} was retained by a New York acid washed peat in a hydrated form. However, Cu^{++} was bonded covalently to the oxygen of a carboxylate group in the peat, thus rendering it very unavailable to plants. Bloom and McBride [10] also considered chelation of micronutrients into plant available organic complexes not as important as other workers had suggested.

Shuman [105] found that the amounts of micronutrients in the various soil fractions of soils of southeastern United States were extremely variable. He was able, however, to indicate the relative proportions of Zn, Mn, and Cu in various soil fractions. The order of Zn concentrations was clay > iron oxide > silt = sand > organic matter > exchangeable. The order for Mn was organic matter = sand > silt > clay > iron oxides > exchangeable, while for Cu it was organic matter > clay > silt > sand > iron oxides > exchangeable.

The preceding discussion concerning the influences of total soil micronutrient levels and other factors upon plant available soil micronutrient levels should aid in explaining why certain soils are deficient in micronutrients. Acidic sandy soils such as Pine Ridge and Menisino sand are sometimes deficient in Cu [2,68] because they are low in total Cu. However, most deficient soils are deficient because of the influence of other factors such as pH, redox potential and organic matter. Zinc and Fe deficiencies are most likely on highly calcareous soils such as Lakeland, Emerson, Tarno etc. [2,47,68] because the high alkalinity of those soils greatly decreases the solubilities of Zn- and Fe- containing compounds. Copper deficiency is quite prevalent on organic soils [20,64,91] because organic matter very tightly binds Cu. Manganese is more likely to be deficient on poorly drained mineral and organic soils because the rather persistent low redox potentials in such soils encourage the conversion of insoluble MnO_2 to the more soluble Mn^{+2} form which then moves out of the soil with the drainage water. On the other hand, that same reaction may lead to Mn-induced Fe deficiency during very wet periods on soils which are usually quite well drained.

2.3 DIAGNOSTIC TECHNIQUES FOR MICRONUTRIENT STATUS

There are two methods of establishing the status of nutrients. These are soil testing and plant tissue analysis, both of which have their advantages and disadvantages. Nitrogen, P, and K are relatively easy to monitor by either method, due mainly to the relatively large quantities of these nutrients in soils and plants. Viets and Lindsay [114] stated that difficulties in micronutrient soil analysis result primarily from low micronutrient concentrations. Interaction among micronutrients as well as between micro- and macronutrients under the influence of varying environmental conditions further complicates the situation [82,114].

Many workers have attempted to develop micronutrient soil tests. Most of these tests fall into one of four catagories; acid, neutral salt, water, or chelate extractions.

Others have tried using microbial tests or "test" crops susceptible to a particular deficiency.

Tissue tests are quite straight forward in principle. The plant tissue is usually ashed, leaving only the inorganic constituents behind. The sample is then analyzed for the nutrients of interest by the most appropriate method available. The results are then interpreted by whatever means are at hand and a diagnosis made of the plants nutrient status. Other types of tissue tests are now being evaluated. Many of these newer tissue tests involve the assay of a particular plant enzyme that has been found to reflect the status of a particular nutrient [31,32,34].

2.3.1 Soil analysis

Most of the numerous micronutrient soil tests which have been developed are extractions with the aim of measuring both the intensity factors (the readily available concentration) and the capacity factor (the soil's ability to replenish the available forms of a micronutrient) [59]. Some methods make excellent predictions under a wide range of soil conditions, whereas others are dismal failures.

Micronutrient soil tests usually involve growing a crop with and without the addition of the micronutrient, or growing a crop on soils varying greatly in content of the micronutrient and then attempting to correlate plant uptake with the amount of micronutrient extracted. The studies have usually involved pot experiments but occasionally research has been conducted in the field. Degree of standardization of soil test procedures has not been great as each of the many laboratories modifies tests to fit local conditions.

One of the more common tests for Cu on organic soils involves extraction with 1.0N HCl with a one to sixteen soil to solution ratio [118]. Recommendations for fertilizer Cu are made in Michigan using this test and practical experience as to crop responsiveness. Addition of 6.6 kg Cu/ha is recommended for highly responsive crops grown on organic soils containing less than 9 ppm 1.0N HCl extractable Cu [117]. On soil containing 10-20 ppm extractable Cu 3.3 kg/ha are recommended, whereas no Cu is recommended on soil containing more than 20 ppm extractable Cu. Lindsay and Norvell [62] suggested a critical level of 0.2 ug DTPA extractable Cu/g soil on mineral soil, however this recommendation was not based upon yield response data. The DTPA soil test involves shaking 10 g soil for 2 hr with 20 ml of a solution containing 0.005M DTPA (diethylenetriaminepentacetic acid), 0.1M TEA (triethanolamine) and 0.01M $CaCl_2$ buffered at pH 7.3.

McGregor [68] investigated several Cu soil tests to determine which was most reliable for Manitoba mineral soils. He found that the amount of Cu extracted with a solution containing 0.01M Na_2DP · [disodium ethylenediamine di(o-hydroxyphenylacetate) more commonly referred to as Na_2EDDHA] and 1.0M NH_4OAc buffered at pH 7.0 correlated well with Cu concentration and uptake by flax, with r^2 values of 0.75 and 0.93, respectively. A soil critical level of 1.3 ppm Na_2EDDHA extractable Cu was suggested. McGregor also found a good relationship between DTPA (buffered at pH 7.0 with 1.0 hr shaking time) extractable Cu and Cu concentration and uptake by flax, with r^2 values of 0.69 and 0.91, respectively.

Available soil zinc levels were first successfully estimated by a two-phase extraction procedure involving aqueous ammonium acetate and dithizone in carbon tetrachloride [114]. This method has since been abandoned due to its tedious nature [59]. An extraction procedure involving 0.1N HCl is currently used in Indiana, Michigan, Missouri, Nebraska, Ohio, South Dakota and Wisconsin. The 0.1N HCl method is quite reliable on acid soils [118] although it does extract Zn which is not available to plants [59]. The 0.1N HCl method can not be used on calcareous soils because it extracts considerable Zn from carbonates which is not plant available. Extracting with a solution containing EDTA and ammonium carbonate buffered at pH 8.6 has been found to be a reliable Zn soil test and is currently used in Minnesota [118]. Lindsay and Norvell [62] found that their DTPA soil test was also a good indicator of the Zn status of neutral to alkaline soils and specified 0.8 ug DTPA extractable Zn/g soil as the critical level. McGregor [68] found that DTPA (buffered at pH 8 with 1 hr of shaking) was the best extractant for Zn from Manitoba soils and estimated a critical level of 1.3 ug Zn/g soil for flax.

Analysis of soils for Fe status has been studied less than Cu and Zn [24] and only one method, the DTPA test of Lindsay and Norvell, appears to have come into regular usage. The DTPA test with a critical level of 4.5 ug Fe/g soil is used in Kansas, North Dakota and probably several other states [118].

Plant available soil Mn has most often been estimated by measuring exchangeable and/or readily reducible Mn. The method as described by Adams [1] involves using hydroquinone as a reducing agent in conjunction with extracting agents which measure exchangeable Mn. Lindsay and Norvell [62] felt that the DTPA soil test could also be useful for determining Mn availability and they suggested a soil critical level of 1.0 ug Mn/g soil.

2.3.2 Plant Analysis

Total micronutrient concentrations in plant tissue are usually measured by either dry ashing in a muffle furnace or wet ashing using a HNO_3-$HClO_4$ digestion [50,51,52] and then analyzing the ash, commonly by atomic absorption, although other methods are in use [50,51,52]. Extensive research has established the relationships between plant micronutrient concentrations and plant performance for a wide variety of crops. Thus, the status of a particular micronutrient in a crop can be estimated by comparing its plant concentration to the established relationship.

The relationship between plant micronutrient concentration and plant performance is often described by using the term 'critical level'. A critical level of micronutrient is usually defined as the plant concentration when yield is 5-15% below maximum, assuming that no other factors are limiting yields [51,76]. Sometimes the relationship between plant micronutrient concentration and plant performance is described by using concentration ranges such as deficient, low, adequate, high and toxic. Critical levels and concentration ranges of several crops are listed in Table 1 for Cu, Zn, Mn and Fe.

The values in Table 1 indicate that there is no real agreement among researchers as to the nutritional levels within a crop. For example, Melsted et al [70] estimated the Cu critical level of wheat as 5.0 ug Cu/g whereas Gupta and MacLeod [43] suggested an optimum concentration of 3.2-3.3 ug Cu/g. The difference in these suggested critical levels likely resulted from many factors, not the least of which were differences in the requirements of the particular

TABLE 1

Micronutrient plant critical levels and concentration ranges from the literature

Plant and growth stage	Element	Concentration plant (ppm)	Comments	Ref
Barley, boot stage	Cu	4.8	optimum	43
Barley, six weeks	Cu	5.2	critical level	2
Barley, harvest	Cu	6.2-11.9	normal	94
Barley, six weeks	Zn	12.5	critical level	2
Barley, five-leaf stage	Zn	290	upper critical level	26
Barley, flag leaf and upper stem at heading	Zn	13-24	normal	8
Barley, six weeks	Mn	28.0-39.4	normal	2
Flax, eight weeks	Cu	2.0	deficient	68
Flax, eight weeks	Zn	9.0	deficient	68
Flax, tops	Mn	6.0	deficient	55
Flax, tops	Mn	50.0	normal	55
Oats, 6-9 weeks	Cu	3.0	deficient	94
Oats, boot stage	Cu	3.2-3.3	optimum	43
Oats, flowering	Zn	<20.0	low	8
Oats, flag and penultimate leafs at heading	Mn	12-15	deficient	67
Wheat, boot stage	Cu	3.2-3.3	optimum	43
Wheat, boot stage	Cu	5.0	critical level	70
Wheat, boot stage	Zn	15.0	critical level	70
Wheat, boot stage	Fe	25.0	critical level	70
Wheat, boot stage	Mn	30.0	critical level	70

varieties grown. Many workers have found nutrient level difference among various crop species, as noted in Table 1. Varietal differences have also been noted [7,15,59,70]. It is also apparent in Table 1 that stage of growth greatly influences plant micronutrient level. Some variation among researchers in suggested critical levels may have resulted from variation in growing conditions. However, variations among crop species and varieties in micronutrient requirements are perhaps most important.

2.3.2.1 Species Variability

Micronutrients affect species differently. It is not uncommon for some plants to thrive while adjacent plants of another species are severely deficient in a particular nutrient [8]. Roth et al [95] found that oats and soybeans reacted differently to Cu fertilization. Toxicity occurred at tissue Cu concentrations greater than 22 ug Cu/g for oats whereas Cu toxicity did not occur in soybeans until the tissue Cu concentrations were greater than 220 ug Cu/g. Nambiar [77,78] reported differing sensitivities to Cu deficiency among wheat, oats and barley with one variety of wheat and one variety of barley being less sensitive to deficiency than six other wheat varieties and the one oat variety tested.

Gladstone et al [39] reported very large species variation. For example, legumes generally contained considerably more Cu than cereals. They also found that in all 24 crops tissue Cu concentration decreased with increasing plant age.

2.3.2.2 Varietal Variability

Varieties within a species also vary in critical levels and in efficiency of use of micronutrients. Nambiar [78] reported that Cu concentration at mid-tillering in young leaves of six varieties of *Triticum aestivum* varied from 0.42 to 0.86 ug Cu/g with a least significant difference of 0.35 ug Cu/g. Nambiar [77] also reported variation among the six varieties in time of appearance of foliar Cu deficiency symptoms.

Boawn *et al* [13] found that number of days to maturity in two varieties of field beans (*Phaseolus vulgaris*) Red Mexican and Sanilac, was decreased by high levels of Zn at the four-compound leaf stage. They also found that the plant Zn concentration necessary for the lowest number of days to maturity was 30-40 ug Zn/g in Red Mexican and 20-30 ug Zn/g in Sanilac.

Ambler and Brown [4] felt that the reason for differential sensitivity to Zn deficiency in two varieties of *Phaseolus vulgaris* was related to uptake of Fe and P. Sensitivity to Zn deficiency was greatest in that variety which contained the most Fe and P. Shukla and Raj [103] indicated that variation in sensitivity to Zn deficiency among wheat varieties (*Triticum* sp.) was due to variation in ability of the root systems to utilize soil Zn. Brown and Jones [18] felt that differences in efficiency of Mn utilization among varieties of *Avena sativa* (oats) were possibly due to variation in degree of substitution of Ca for Mn in nonspecific Mn complexes. Such substitution would enable the Mn to be utilized for Mn specific enzyme sites and thus benefit the plant under Mn stress conditions.

Brown and McDaniel [19] felt that variation among varieties of *Avena byzantina* (oats) in sensitivity to Zn and Cu deficiencies was due in part to variation in ability to take up P, Ca and Fe. They reported that Ca concentrations were higher in tops of Zn deficient plants. Also they stated that Fe concentration was decreased in both varieties by Zn fertilization which caused chlorosis in one variety but not in the other. Phosphorus concentrations were higher in shoots of the variety which developed withertip (Cu deficiency).

2.4 NUTRIENT INTERACTIONS

Optimal plant nutrition is dependent upon a delicate balance among nutrient levels and other environmental factors. Interaction among nutrient elements is very common and also very important. Correction of a nutrient deficiency has often resulted in a deficiency of another nutrient [19].

Phosphorus-zinc interactions have been well documented [12,54,85,90,96,98,111,112,115]. Some workers felt the interaction was due to decreased availability of soil Zn at high P levels [112]. However the more common view is that the interaction is physiological [12,54,85,90,98,111,115], with high P inhibiting plant uptake and/or translocation of Zn. In contrast, Chaudhry et al [22], reported a benefical effect of P fertilization on Zn utilization in a calcareous flooded rice soil. They felt that the P increased the soil solution concentration of Zn thus favouring increased Zn uptake.

Chaudhry et al [23] also showed that Zn fertilization is antagonistic to Cu uptake and can result in Cu deficiency if soil Cu is low. Singh and Steenberg [109] also reported a Zn-Cu interaction, however, they stated that the decrease in Cu was inconsistent.

Nambiar [78] reported that Cu deficiency was more likely with high grain protein varieties of wheat, oats and barley. The N/Cu ratio in grains of the cereals was important in determining the effect of late application of fertilizer Cu, the recovery from deficiency decreasing as the N/Cu ratio increased.

Singh and Steenberg [108] showed that Zn fertilization decreased Mn concentration in roots, sheaths and blades in maize but not in barley. They indicated that Zn-Mn interaction was at the point of translocation of Mn into the root.

Polson and Adams [86] reported that an Fe deficiency resulted from applying high rates of Cu in a sand culture experiment when working with navy beans. Lee _et al_ [58] reported that high Zn inhibited Fe uptake by flax grown in solution culture whereas Fe did not inhibit Zn uptake. They found that only FeEDDHA added to the solution cultures was effective in increasing Fe content of the flax tops at high Zn levels. The same amount of Fe as $FeCl_3$, FeDTPA, or, Rayplex Fe (Fe-polyflavonoid) was not very effective.

Sánchez-Raya _et al._ [99] reported a Mn-Fe interaction in tomato which included two facets. At low Fe, Mn accumulated in the shoots, whereas at high Fe Mn accumulated in the roots. Moraghan and coworkers [72,73,74] reported that flax accumulated Mn to toxic levels when Fe availability was low and addition of 2 ug Fe/g soil as FeEDDHA to the soil was sufficient to correct the Mn toxicity. They also reported that "chlorotic dieback" of flax was due to a deficiency of Zn and imbalance between Zn, Mn and Fe in the plants. Olomu and Racz [82] reported that chlorosis of flax was related to a Mn-Fe imbalance, and suggested that when the plant concentration ratio of Mn/Fe was greater than 4.0 that chlorosis and yield depression occurred.

Brown [16] discussed interactions between Ca and Mn, P, Fe or Cu in both monocots and dicots in a review paper. He stated that part of the reason for the interaction between

Ca and other nutrients was a Ca competition for sites in chelates involved in ion transport within plants.

2.5 MICRONUTRIENT CARRIERS AND PLACEMENT METHODS

Micronutrient carriers fall into four categories based on their form and solubility. These are soluble inorganic forms such as sulfates, insoluble inorganic forms such as phosphates, organic chelates such as EDTA (ethylenediamine-tetraacetic acid) and organic nonchelates such as polyflavonoids [76]. To be effective, a micronutrient fertilizer usually must provide a readily available supply of a particular micronutrient in amounts that are required by the crop during the time in which the crop is actively growing. In order to accomplish this, a highly mobile carrier may be needed for a fast growing crop whereas a carrier which is slowly available may be ideal for slow growing crops. Thus, virtually every micronutrient carrier is adapted for use in some situation.

Micronutrient fertilizer effectiveness is also influenced by placement method. Usually, micronutrient uptake increases with increasing root fertilizer contact. MacGregor et al. [65] found that maize yields were higher when $ZnSO_4$ was plowed down than when the same amount of $ZnSO_4$ was banded. Tissue Zn concentration was also higher for the plowed down treatment. However, Hawkins et al. [46] found that 6.72 kg Zn/ha as finely divided $ZnSO_4 \cdot H_2O$ were equally effective plowed down or disked in. Schnappinger et al.

[101] reported that the maize yield increase from 7.0 kg Zn/ha as $ZnSO_4 \cdot H_2O$ was equivalent to the increase from 4.5 kg Zn/ha as ZnEDTA when either were broadcast and worked into the surface 8 cm of a Zn deficient soil. However they reported in another experiment that 1.12 kg Zn/ha as ZnEDTA banded was as effective as 7.0 kg Zn/ha as $ZnSO_4 \cdot H_2O$ broadcast and worked in. Boawn [11] reported that ZnEDTA was 2 to 2.5 times as effective as $ZnSO_4$ both when banded and when broadcast and plowed down. He also reported that when both carriers were broadcast on the surface only ZnEDTA was effectively leached in by irrigation water.

Chelated micronutrients are less sensitive to placement due to their higher mobility thus greater availability. Singh [106,107] reported evidence that the solution applied Zn and Mn sulfates were relatively immobile, moving only 12 cm and 15 cm, respectively, with 1200 mm of simulated rain. Lahav and Hochberg [56,57] reported that ZnEDTA absorption to soil was negligible. Norvell and Lindsay [80] reported that Zn and CuEDTA were stable at pH 6.75 and 7.3 with approximately 60% of the Zn and 40% of the Cu still attached to EDTA after 30 days. Lahav and Hochberg [56] reported that FeEDDHA was extremely stable and was virtually totally recovered after 2 months incubation with soil.

Prasad _et_ _al_. [87] reported that addition of chelating agents to soil increased concentrations of indigenous micronutrients in soil solution. Lindsay and Norvell [61] also showed that soil solution concentrations of micronutrients increased with addition of EDTA and DTPA.

Farley and Draycott [33] found that coating sugar beet seeds with MnO prevented Mn deficiency early in the growing period but subsequent foliar applications were necessary for normal production. Saric and Saciragic [100] had earlier reported oat yield increases from seed coat applied Co and Cu. On the other hand, Rasmussen and Brown [93] using several Zn chelates found that only Zn polyflavonoid had no undesirable effects when used as a seed treatment. McGregor [68] reported that when Zn- or CuEDTA was applied with flax seed, no flax emerged. It appears that caution should be used when applying chelated micronutrients with seed.

Hedayat [47] reported that Zn uptake by blackbeans (*Phaseolus vulgaris*) increased when a constant amount of $ZnSO_4$ was mixed with an increasing volume of soil. He also reported that in a pot experiment with blackbeans 2 ug Zn/g soil as $ZnSO_4$ mixed throughout was more effective in increasing Zn uptake than banding it below the seed, while applying $ZnSO_4$ in a point below the seed was totally ineffective. In a similar experiment with barley, Akinyede [2], found that the order of relative effectiveness in Zn uptake from $ZnSO_4$ was mixed throughout > banded with the seed > banded below the seed > point below the seed.

Banin and Navrot [6] presented information concerning a novel micronutrient fertilizer. They used montmorillonite saturated with Cu, Zn and Mn as a balanced source of all three nutrients. Efficiency was found to be very comparable to EDTA chelates and superior to sulfates at equal rates. Montmorillonite had an added advantage of slowly releasing macronutrients preventing rapid fixation and permitting a longer period of availability. Iron montmorillonite was also effective in slowly providing Fe to crops in calcareous soils [79].

Gilkes [38] reported that application of $CuSO_4$ and ZnO with ordinary superphosphate resulted in formation of Cu and Zn compounds which were 40% and 90% soluble in water respectively. This resulted in slow release of Cu and Zn from the acid fertilizer granules. Mortvedt and Giordano [75] stated that $MnSO_4$ or MnO were more available when combined with orthophosphates than with polyphosphates. They also reported that MnEDTA applied with phosphate fertilizer was effective in overcoming a Mn deficiency.

Norvell and Lindsay [80] found that MnEDTA was very unstable with less than 3% of the Mn remaining with EDTA after 20 hrs at pH 5.7. Rumpel <u>et al</u> [97] reported that although both finely ground $MnSO_4$ and MnO were satisfactory fertilizers MnEDTA actually depressed plant yield.

The influence of placement method upon micronutrient efficiency varies among carriers. If the method of the micronutrient application is restricted by cultivation and/or seeding practices, this must be considered when a choice of carrier is made. Broadcast application worked in by disking is usually the best method. When this method is used virtually any carrier is acceptable. However, if it is not possible to work in a broadcast application, only the soluble chelated forms such as EDTA or EDDHA are likely to be sufficiently mobile to penetrate into the rooting zone. Band application of chelated and inorganic micronutrient fertilizers is usually less effective than mixing throughout. This method of application has the added disadvantage of formation of insoluble compounds with macronutrient fertilizers, particularily with those containing P. Chelated micronutrients are sometimes as effective when banded, since they move out in the soil with the movement of water, thus affording a larger root interaction zone. It should also be apparent that the optimal rate of micronutrient application varies among carriers and method of application. Optimal rates are usually lower with chelated than with inorganic fertilizers. Optimal rates are also considerably lower when inorganic carriers are mixed throughout as compared to banded.

2.6 RESIDUAL EFFECT OF MICRONUTRIENT FERTILIZERS

Residual availability of a micronutrient fertilizer to subsequent crops is very important when it is considered that most of the fertilizer is not utilized by crops in the year of application. Terman et al [113] in a pot experiment with corn found that Zn applied alone and in combination with P and N carriers had definite residual effects to a second crop of corn. Norvell and Lindsay [80] in incubation studies with Fe-, Cu-, and ZnEDTA found initial rapid decreases in the percent of the chelate remaining with the original metal. However, by 30 days of incubation there was very little change in the chelated metals with the percent of metal chelated dependent on the inculation pH.

Schnappinger et al [101,102] reported increases in corn yield as a result of the residual effect of 7.0 and 14.0 kg Zn/ha as $ZnSO_4$ and 4.4 kg Zn/ha as ZnEDTA which had been broadcast and worked into the surface 8 cm for a corn crop the previous year. MacGregor et al [65] reported that extracts from soils treated eight years previously with $ZnSO_4 \cdot 7H_2O$ or ZnEDTA contained more Zn than check treatments. They indicated that Zn deficiencies that occurred five years after Zn fertilization were actually due to high levels of P fertilization.

Follett and Lindsay [37] reported that in incubation experiments with 11 soils extractability by DTPA 14 weeks after addition of Zn, Fe, Mn and Cu sulfates and FeEDDHA was only 44, 0, 14, 61, and 26% respectively, of that at the time of application. Residual effects from micronutrient applications definitely occur and Follet and Lindsay [37] indicated that extraction with DTPA is a good way to monitor such effects.

Chapter III

STUDY I: COPPER NUTRITION OF CEREAL AND OILSEED CROPS ON ORGANIC SOIL IN THE ENVIRONMENTAL CHAMBER

3.1 INTRODUCTION

It is known that Cu deficiencies in cereal and oilseed crops in Manitoba occur most often on acidic, sandy soils and particularily on organic soils. However, soil analyses have not been particularily useful in identifying specific situations in which Cu deficiency is likely. Plant analyses, on the other hand, are likely to be more useful as diagnostic tools. Unfortunately, the relationships between plant Cu concentrations and plant performance have not been established for cereal and oilseed crops commonly grown in Manitoba. Study I was conducted to establish plant Cu critical levels in barley, oats, wheat, flax and rapeseed. Relative susceptibility of those crops to Cu deficiency was also investigated.

3.2 METHODS AND MATERIALS

3.2.1 Soil Properties

The soil used in this experiment was a Terric Mesisol from the Stead area of Manitoba which was known to be very Cu deficient from a field experiment conducted in the summer of 1978. The soil was rototilled in the field to encourage uniformity, and sealed into large plastic bags to prevent moisture loss. The soil was later removed from the bags, thoroughly mixed and resealed into the plastic bags until initiation of the experiment.

Volumetric water content and air-filled pore space at field capacity as well as bulk density were estimated by filling a cylinder of known volume with soil, saturating the soil with water and then weighing to determine a saturated weight. Each cylinder was then allowed to drain through Whatman #42 filter paper for two days and reweighed. The saturated weight minus the weight after two days divided by the volume of the cylinder was taken as the air-filled pore space at "field capacity". After the two-day weighing, all soil in each cylinder was oven dried, the oven dry weight subtracted from the "field capacity" weight and then divided by the volume of the cylinder to arrive at the volumetric water content at "field capacity". Bulk density was also calculated from soil oven dry weight divided by cylinder volume. Total pore space would be the sum of volumetric water content plus air-filled pore space at field capacity.

A standard combination glass-calomel pH electrode was used to measure pH of a 3 to 1, water to soil paste. Conductivity of the same paste was determined with a Radiometer conductivity meter having a standard conductivity cell.

Nitrate-N was determined by Harper's modified phenoldisulfonic acid method [45]. Five g of air dry soil were extracted with 50.0 ml of a solution containing 0.02M $CuSO_4$ and 0.06% Ag_2SO_4. Nitrate was measured colorimetrically as the nitrated form of phenoldisulfonic acid in an alkaline solution using a Cecil Instruments 202 Ultraviolet Spectrophotometer at 415nm.

Phosphorus was measured using Bray's [83] 0.03N NH_4F, 0.025N HCl extracting solution with colour development by molybdic acid and measured at 660nm on a Cecil Instruments 202 Ultraviolet Spectrophotometer.

Sulfate-S was analyzed by the method used in The Manitoba Provincal Soil Testing Laboratory, in which a 1:20 soil to 0.001M $CaCl_2$ mixture is shaken for 30 min and the mixture filtered through Whatman #42 filter paper. An aliquot from the filtrate was diluted 1 to 41 with distilled water and reacted with $BaCl_2$ at pH 2.5-3.0. Exactly enough methylthymol blue to complex the amount of Ba originally present was added and the pH adjusted to between 12.5 and 13. The amount of methythymol blue not complexed with Ba (or in other words the amount of sulfate) was measured at 460nm on a Technicon AutoAnalyzer II.

Exchangeable Ca^{+2}, Mg^{+2}, and K^{+} were estimated by shaking one part of soil with 20 parts of 1.0N NH_4OAc solution containing 250 ppm Li for one hour and then filtering through

Whatman #1 filter paper. Concentrations of Ca, Mg and K in the filtrate were measured with a Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

Plant available Cu, Mn, Zn and Fe were estimated using Lindsay and Norvell's DTPA method [62] as previously discussed except that 2.0 g of air dry soil was used instead of 10.0 g with 20.0 ml extracting solution. Metal concentrations in the DTPA extracting solution were measured on a Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

3.2.2 Experiment Design

Barley (*Hordeum vulgare* var. Conquest), oats (*Avena sativa* var. Hudson) and wheat (*Triticum aestevum* var. Neepawa) were grown in Experiment 1 until early heading or for 45, 49 and 52 days, respectively, in a Conviron Model PGW36 environmental chamber under a 15-hr photoperiod, a light intensity at plant canopy height of 500-550 microEinsteins / m^2 s (400-700 nm) and day/night temperatures of 21/17^o C. In Experiment 2, flax (*Linum usitatissimum* var. Dufferin) and rapeseed (*Brassica campestris* var. Torch) were grown under the same conditions for 43 days.

The polyethylene pots and all glassware used in the growth chamber experiments were cleaned by first washing with detergent, then rinsing in deionized water, soaking in 1% Na_2H_2EDTA, rerinsing in deionized water, soaking in 1*M* HCl and finally rinsing again in deionized water.

TABLE 2

Treatments used in growth chamber

Treatment	growth chamber experiment #1	growth chamber experiment #2
	ug Cu/g oven dry soil as $CuSO_4$	
#1	0	0
#2	2.9	2.0
#3	5.8	4.0
#4	11.5	8.0
#5	23.0	16.0
#6	46.0	32.0
#7	92.0	64.0
#8	----	128.0
	All treatments ug/g	
N as NH_4NO_3	1820	2435
P as $(NH_4)H_2PO_4$	115	230
K as K_2SO_4	777	1550
S as K_2SO_4	318	636

The fertilizer levels shown in Table 2, with the exception of N were uniformily mixed with the entire soil volume of each pot by spraying the fertilizer in solution form onto the soil spread thinly on a large plastic sheet and then thoroughly mixing. Nitrogen was applied initially in the same manner as other nutrients as NH_4NO_3 and $NH_4H_2PO_4$ at 620 and 1240 ug/g for experiment 1 and 2, respectively. The remaining N was added during watering at 2 to 3-week intervals as dissolved NH_4NO_3. Copper was supplied as $CuSO_4$, P as $NH_4H_2PO_4$, K and S as K_2SO_4 all as reagent grade chemicals.

Each pot received 1800 g of moist organic soil at 228% moisture (oven dry weight basis) or 548.6 g oven dry soil packed to a volume of 4.1 liters or a bulk density of approximately 0.13 g/cm^3. Fifteen barley, oat or wheat seeds per pot were planted 1.5 cm deep and thinned to 10 plants per pot 8 days after seeding. Fifteen to 20 flax and rape seeds per pot were planted 1.5 cm deep and thinned 16 days later to 10 and 5 plants, respectively. The experiments were initiated by wetting to 400% moisture (oven dry weight basis) with deionized water. Thereafter, soil moisture was maintained between 40 and 70% volumetric water content or 300 and 525% moisture on an oven dry weight basis. Treatments for each crop were replicated 3 times in a randomized complete block design.

Plants were harvested just above the soil surface, dipped in deionized water for approximately one minute, and dried in closed paper bags in a forced air oven at 85° C for 40 hours. Upon removal from the oven, the bags were placed in desiccators and cooled before weighing. Total shoot dry matter production was estimated by subtracting from those weights the weight of the paper bags after having been emptied and redried at 85° C for 2 hrs. Dried plant samples were fragmented by hand in the case of flax or ground in a salad processor having stainless steel and plastic parts for all other crops and stored in paper envelopes until analysis.

3.2.3 Plant Analyses

Two g of air dry plant material were digested in an acid mixture consisting of 10.0 ml conc HNO_3 and 5.0 ml 70% $HClO_4$ using a micro-Kjeldahl apparatus. The ash was filtered through Whatman #42 filter paper into 25.0 ml volumetric flasks, and diluted to volume with deionized water. Copper, Mn, Zn and Fe were determined by aspirating solution directly from the volumetric flasks into a Perkin-Elmer 303 Atomic Absorption Spectrophotometer. Calcium, Mg, and K were determined by taking a 1-ml aliquot from a volumetric flask, adding 2.5 ml of a 2500 ppm $LiNO_3$ solution, diluting to 25.0 ml with deionized water and aspirating the diluted solution into a Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

Plant P was determined by the method of Stainton *et al* [110] using a 0.5 ml aliquot from original diluted digest. Plant S was determined by a $BaSO_4$ turbidometric method in which a 1-ml aliquot from the original diluted digest was added to 24.0 ml deionized water and 3.0 ml acid "seed" solution. The acid "seed" solution contained 50 ppm S in 6*N* HCl which enabled formation of sufficient $BaSO_4$ precipitate for the sensitivity of the method. One g $BaCl_2 \cdot 2H_2O$ was then added and the turbidity measured after a reaction time of 5 minutes with a Cecil Instruments 202 Ultraviolet Spectrophotometer at 420 nm. Plant N was determined from a separate sample using a modification of the Kjeldahl method given by Jackson [48] in which the catalyst mixture consisted of 0.3 g $CuSO_4$ plus 10.0 g K_2SO_4 and 1.0 g air dry ground plant tissue was used.

3.3 RESULTS AND DISCUSSION

3.3.1 Soil Characteristics

Chemical and physical properties of the soils used in experiments 1 and 2 are listed in Table 3. Bulk density of the soil in the field was 0.13 g/cm^3, about one tenth as large as the bulk density of a typical mineral soil. It should be noted that soil in the pots was also packed to a bulk density of 0.13 g/cm^3. Comparisons between total potentially available macronutrients and maximum total macronutrient amounts taken up into plant shoots (Table 4)

TABLE 3

Soil characteristics and available nutrients for growth chamber experiments

	growth chamber experiment #1	growth chamber experiment #2
Soil	Terric Mesosol	
Bulk density	0.13 g/cm^3	
Weight of soil per pot	548.6 g	
Pore space at "field capacity"	0.10 g/cm^3	
Volumetric water at "field capacity"	0.76 ml/cm^3	
pH	6.0	6.1
Conductivity (mmho)	1.0	1.1
NO_3-N (ug/g)	361	307
PO_4-P (ug/g)	24.2	19.2
SO_4-S (ug/g)	677	1025
Ca (exchangeable mg/g)	0.93	0.92
Mg (exchangeable mg/g)	0.34	0.36
K (exchangeable ug/g)	286	271
Cu (DTPA extractable ug/g)	0.6	0.8
Mn (DTPA extractable ug/g)	7.5	7.5
Zn (DTPA extractable ug/g)	5.6	5.6
Fe (DTPA extractable ug/g)	184	185

indicate that the soil was deficient in N, P, K, and perhaps Ca and Mg but was capable of supplying more than enough S.

TABLE 4

Comparison between total potentially available nutrient and the maximum nutrient uptake in each experiment in the growth chamber

Nutrient	Experiment number	Available Nutrient (mg/pot)	Fertilizer added (mg/pot)	Maximum uptake (mg/pot)	Crop
N	1	198	998	695	barley
N	2	168	1336	832	rapeseed
P	1	13	63	51.8	barley
P	2	11	126	84.2	flax
K	1	157	426	400	oats
K	2	149	850	480	rapeseed
S	1	371	174	130	oats
S	2	562	349	170	rapeseed
Ca	1	510	---	160	oats
Ca	2	505	---	670	rapeseed
Mg	1	187	---	220	oats
Mg	2	197	---	340	rapeseed
Zn	1 and 2	3.1	---	0.63	rapeseed
Mn	1 and 2	4.1	---	5.8	flax
Fe	1 and 2	102	---	1.34	flax

However, with the possible exceptions of Ca and Mg, supplemental nutrients more than filled the voids. Calcium and Mg may have been deficient and there may not have been sufficient P and K to satisfy uptake into roots. But, it will be seen later that all plants recieving Cu were very healthy suggesting that no serious deficiencies in nutrients other than Cu occurred. The DTPA extractable soil micronutrient levels can not be assessed at this time, since the bulk density of this soil was very low and since the extracting solution-soil ratio was different than that used by Lindsay and Norvell [62].

3.3.2 Visual Cu Deficiency Symptoms

Copper deficiency symptoms occurred in all 5 crops when no Cu was added. Deficiency symptoms also occurred in the 2.9 and 5.8 ug Cu/g treatments for barley, oats and wheat as well as in the 11.5 ug Cu/g treatment for wheat. In the cereal crops, the leaf blades bent down at approximately right angles near their tips and became grayish along the leaf margins from the bent areas to the leaf tips. Later, those regions of the leaf blades became necrotic beginning along the leaf margins. The symptoms did not vary appreciably among the various cereal crops although the affected areas of the oat leaf blades tended to be more whitish than grayish.

Deficiency symptoms in flax receiving no Cu were evident virtually from the time of emergence until harvest. The first symptom was interveinal chlorosis and a few days after emergence stunting was noticeable in the 0.0 Cu treatment. In addition, leaf blades on the chlorotic plants were at

Figure 1: Flax plant showing necrosis of lower leaves due to Cu deficiency

Figure 2: Cu deficient rapeseed plant

Figure 3: Enlarged leaf of Cu deficient rapeseed plant

Figure 4: Comparison between control and 2.0 ug Cu treatments in rapeseed

angles greater than 90^{o} to the stems, compared to non-chlorotic leaf blades which were about 90^{o} to the stem. Treatments 2 to 6 eventually developed some degree of interveinal chlorosis. The lower leaves on the older stalks of treatments 1 to 3 eventually became necrotic (Figure 1). The appearance of Cu deficiency symptoms in treatments 1 to 6 suggest that the flax was very susceptible to Cu deficiency.

Rapeseed treatments 1 and 2 exhibited interveinal chlorosis shortly after emergence although only rapeseed receiving no Cu retained any visual deficiency symptoms. However, flowering was delayed slightly in treatments 2, 3 and 4. Copper deficiency symptoms in rapeseed included larger than normal leaves and compressed flower infloresence (Figure 2, 3 and 4). Addition of 2.0 ug Cu/g soil was sufficient to alleviate visual deficiency symptoms in rapeseed (Figure 4). Therefore rapeseed appeared to be very tolerant of Cu stress.

3.3.3 Dry Matter Yields and Plant Cu Concentrations

Yield and plant nutrient concentrations are shown in Tables 5 through 34. Within each vertical column numbers followed by the same letter are not significantly different at the 5% level according to Duncans multiple range test [30].

3.3.3.1 Barley

Barley shoot dry matter yield (Table 5) increased significantly with the addition of up to 5.8 ug Cu/g soil. However, addition of more than 5.8 ug Cu/g soil did not further increase yields. This was consistent with appearance of visual deficiency symptoms in only treatments 1 and 2. In contrast to dry matter yield, both Cu concentration and Cu uptake increased with every increment of supplemental Cu.

Dry matter yield of barley shoots is plotted against the corresponding shoot Cu concentration for each pot in Figure 5. No further yield increases occurred when barley shoots contained more than 3.7 ug Cu/g plant material suggesting that Cu sufficiency occurred at the higher rates of Cu addition. Thus, the curve could be used to elucidate Cu nutritional status of barley.

Shoot Cu concentrations in excess of 3.7 ug Cu/g were considered as sufficient for normal growth. The shoot Cu concentration was 2.3 ug Cu/g when dry matter yield was 15% lower than maximum. Copper concentrations below 2.3 ug Cu/g were considered as deficient whereas concentrations between 2.3 and 3.7 ug Cu/g plant material were considered as low.

Akinyede [2] found the Cu critical level for this same variety of barley to be 5.2 ug Cu/g plant material which is considerably higher than the levels in the current study. Reasons for the discrepancy are not at all clear.

TABLE 5

Effect of $CuSO_4$ rate upon dry matter yield, Cu concentration and Cu total uptake of barley shoots

ug Cu/g oven dry soil	Dry matter yield (g/pot)	Cu conc in shoots (ug/g)	Total Cu uptake into shoots (ug/pot)
0.0	13.7 c	1.4 g	20 g
2.9	22.4 b	2.0 f	45 f
5.8	26.0 a	2.9 e	86 e
11.5	26.3 a	4.1 d	110 d
23.0	27.4 a	4.7 c	130 c
46.0	27.0 a	5.5 b	150 b
92.0	27.0 a	6.5 a	170 a

TABLE 6

Effect of $CuSO_4$ rate upon dry matter yield, Cu concentration and Cu total uptake of oats shoots

ug Cu/g oven dry soil	Dry matter yield (g/pot)	Cu conc in shoots (ug/g)	Total Cu uptake into shoots (ug/pot)
0.0	11.0 c	1.2 e	14 f
2.9	27.3 b	1.3 e	36 e
5.8	28.8 b	1.5 e	43 e
11.5	32.8 a	1.9 d	63 d
23.0	31.7 a	2.6 c	84 c
46.0	34.5 a	3.1 b	110 b
92.0	34.1 a	4.2 a	140 a

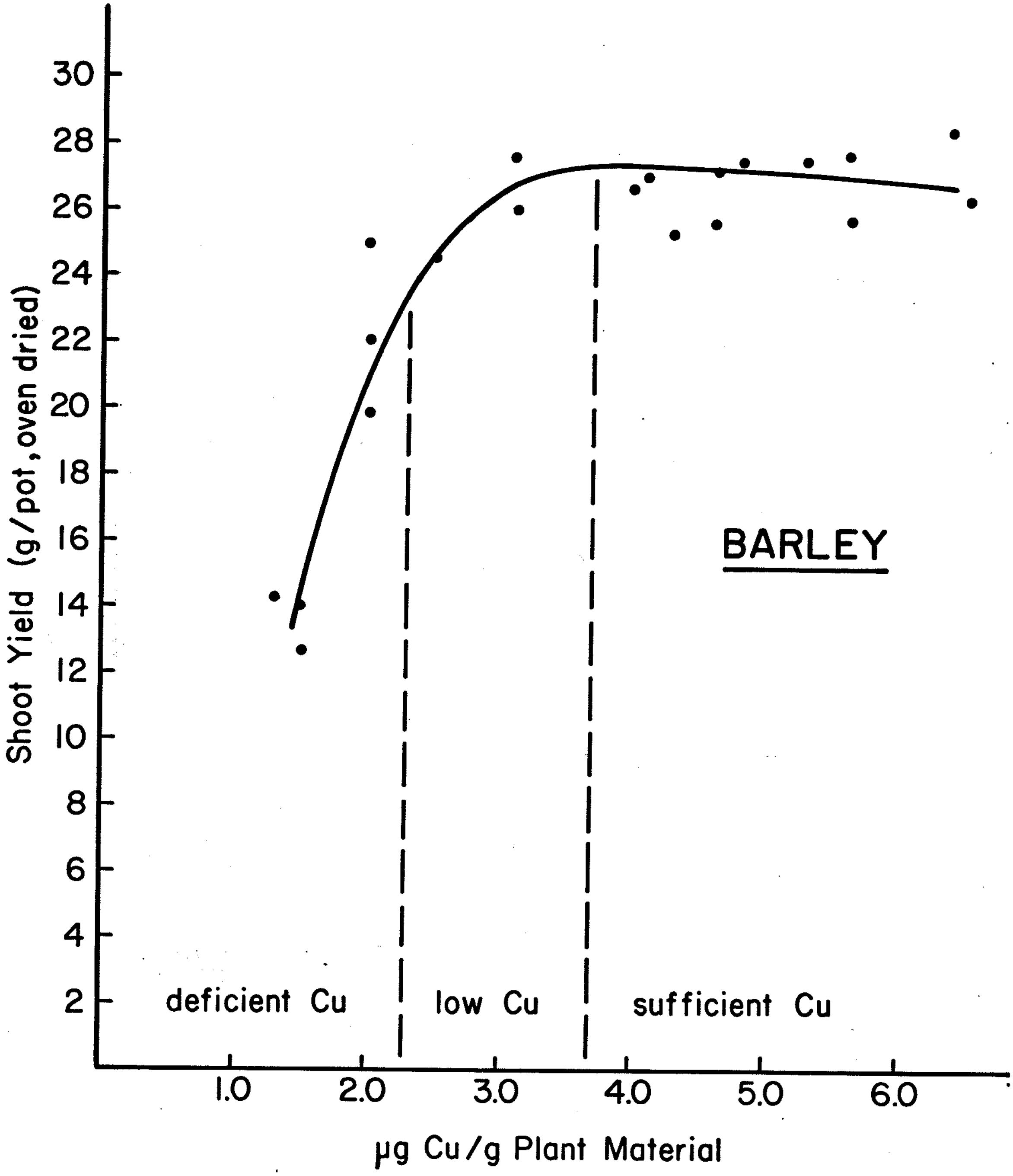


Figure 5: Effect of shoot Cu concentration on barley yield[1]

1. Each curve in this study was obtained by regression analysis and the local maxima of the trinomial function was designated as the maximum dry matter yield of each crop.

However, it is entirely possible that only the very upper portion of the Cu response curve was present in Akinyede's study which would over estimate the Cu critical level. The lack of Cu deficiency symptoms when no Cu was applied would support the conclusion that only the upper portion of the response curve was present.

3.3.3.2 Oats

Oat shoot dry matter yield (Table 6) increased substantially with the addition of 2.9 ug Cu/g soil. Although addition of 5.8 ug Cu/g soil did not increase yield above that of 2.9 ug Cu/g soil, a further significant yield increase was obtained with the addition of 11.5 ug Cu/g soil. No further yield increase occurred above 11.5 ug Cu/g soil. Visual symptoms of deficiency were alleviated with the addition of 5.8 ug Cu/g soil although yield increased up to 11.5 ug Cu/g.

Plant Cu concentration did not increase until 11.5 ug Cu/g soil were added. However, each increment of supplemental Cu above 11.5 ug Cu increased shoot Cu concentrations. The lack of increase in plant Cu concentration when 2.9 and 5.8 ug Cu/g soil were added likely resulted from dilution since dry matter yield increased greatly at lower levels of Cu addition. Total Cu uptake into oat shoots increased with each increment of supplemental Cu with the exception of that treatment receiving 5.8 ug Cu/g soil.

The graph of dry matter yield versus shoot Cu concentration (Figure 6) suggests that tissue Cu concentrations greater than 2.5 ug Cu/g plant material were sufficient for normal growth. A shoot Cu concentration of 1.7 ug Cu/g was considered to be the upper limit of deficiency. Copper concentrations between these two limits were considered low. These values are quite consistent with literature values although the sufficiency level in this study was slightly lower than reported by Gupta and MacLeod [43].

3.3.3.3 Wheat

Dry matter yield of wheat shoots (Table 7) was considerably lower than barley and oat yields when no Cu was added suggesting that wheat was more susceptible to Cu deficiency than barley or oats. As might be expected, the first increment of supplemental Cu resulted in a very large increase in wheat shoot yield. Although wheat shoot yield did not increase with every increment of supplemental Cu, the highest Cu level, 92 ug Cu/g soil, resulted in a yield which was significantly higher than that for 11.5 ug Cu/g soil. Therefore it was possible that the Cu sufficiency level was not reached. Visual deficiency symptoms were eliminated however with the 11.5 ug Cu/g soil treatment. Similar to the results for oats, tissue Cu concentration did not change significantly until 11.5 ug Cu/g soil was added. Addition of 23.0 and 46.0 ug Cu/g soil resulted in further increases in plant Cu concentrations, although there was no increase

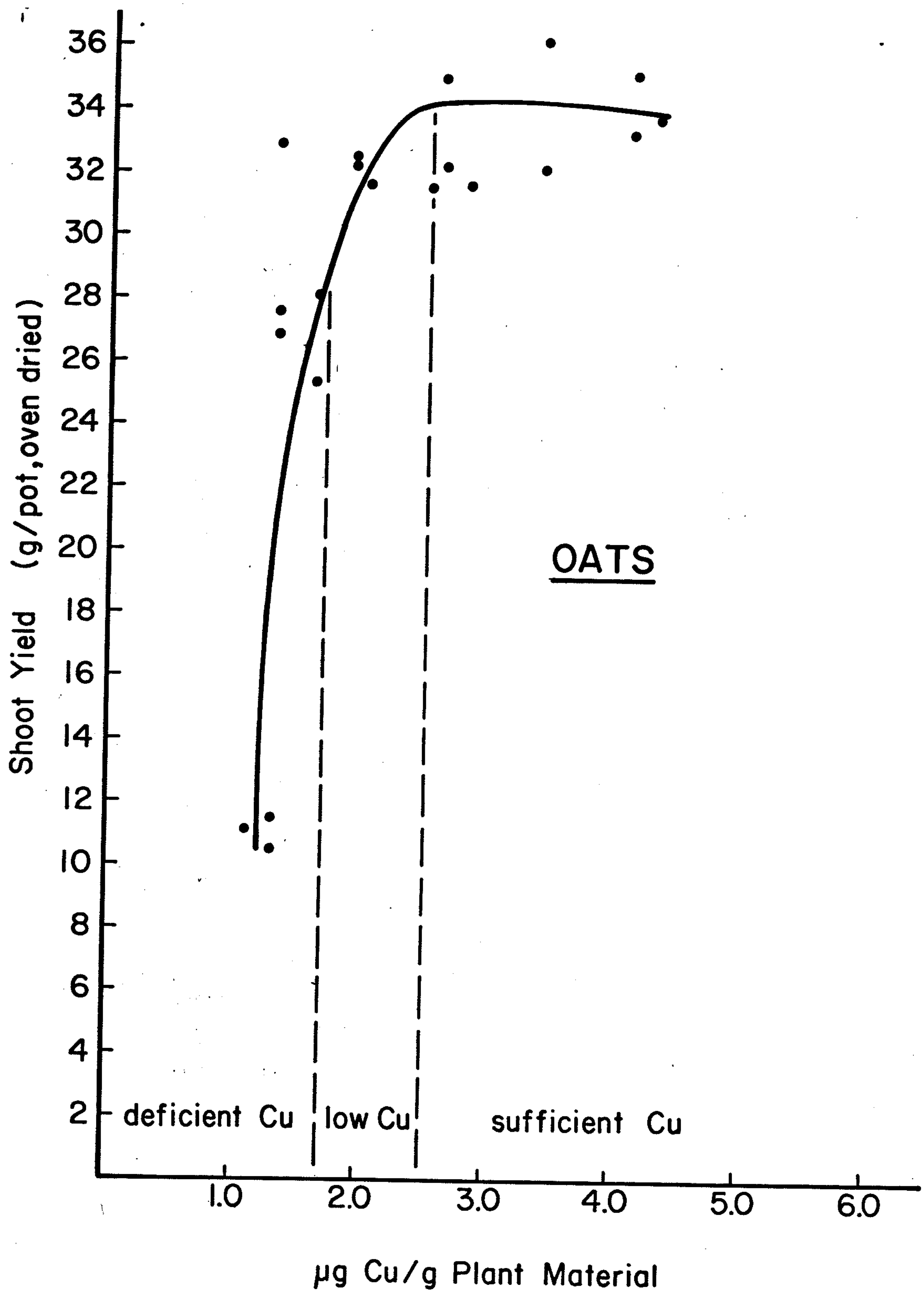


Figure 6: Effect of shoot Cu concentration on oat yield

TABLE 7

Effect of $CuSO_4$ rate upon dry matter yield, Cu concentration and Cu total uptake of wheat shoots

ug Cu/g oven dry soil	Dry matter yield (g/pot)	Cu conc in shoots (ug/g)	Total Cu uptake into shoots (ug/pot)
0.0	1.8 e	1.7 d	3.0 f
2.9	14.9 d	1.6 d	23 e
5.8	21.8 c	1.8 d	40 d
11.5	28.3 b	2.6 c	74 c
23.0	29.5 ab	3.4 b	100 b
46.0	31.6 ab	4.0 a	130 a
92.0	33.8 a	4.2 a	140 a

TABLE 8

Effect of $CuSO_4$ rate upon dry matter yield, Cu concentration and Cu total uptake of flax shoots

ug Cu/g oven dry soil	Dry matter yield (g/pot)	Cu conc in shoots (ug/g)	Total Cu uptake into shoots (ug/pot)
0.0	0.9 e	1.3 ef	1.2 f
2.0	2.1 de	1.1 f	2.2 f
4.0	5.0 d	1.0 f	5.2 f
8.0	9.6 c	1.5 e	14 d
16.0	13.3 b	1.9 d	25 d
32.0	16.8 a	2.5 c	42 c
64.0	19.5 a	3.3 b	64 b
128.0	18.7 a	4.6 a	86 a

through the addition of 92.0 ug Cu/g soil over that obtained with 46.0 ug Cu/g soil. Total Cu uptake increased significantly with each increment of supplemental Cu up to the 46.0 ug Cu/g soil. The uptake of Cu when 92.0 ug Cu/g soil were added was not significantly greater than that obtained when 46.0 ug Cu/g soil were added.

Dry matter yield of wheat shoots is plotted against shoot Cu concentration in Figure 7. Unlike the four other crops dry matter yield continued to increase with increasing plant Cu concentration. The absences of visual deficiency symptoms with the 11.5 ug Cu/g soil treatment as well as the high yields that were obtained, approximately double those of Akinyede [2], led to the assumption that no further yield increase would be expected at Cu levels above the 4.9 ug Cu/g.

This assumption placed the lower limit of sufficiency at 4.9 ug Cu/g. The upper limit of deficiency or the plant Cu concentration corresponding to a yield 15% below the maximum yield would be 3.0 ug Cu/g. Wheat shoot Cu concentrations between 3.0 and 4.9 ug Cu/g were considered as low. These nutritional levels are high compared to Gupta and MacLeod's [43] optimum level of 3.2 - 3.3 ug Cu/g plant material but are in excellent agreement with those of Melsted et al [70] who reported a critical level from field samples of 5 ug Cu/g.

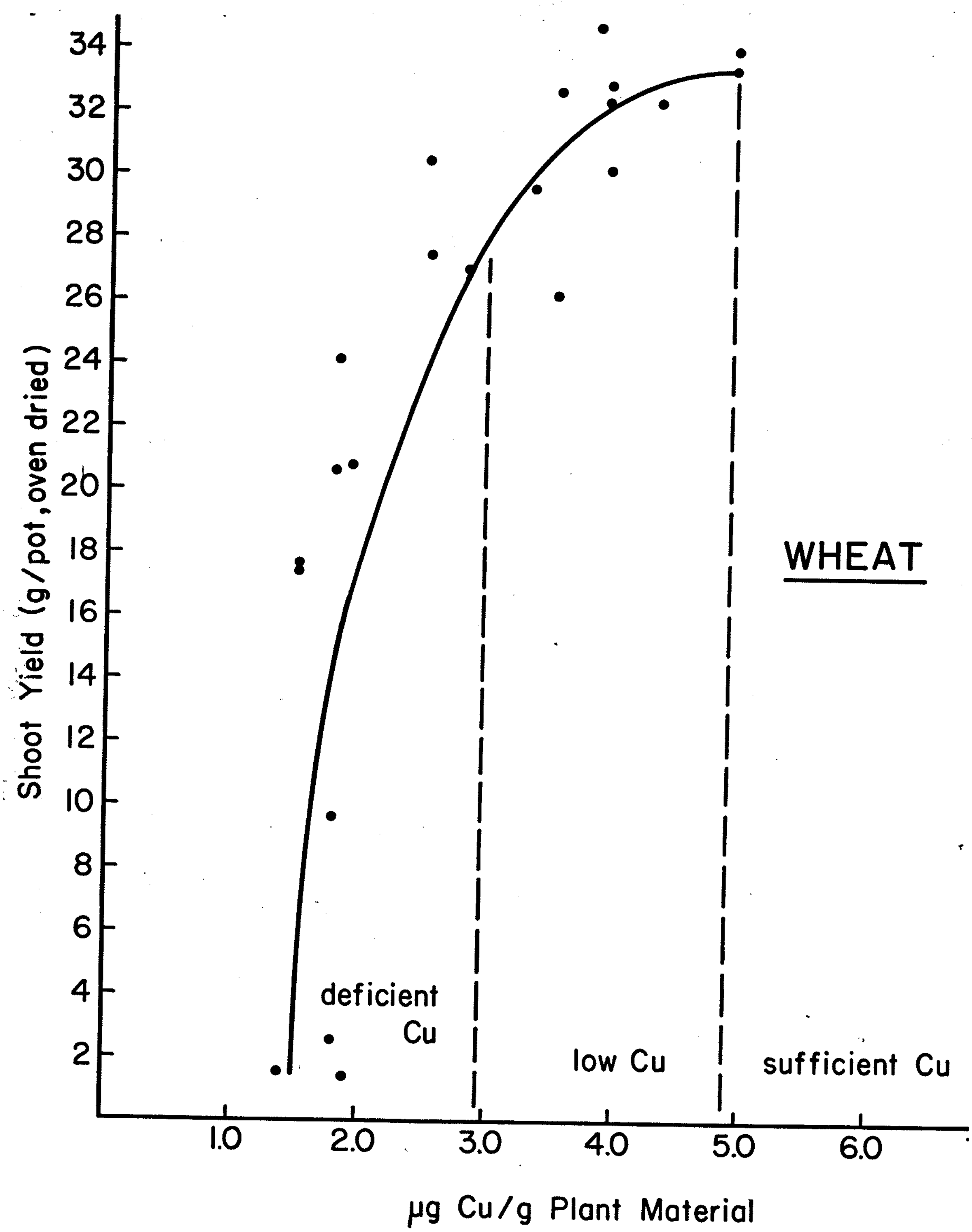


Figure 7: Effect of shoot Cu concentration on wheat yield

3.3.3.4 Flax

Dry matter yield of flax shoots (Table 8) increased from 0.9 g/pot for the check treatment to a maximum of 19.5 g/pot for the 64.0 ug Cu/g soil treatment. Yields of flax increased more as a function of the level of supplemental Cu than for any of the other crops in the study. The dry matter yields were not changed by addition of more than 32 ug Cu/g soil even though some interveinal chlorosis was present in the 32 ug Cu/g soil treatment.

Flax shoot Cu concentration and uptake were not significantly increased until 8 ug Cu/g soil were added. However, each level of supplemental Cu higher than 8 ug Cu/g soil resulted in increases in flax shoot concentration and uptake of Cu. This indicates that flax was a poor accumulator of Cu.

Flax shoot dry matter yield increased as Cu concentration increased up to a concentration of 3.5 ug Cu/g plant material (Figure 8). Copper concentrations higher than 3.5 ug Cu/g did not result in higher dry matter yields. The response curve could therefore be used to elucidate the Cu nutritional status in flax. Copper concentrations in excess of 3.5 ug Cu/g were considered sufficient for normal growth. The upper limit of deficiency was 2.4 ug Cu/g. Concentrations between 2.4 and 3.5 ug Cu/g were considered as low.

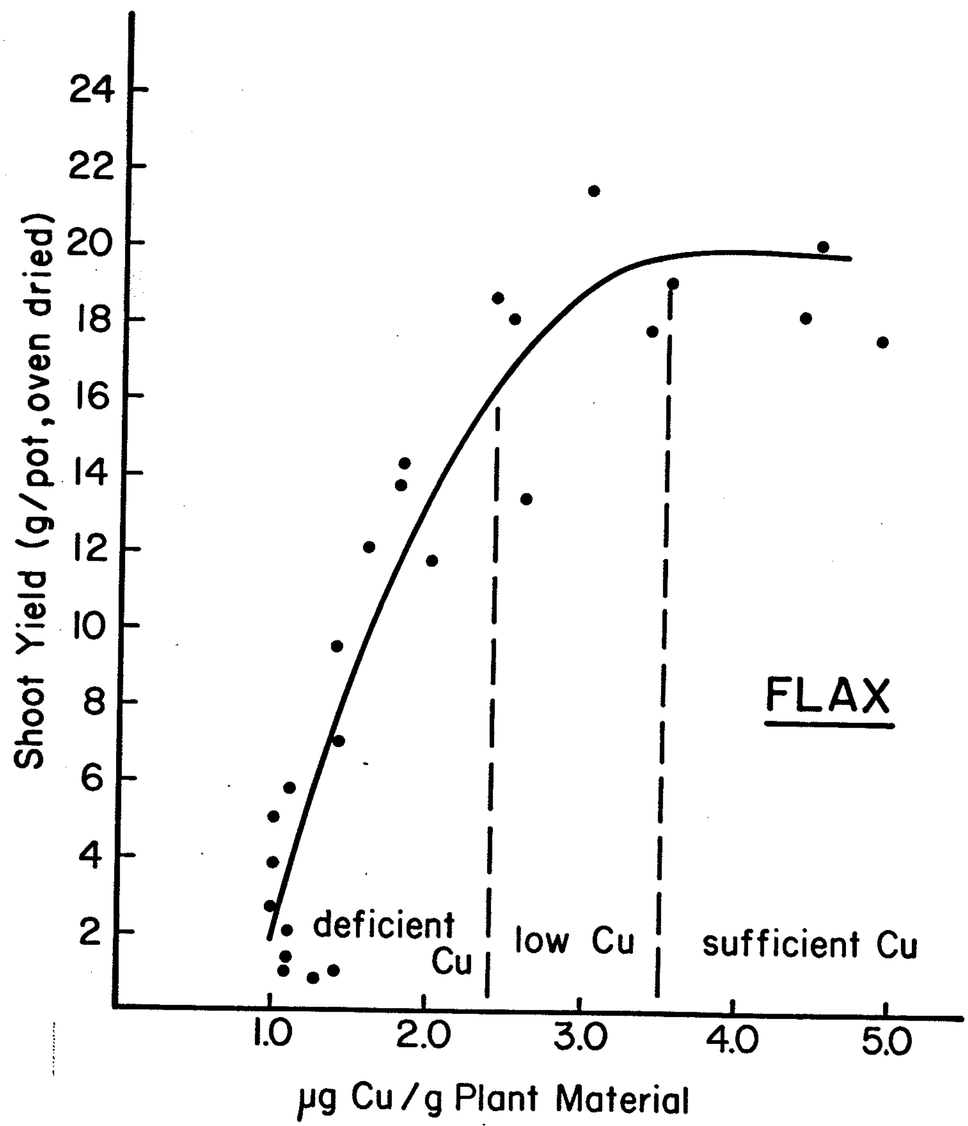


Figure 8: Effect of shoot Cu concentration on flax yield

3.3.3.5 Rapeseed

Dry matter yield of rapeseed shoots (Table 9) was increased by the addition of 2 ug Cu/g soil. However, addition of more than 2 ug Cu/g soil did not influence rapeseed growth. Response in dry matter yield to Cu agreed well with visual appearance of the plants. Only plants receiving no supplemental Cu exhibited deficiency symptoms. Copper concentration in rapeseed shoots increased as rate of supplemental Cu increased in the absence of dry matter yield increases. Total Cu uptake into rapeseed shoots behaved similarily to Cu concentration.

Dry matter yield of rapeseed shoots is plotted against shoot Cu concentration in Figure 9. The low dry matter yield of rapeseed shoots containing approximately 1.0 ug Cu/g plant material suggests that this rapeseed was deficient in Cu. The rapid increase followed by leveling off in rapeseed shoot yield with increasing shoot Cu concentration indicate that this curve can be used to elucidate nutrition ranges for Cu in rapeseed. The response curve suggests that a Cu concentration in excess of 2.7 ug Cu/g plant material was sufficient for normal growth of rapeseed. The upper limit of deficiency was 1.7 ug Cu/g plant material. Copper concentrations between 1.7 and 2.7 ug Cu/g plant material were considered low.

TABLE 9

Effect of $CuSO_4$ rate upon dry matter yield, Cu concentration and Cu total uptake of rapeseed shoots

ug Cu/g oven dry soil	Dry matter yield (g/pot)	Cu conc in shoots (ug/g)	Total Cu uptake into shoots (ug/pot)
0.0	12.3 b	1.0 e	13 e
2.0	24.1 a	1.6 d	40 d
4.0	27.1 a	1.9 d	53 cd
8.0	25.5 a	2.3 cd	58 cd
16.0	23.6 a	2.3 cd	55 cd
32.0	26.2 a	3.0 bc	78 bc
64.0	25.2 a	3.6 b	91 b
128.0	28.0 a	4.5 a	130 a

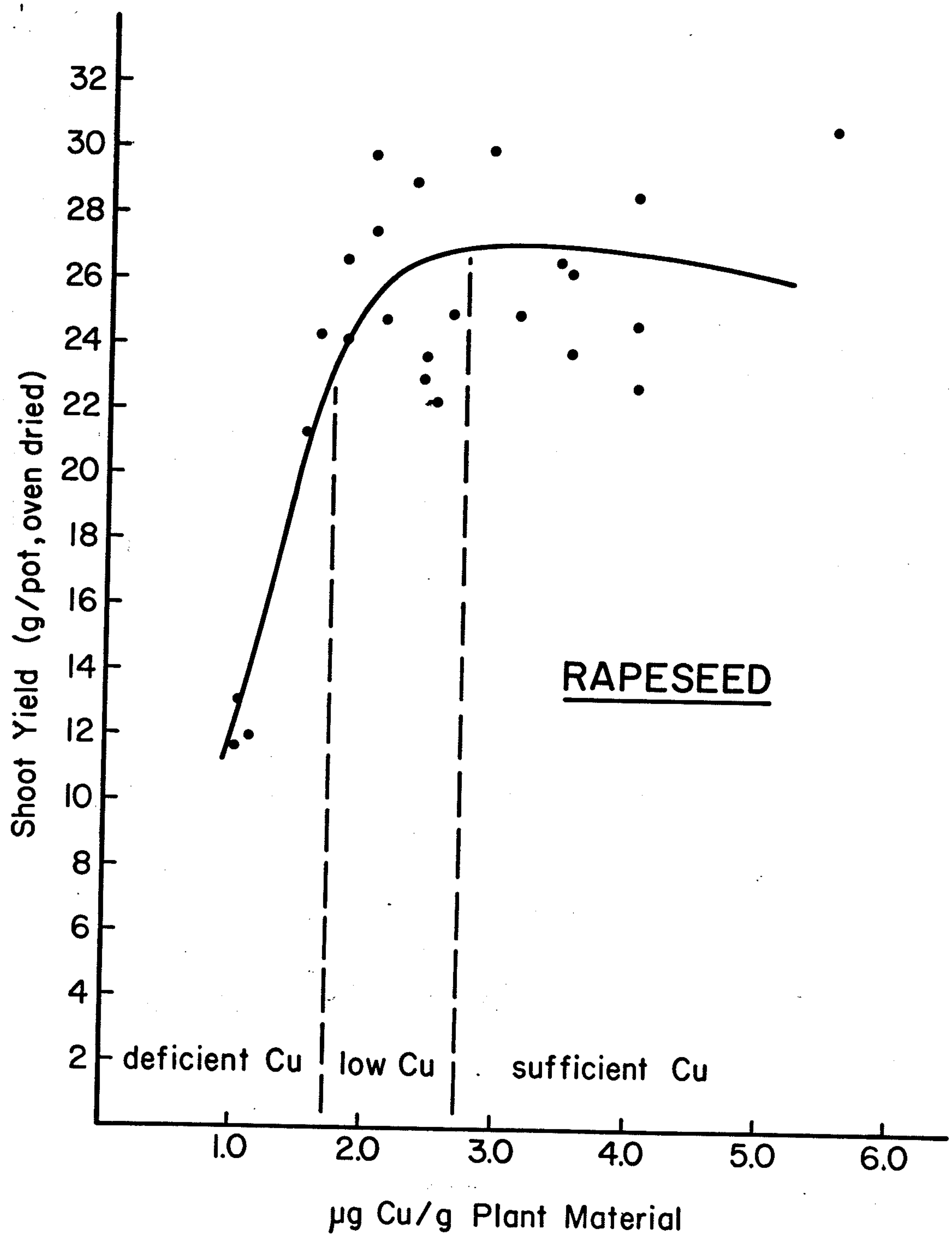


Figure 9: Effect of shoot Cu concentration on rapeseed yield

Rapeseed appeared to be slightly less efficient than barley in taking up Cu, slightly more efficient than oats and definitely more efficient than wheat or flax, on the basis of total Cu uptake for the first two increments of supplemental Cu. The first increment of supplemental Cu increased shoot Cu concentrations in only barley and rapeseed, indicating that barley and rapeseed were good accumulators of Cu. However, the critical Cu concentrations in rapeseed shoots were lower than those in barley and about the same as those in oats. Consequently, rapeseed appeared to be the most efficient in Cu nutrition.

3.3.4 Relative Tolerance to Copper Stress

The 5 crops grown in this study all responded to the addition of fertilizer Cu. A statement can therefore be made as to the tolerance of the crops to Cu stress. Unlike all other crops Cu deficiency symptoms in rapeseed were eliminated through the addition of only 2 ug Cu/g soil, suggesting that rapeseed was most tolerant to Cu stress. In addition, the graph of rapeseed shoot dry matter yield versus shoot Cu concentration suggests that rapeseed was most resistant to Cu deficiency since only five Cu concentrations were in the deficiency range (Figure 9). This statement is strengthened when it is considered that dry matter yields associated with two of those five deficient Cu concentrations were not significantly different from dry matter yields associated with plant Cu concentrations in the low or sufficient range. That result is not surprising since it was concluded in the previous section that rapeseed was the most efficient in Cu nutrition.

Barley was only slightly less tolerant of Cu stress than rapeseed. Only those treatments receiving 5.8 ug Cu/g soil or less exhibited Cu deficiency symptoms. In addition, it can be seen in Figure 5 that Cu concentrations were in the deficiency range in only six replicates.

Oats behaved much the same as barley in that only oats receiving up to 11.5 ug Cu/g soil exhibited Cu deficiency symptoms. However, it was concluded that oats were slightly more susceptible to Cu efficiency since Cu concentrations in eight replicates were in the deficiency range (Figure 6).

Wheat was the most susceptible to Cu deficiency of the cereal crops. Although visual deficiency symptoms occurred only in those treatments receiving up to 11.5 ug Cu/g soil the symptoms were very severe in the check treatment where dry matter yield was only 1.8 g/pot. Maximum yield was not attained until 92 ug Cu/g soil were added. Also, Cu concentrations in twelve replicates as plotted in Figure 7 were in the Cu deficiency range.

Flax was the most Cu inefficient crop grown. Visual Cu deficiency symptoms occurred in flax receiving up to 32 ug

Cu/g soil. Addition of low levels of Cu did not result in large yield increases as in wheat. Shoot Cu concentrations in sixteen of the replicates were in the Cu deficient range.

It can be concluded that for the varieties grown and under the conditions in the present study, the order of tolerance to Cu stress was rapeseed > barley > oats > wheat > flax. Other conditions and varieties might have resulted in a different order of tolerance.

3.3.5 Effect of Cu Fertilization on Plant Uptake of Other Nutrients

3.3.5.1 Nitrogen

Nitrogen concentrations in the shoots of all crops (Tables 10, 11, 12, 13, and 14) were lower when Cu was added. Nitrogen analysis was not possible for the check treatment of wheat and flax as well as the 2.0 ug Cu/g treatment for flax, due to insufficient dry matter yield. Nitrogen concentrations in barley, oats and wheat decreased for the first two treatments which could be analyzed. However, no further changes occurred at higher rates of Cu. Nitrogen concentration in rapeseed decreased as a result of the first increment of Cu but was was not influenced by further increments of Cu. Copper fertilization did not influence N concentrations in flax for those treatments which could be analyzed. Nitrogen uptake was not affected by Cu deficiency in barley, this being a result of high N concentration in the check treatment in conjunction with the reduced yield. Nitrogen uptake in all other crops increased as a result of dry matter yield increases, suggesting that the decrease in N concentration with increasing Cu resulted from dilution.

Ward et al [116] indicated a N sufficiency level in spring cereals at head emergence between 20.0 and 30.0 mg N/g plant material. The N levels in this study indicate that adequate amounts were present in all five crops.

3.3.5.2 Phosphorus

Phosphorus concentrations in the shoots of all crops (Tables 10, 11, 12, 13, and 14) were lower when Cu was added. But, there were usually no differences in plant P concentrations among the various treatments which included supplemental Cu. The lower plant P concentrations when Cu was applied likely resulted from dilution. As might be expected, total P uptake into the shoots usually increased with increasing Cu, because of increases in dry matter yields. With the exception of the check treatment in wheat, P levels in the cereal crops were similiar. The higher P concentrations in wheat receiving no Cu likely resulted from the very low dry matter yield in that treatment. Phosphorus concentrations in rapeseed were generally higher than in the cereals. However, the highest P concentrations occurred in flax.

TABLE 10

N and P uptake into barley shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	N Conc. in shoots (mg/g)	Total N Uptake into shoots (mg/pot)	P Conc. in shoots (mg/g)	Total P Uptake into shoots (mg/pot)
0.0	45.2 a	617 a	3.32 a	45.2 bc
2.9	29.2 b	648 a	1.76 bc	39.1 d
5.8	25.4 c	662 a	1.68 c	43.6 c
11.5	26.4 c	695 a	1.71 bc	45.0 ab
23.0	24.2 c	664 a	1.79 bc	49.0 ab
46.0	25.5 c	686 a	1.91 b	51.5 a
92.0	25.0 c	675 a	1.92 b	51.8 a

TABLE 11

N and P uptake into oats shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	N Conc. in shoots (mg/g)	Total N Uptake into shoots (mg/pot)	P Conc. in shoots (mg/g)	Total P Uptake into shoots (mg/pot)
0.0	40.5 a	448 b	3.24 a	35.8 c
2.9	23.6 b	643 a	1.43 b	39.1 bc
5.8	21.8 bc	621 a	1.40 b	39.7 bc
11.5	19.4 c	635 a	1.19 b	39.1 bc
23.0	20.4 bc	648 a	1.31 b	41.5 ab
46.0	18.7 c	642 a	1.23 b	42.2 ab
92.0	19.6 c	666 a	1.31 b	44.7 a

TABLE 12

N and P uptake into wheat shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	N Conc. in shoots (mg/g)	Total N Uptake into shoots (mg/pot)	P Conc. in shoots (mg/g)	Total P Uptake into shoots (mg/pot)
0.0	---[1]	---	6.61 a	11.7 d
2.9	34.6 a	503 b	2.46 b	34.3 c
5.8	28.5 b	619 a	1.77 c	38.3 bc
11.5	22.9 c	646 a	1.49 c	42.2 ab
23.0	23.4 c	688 a	1.54 c	45.3 a
46.0	21.9 c	690 a	1.37 c	43.3 ab
92.0	20.1 c	680 a	1.31 c	44.4 a

TABLE 13

N and P uptake into flax shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	N Conc. in shoots (mg/g)	Total N Uptake into shoots (mg/pot)	P Conc. in shoots (mg/g)	Total P Uptake into shoots (mg/pot)
0.0	---	---	12.8 a	12.0 d
2.0	---	---	8.46 b	17.2 d
4.0	49.0 a	248 c	6.45 c	31.8 c
8.0	43.2 a	414 b	6.30 cd	59.9 b
16.0	39.6 a	522 b	5.70 cde	75.3 a
32.0	40.4 a	679 a	4.65 de	76.6 a
64.0	38.6 a	753 a	4.36 e	84.2 a
128.0	39.3 a	733 a	4.26 e	79.4 a

1. Where no N concentrations are reported there was insufficient sample for analysis.

TABLE 14

N and P uptake into rapeseed shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	N Conc. in shoots (mg/g)	Total N Uptake into shoots (mg/pot)	P Conc. in shoots (mg/g)	Total P Uptake into shoots (mg/pot)
0.0	50.9 a	625 c	4.86 a	59.3 a
2.0	34.0 b	813 ab	2.42 b	57.7 a
4.0	30.9 b	831 a	2.19 b	59.0 a
8.0	32.8 b	832 a	2.30 b	58.5 a
16.0	32.3 b	758 ab	2.16 b	50.5 a
32.0	28.5 b	739 b	2.14 b	55.8 a
64.0	31.3 b	788 ab	2.17 b	54.6 a
128.0	29.0 b	804 ab	1.98 b	54.9 a

Phosphorus levels in this study were lower than would normally be expected. Ward et al [116] indicated P deficiency in barley, oats and wheat can be expected if the concentration P at the stage when the head emerges from the boot is less than 1.5 mg P/g plant material. Racz et al [92] in a field study with various harvest dates reported P concentrations in flax and rapeseed of 1.6 and 2.9 mg P/g, respectively, at 49 days after seeding for a treatment in which P had been added at 22 kg/ha. The lowest P concentration in oats of 1.19 mg P/g is considerably lower than the deficiency level of Ward et al. Phosphorous concentrations in rapeseed were somewhat lower than those reported by Racz et al [92]. However, no P deficiency symptoms were apparent in any crops. In fact, plants receiving adequate Cu were lush and green and yielded well in comparison to yields in other studies conducted under similar conditions. It was assumed, therefore, that low P did not significantly influence Cu nutrition.

3.3.5.3 Potassium

Potassium concentrations in barley and rapeseed shoots (Tables 15 and 19) were not influenced by Cu fertilization. Potassium concentrations in oat, wheat and flax shoots decreased with the first increment of supplemental Cu, but usually did not vary among treatments which included supplemental Cu (Tables 16, 17 and 18).

Ward *et al* [116] suggested that barley, oats and wheat were K deficient if the tissue concentration at the head emergence stage was less than 12.5 mg K/g plant material. Potassium levels in this study were lower than this level for all barley and oats which received supplemental Cu, and for wheat which received more than 2.9 ug Cu/g soil. Potassium concentrations in flax and rapeseed shoots were generally higher than in the cereals. Potassium critical levels for flax and rapeseed could not be found in the literature. However, the lack of K deficiency symptoms and the high dry matter yields in comparison to yields under similar conditions in other experiments indicated that low K did not have a significant effect on growth of any crop in this study.

Total K uptake often increased with increasing supplemental Cu (Tables 15, 16, 17, 18 and 19). These increases probably resulted from increasing dry matter production.

3.3.5.4 Iron

Shoot concentrations of Fe in barley, oats and wheat decreased for the first two or three increments of supplemental Cu (Tables 20, 21 and 22). Iron concentration in flax shoots was not influenced by the first few increments of Cu but was increased with the addition of 8 ug Cu/g soil (Table 23). Addition of more than 8 ug Cu/g soil did not influence Fe concentration in flax shoots. It is interesting to note that the Fe concentration in flax shoots

TABLE 15

K uptake into barley shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	K Conc. in shoots (mg/g)	Total K Uptake by shoots (mg/pot)
0.0	12 a	170 b
2.9	11 a	250 a
5.8	11 a	300 a
11.5	8.5 a	230 ab
23.0	11 a	300 a
46.0	9.1 a	250 a
92.0	11 a	290 a

TABLE 16

K uptake into oats shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	K Conc. in shoots (mg/g)	Total K Uptake by shoots (mg/pot)
0.0	15 a	170 d
2.9	8.8 c	240 cd
5.8	12 ab	340 ab
11.5	12 ab	400 a
23.0	11 bc	350 ab
46.0	8.0 c	280 bc
92.0	11 bc	380 a

TABLE 17

K uptake into wheat shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	K Conc. in shoots (mg/g)	Total K Uptake by shoots (mg/pot)
0.0	46 a	82 b
2.9	23 b	320 a
5.8	12 bc	250 a
11.5	10 bc	290 a
23.0	12 bc	350 a
46.0	7.6 c	240 a
92.0	9.2 c	310 a

TABLE 18

K uptake into flax shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	K Conc. in shoots (mg/g)	Total K Uptake by shoots (mg/pot)
0.0	31 a	29 e
2.0	18 bc	38 e
4.0	21 b	100 d
8.0	17 bc	160 c
16.0	17 bc	230 b
32.0	17 bc	280 a
64.0	14 c	270 ab
128.0	16 c	290 a

TABLE 19

K uptake into rapeseed shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	K Conc. in shoots (mg/g)	Total K Uptake by shoots (mg/pot)
0.0	11 a	140 c
2.0	11 a	280 bc
4.0	14 a	380 ab
8.0	14 a	350 ab
16.0	13 a	300 b
32.0	14 a	360 ab
64.0	15 a	360 ab
128.0	17 a	480 a

increased at the same time as the Cu concentration in flax shoots increased from 1.0 to 1.5 ug Cu/g. Iron concentration in rapeseed shoots was not influenced by Cu fertilization (Table 24). Melsted <u>et al</u> [70] listed the Fe critical level for wheat at boot stage as 25 mg Fe/g plant material. All crops in the present study had Fe concentrations above this level. Iron critical levels for flax and rapeseed could not be found in the literature. However, it is unlikely that Fe was deficient in any crop since no Fe deficiency symptoms occurred and yields were high.

Uptake of Fe by barley (Table 20) was not influenced by addition of Cu. The first increment of supplemental Cu increased Fe uptake into oat and rapeseed shoots (Tables 21 and 24), although further increments of Cu had little influence on Fe uptake into those crops. Iron uptake into wheat and flax shoots generally increased as rate of Cu fertilization increased (Tables 22 and 23). Increases in Fe uptake with increasing supplemental Cu likely resulted primarily from increasing dry matter production although some of the increase in flax was likely caused by increases in Fe concentration. Since Fe uptake was either increased or not affected by Cu fertilization, it is reasonable to assume that the decrease in Fe concentration with increasing Cu additions likely resulted from dilution.

TABLE 20

Fe and S uptake into barley shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Fe Conc. in shoots (ug/g)	Total Fe Uptake into shoots (ug/pot)	S Conc. in shoots (mg/g)	Total S Uptake into shoots (mg/pot)
0.0	67.9 a	928 a	6.1 a	84 a
2.9	39.2 bc	871 a	3.9 b	87 a
5.8	41.7 b	1090 a	3.7 b	98 a
11.5	37.1 bc	977 a	3.9 b	100 a
23.0	31.3 c	858 a	3.3 b	90 a
46.0	31.3 c	843 a	3.6 b	96 a
92.0	30.5 c	823 a	3.6 b	97 a

TABLE 21

Fe and S uptake into oats shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Fe Conc. in shoots (ug/g)	Total Fe Uptake into shoots (ug/pot)	S Conc. in shoots (mg/g)	Total S Uptake into shoots (mg/pot)
0.0	61.7 a	681 b	6.7 a	74 c
2.9	39.2 b	1070 a	4.1 b	110 ab
5.8	35.4 bc	1010 a	3.3 b	94 b
11.5	31.7 c	1040 a	3.4 b	110 ab
23.0	31.7 c	1000 a	3.6 b	110 ab
46.0	31.3 c	1080 a	3.7 b	130 a
92.0	32.5 c	1110 a	3.7 b	130 a

TABLE 22

Fe and S uptake into wheat shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Fe Conc. in shoots (ug/g)	Total Fe Uptake into shoots (ug/pot)	S Conc. in shoots (mg/g)	Total S Uptake into shoots (mg/pot)
0.0	70.0 a	124 d	2.4 ab	4.1 c
2.9	51.7 b	768 c	2.8 a	43 b
5.8	45.5 c	989 b	2.6 ab	58 ab
11.5	40.0 d	1130 ab	2.1 cd	58 ab
23.0	44.6 c	1310 a	2.2 cd	64 a
46.0	38.8 d	1220 a	2.0 cd	63 a
92.0	37.9 d	1280 a	1.9 d	64 a

TABLE 23

Fe and S uptake into flax shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Fe Conc. in shoots (ug/g)	Total Fe Uptake into shoots (ug/pot)	S Conc. in shoots (mg/g)	Total S Uptake into shoots (mg/pot)
0.0	53.3 ab	49.3 d	5.5 a	5.2 d
2.0	45.4 b	95.0 d	5.8 a	12 d
4.0	42.1 b	209 d	5.1 a	25 c
8.0	72.1 a	708 c	5.1 a	49 c
16.0	72.1 a	962 bc	5.0 a	66 b
32.0	69.2 a	1140 ab	4.1 b	67 b
64.0	67.5 a	1300 a	4.1 b	79 a
128.0	71.7 a	1340 a	3.7 b	69 ab

TABLE 24

Fe and S uptake into rapeseed shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Fe Conc. in shoots (ug/g)	Total Fe Uptake into shoots (ug/pot)	S Conc. in shoots (mg/g)	Total S Uptake into shoots (mg/pot)
0.0	40.8 a	499 c	7.1 a	88 b
2.0	34.6 a	833 ab	6.1 a	150 a
4.0	30.9 a	834 ab	5.9 a	160 a
8.0	32.1 a	815 ab	6.1 a	160 a
16.0	31.3 a	733 b	6.6 a	160 a
32.0	31.7 a	826 ab	6.7 a	170 a
64.0	30.0 a	755 ab	6.4 a	160 a
128.0	33.4 a	939 a	6.2 a	170 a

3.3.5.5 Sulfur

Sulfur concentrations in barley and oat shoots decreased with the first increment of supplemental Cu but did not vary among those treatments which included supplemental Cu (Tables 20 and 21). Sulfur concentrations in wheat shoots (Table 22) did not decrease until 11.5 ug Cu/g soil had been added, whereas 32.0 ug Cu/g soil were necessary to decrease S concentrations in flax shoots (Table 23). Copper fertilization had no influence on S concentration in rapeseed shoots (Table 24). Ward et al [116] suggest that the S sufficiency range for barley, oats and wheat at head emergence stage was 1.5 to 4.5 mg/g plant material. All cereal crops in this study were adequately supplied with S. Anderson [5] suggested a critical level of 1.0 mg S/g plant material for rapeseed 36 days after emergence. No S critical levels for flax could be found, however it is unlikely that S was deficient in this crop.

Total S uptake into barley shoots was not influenced by the addition of Cu (Table 20). Sulfur uptake into oat and rapeseed (Tables 21 and 24) increased with the first increment of supplemental Cu but usually did not increase with the additions of more Cu. Sulfur uptake into wheat and flax shoots not only increased with first increment of Cu but also increased somewhat with additional Cu (Tables 22 and 23). Those increases in Cu uptake likely resulted from increased dry matter production and suggested that the decreases in shoot S concentration with increasing Cu were due to dilution.

3.3.5.6 Zinc

Zinc concentrations in shoots of barley, oats, wheat and flax decreased substantially with the first increment of Cu (Tables 25, 26, 27 and 28). However, additional increments of Cu decreased Zn concentrations only slightly or had no influence. Zinc concentrations in rapeseed shoots were not influenced by the addition of fertilizer Cu (Table 29). Ward et al [116] listed the critical level for barley, oat, and wheat shoots at heading as 15 ug Zn/g plant material. Akinyede [2] suggested a critical level of 12.5 ug Zn/g plant material for barley at heading. McGregor [68] has suggested that eight week old flax shoots may be suspected of being Zn deficient if they contain less than 13 ug Zn/g plant material. Zinc levels in this study were above those values, therefore it was felt that Zn was adequate in the cereal crops and flax. No Zn critical levels were found for rapeseed, however, rapeseed was likely not deficient in Zn for reasons already mentioned for the other nutrients.

Total Zn uptake into the shoots of all five crops increased with increasing Cu, likely as the result of increases in dry matter production (Tables 25, 26, 27, 28 and 29). The increases in total Zn uptake suggest that the decreases in Zn concentration with increasing supplemental Cu resulted from dilution.

TABLE 25

Zn and Mn uptake into barley shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Zn Conc. in shoots (ug/g)	Total Zn Uptake into shoots (ug/pot)	Mn Conc. in shoots (ug/g)	Total Mn Uptake into shoots (ug/pot)
0.0	28.8 a	393 c	54.6 a	744 a
2.9	18.8 b	424 bc	27.5 b	620 a
5.8	18.8 b	489 bc	25.0 bc	653 a
11.5	20.0 b	527 ab	25.0 bc	659 a
23.0	19.2 b	527 ab	22.9 c	629 a
46.0	21.7 b	586 a	22.9 c	617 a
92.0	20.9 b	564 a	23.8 bc	643 a

TABLE 26

Zn and Mn uptake into oats shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Zn Conc. in shoots (ug/g)	Total Zn Uptake into shoots (ug/pot)	Mn Conc. in shoots (ug/g)	Total Mn Uptake into shoots (ug/pot)
0.0	28.0 a	308 c	72.1 a	796 d
2.9	16.3 b	444 ab	53.8 b	1470 ab
5.8	14.2 bc	404 b	44.6 c	1280 bc
11.5	12.9 c	424 ab	37.9 c	1240 c
23.0	14.2 bc	451 ab	39.6 c	1260 c
46.0	13.4 c	461 ab	43.8 c	1510 a
92.0	13.8 c	471 a	45.0 c	1530 a

TABLE 27

Zn and Mn uptake into wheat shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Zn Conc. in shoots (ug/g)	Total Zn Uptake into shoots (ug/pot)	Mn Conc. in shoots (ug/g)	Total Mn Uptake into shoots (ug/pot)
0.0	31.7 a	56.1 c	37.1 a	65.0 d
2.9	21.3 b	307 b	25.8 b	367 c
5.8	22.1 b	479 a	21.7 bc	473 b
11.5	15.4 c	436 a	19.2 c	543 ab
23.0	15.4 c	453 a	18.4 c	540 ab
46.0	13.8 c	435 a	17.1 c	542 ab
92.0	12.5 c	429 a	17.5 c	593 a

TABLE 28

Zn and Mn uptake into flax shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Zn Conc. in shoots (ug/g)	Total Zn Uptake into shoots (ug/pot)	Mn Conc. in shoots (ug/g)	Total Mn Uptake into shoots (ug/pot)
0.0	49.8 a	46.8 e	165 b	155 d
2.0	39.1 b	82.4 de	189 b	398 d
4.0	32.5 bc	161 d	191 b	950 d
8.0	35.9 bc	344 c	268 a	2730 c
16.0	32.5 bc	432 b	312 a	4160 b
32.0	30.9 c	509 ab	318 a	5300 ab
64.0	28.8 c	557 a	296 a	5740 a
128.0	30.0 c	560 a	314 a	5880 a

TABLE 29

Zn and Mn uptake into rapeseed shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Zn Conc. in shoots (ug/g)	Total Zn Uptake into shoots (ug/pot)	Mn Conc. in shoots (ug/g)	Total Mn Uptake into shoots (ug/pot)
0.0	26.7 a	328 c	63.8 a	786 c
2.0	23.8 a	575 ab	51.3 b	1230 ab
4.0	22.1 a	598 ab	51.7 b	1390 a
8.0	21.7 a	554 ab	49.6 b	1260 ab
16.0	20.0 a	471 b	49.6 b	1160 ab
32.0	22.1 a	579 ab	44.2 b	1150 ab
64.0	20.8 a	523 ab	43.4 b	1090 b
128.0	22.1 a	627 a	47.9 b	1350 ab

3.3.5.7 Manganese

Manganese concentrations in barley, oats, wheat and rapeseed (Tables 25, 26, 27 and 29) decreased with the first increment of supplemental Cu. Thereafter only barley, oats and wheat Mn concentrations decreased with further increments of Cu. Manganese concentrations in flax shoots increased substantially when more than 8.0 ug Cu/g soil was added which corresponded to the increase in Cu concentration in flax shoots from 1.0 to 1.5 ug cu/g plant material. Manganese concentrations in flax behaved similar to Fe concentrations, increasing with the first increase in Cu concentration in flax shoots. Total uptake of Mn in barley shoots was not influenced by supplemental Cu additions (Table 25). Oats, wheat, flax and rapeseed shoot uptake of Mn increased when supplemental Cu was added (Tables 26, 27, 28 and 29). The increased uptake was likely a result of increased dry matter production for oats, wheat and rapeseed. Flax Mn uptake was influenced by both increased shoot Mn concentration and increase in dry matter production.

3.3.5.8 Calcium

Calcium concentration in shoots of barley, oats and rapeseed (Tables 30, 31 and 34) generally decreased with increasing supplemental Cu. Wheat shoot Ca concentration decreased for the first increment of Cu but was not influenced by higher levels of Cu (Table 32). Although the Ca concentration was significantly lower in flax receiving 4 ug Cu/g soil, Cu level had no consistent effect on Ca concentrations in flax (Table 33). Ward et al [116] listed low Ca levels for barley, oat and wheat shoots at heading as < 3.0, < 2.0 and < 2.0 mg Ca/g plant material, respectively. All cereals in this study were likely adequately supplied with Ca. Flax and rapeseed shoots contained considerably more Ca than oat and wheat shoots. Therefore, flax and rapeseed were likely also adequately supplied with Ca.

Total Ca uptake by shoots of wheat and flax increased with increasing supplemental Cu (Tables 32 and 33). Total Ca uptake into oat and rapeseed increased with the first increment of supplemental Cu but was not influenced by higher levels of Cu (Tables 31 and 34). Calcium uptake into barley shoots was not influenced by supplemental Cu (Table 30). The increases in Ca uptake resulted from of increases in dry matter production. Decreases in Ca concentration with increasing Cu probably were caused by dilution since total Ca uptake did not decrease with increasing Cu.

TABLE 30

Ca and Mg uptake into barley shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Ca Conc. in shoots (mg/g)	Total Ca Uptake into shoots (mg/pot)	Mg Conc. in shoots (mg/g)	Total Mg Uptake into shoots (mg/pot)
0.0	8.2 a	112 c	6.3 a	86 b
2.9	5.9 b	130 ab	5.0 b	110 a
5.8	5.4 bc	140 ab	4.9 b	130 a
11.5	4.4 d	110 bc	3.5 c	92 b
23.0	5.4 c	150 a	4.7 b	130 a
46.0	4.7 d	130 bc	4.5 b	120 a
92.0	4.7 d	130 bc	4.5 b	120 b

TABLE 31

Ca and Mg uptake into oats shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Ca Conc. in shoots (mg/g)	Total Ca Uptake into shoots (mg/pot)	Mg Conc. in shoots (mg/g)	Total Mg Uptake into shoots (mg/pot)
0.0	5.4 a	60 c	7.3 a	80 c
2.9	3.9 b	110 b	5.7 bc	150 b
5.8	3.8 bc	110 b	4.9 bc	140 b
11.5	4.8 ab	160 a	6.6 ab	220 a
23.0	3.1 c	97 bc	4.6 bc	150 b
46.0	2.8 c	97 bc	4.1 c	140 b
92.0	3.2 c	110 b	4.9 bc	170 b

TABLE 32

Ca and Mg uptake into wheat shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Ca Conc. in shoots (mg/g)	Total Ca Uptake into shoots (mg/pot)	Mg Conc. in shoots (mg/g)	Total Mg Uptake into shoots (mg/pot)
0.0	16 a	28 d	20 a	35 a
2.9	3.6 b	53 c	14 b	190 a
5.8	3.1 bc	69 abc	3.3 c	73 a
11.5	2.1 d	59 bc	2.4 c	69 a
23.0	2.4 cd	71 abc	2.7 c	80 a
46.0	2.6 cd	81 a	2.2 c	71 a
92.0	2.3 cd	77 ab	2.7 c	93 a

TABLE 33

Ca and Mg uptake into flax shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Ca Conc. in shoots (mg/g)	Total Ca Uptake into shoots (mg/pot)	Mg Conc. in shoots (mg/g)	Total Mg Uptake into shoots (mg/pot)
0.0	11 a	11 c	8.5 a	7.9 c
2.0	9.6 a	20 c	8.0 a	16 c
4.0	6.6 b	33 c	7.7 a	38 c
8.0	11 a	84 b	8.3 a	83 b
16.0	11 a	140 ab	7.4 a	98 b
32.0	11 a	190 a	7.8 a	130 a
64.0	11 a	210 a	6.9 a	130 a
128.0	9.1 ab	170 a	7.2 a	130 a

TABLE 34

Ca and Mg uptake into rapeseed shoots as influenced by $CuSO_4$ rate

ug Cu/g oven dry soil	Ca Conc. in shoots (mg/g)	Total Ca Uptake into shoots (mg/pot)	Mg Conc. in shoots (mg/g)	Total Mg Uptake into shoots (mg/pot)
0.0	27 ab	340 c	7.9 bc	96 e
2.0	25 bc	600 ab	8.7 b	210 bc
4.0	25 bc	670 ab	8.5 bc	230 b
8.0	24 bc	625 ab	7.5 bc	190 cd
16.0	31 a	730 a	15 a	340 a
32.0	23 c	600 ab	7.5 bc	200 cd
64.0	21 c	530 b	6.9 bc	170 d
128.0	21 c	574 b	6.5 c	180 d

3.3.5.9 Magnesium

Magnesium concentration in barley and oat shoots (Tables 30 and 31) decreased with the first increment of supplemental Cu but was not influenced by any higher increments of Cu. Wheat shoot Mg concentration decreased for the first two increments of Cu but was not influenced by subsequent increments (Table 32). Flax and rapeseed shoot Mg concentrations were usually not influenced by Cu additions (Tables 33 and 34). The 16.0 ug Cu/g soil treatment in rapeseed was unusual in that the Mg concentration was 15.0 mg Mg/g plant material, approximately double any of the other rapeseed treatments for rapeseed. It is of interest that this treatment had the lowest dry matter production for the treatments of rapeseed receiving Cu. The reasons for this anomaly are not known. Ward _et al_ [116] listed the sufficiency range for barley, oat and wheat shoots at heading as 1.5 to 5.0 mg Mg/g plant material. Cereals in this study were within this range whereas the oilseeds contained an adequate supply of Mg.

Total uptake of Mg in wheat shoots was not influenced by supplemental Cu (Table 32). Magnesium uptake into shoots of barley, oats and rapeseed (Tables 30, 31 and 34) was increased by the first increment of supplemental Cu but usually was not influenced by further increments of Cu. Magnesium uptake into flax shoots increased with increasing supplemental Cu (Table 33). The increases in Mg uptake with increasing Cu probably resulted from increases in dry matter production. As with Ca, decreases in Mg concentrations with increasing Cu likely resulted from dilution since Mg uptake either was not affected or increased with increasing Cu.

Chapter IV

STUDY II: EFFECT OF ZN PLACEMENT, RATE AND CARRIER ON GROWTH AND ZN UPTAKE OF CEREAL AND OILSEED CROPS

4.1 INTRODUCTION

Previous research in Manitoba and elsewhere had established that Zn deficiency is more likely to occur on highly calcareous soils than on soils containing no lime. However, the only responses to Zn fertilization had been obtained in the growth chamber with flax [68] and in the field with blackbeans [64]. The present research was initiated to determine the extent and severity of Zn deficiency in the field in cereal as well as oilseed crops, the most commonly grown crops in Manitoba. The experiments were conducted in 1977 and 1978 on the highly calcareous soil, Lakeland clay loam. It was felt that if no growth responses to Zn fertilization were obtained on a highly calcareous soil, it could be assumed that Zn deficiency is not very prevalent in cereal and oilseed crops in Manitoba. Another important objective of the research was to evaluate the relative efficiences of various Zn carriers, placement methods and rates by measuring the influence of those factors upon Zn uptake.

4.2 METHODS AND MATERIALS

4.2.1 Soil Properties

The field sites in both 1977 and 1978 were on the farm of I. Campbell located at SW 1/4 2-16-2E. The soil was in the Lakeland Series which was mapped by Pratt et al [88] as a Gleyed Rego Black soil developed on strongly calcareous deltaic deposits.

Conductivity and pH determinations were similar to those discussed in Section 3.2.1 except that a 1:1 water to soil paste instead of a 3:1 water to soil paste was used. Nitrate-N, SO_4-S, as well as exchangeable Ca^{+2}, Mg^{+2} and K^+ were all determined as described in Section 3.2.1. Plant available soil P levels were estimated by shaking 5 g of soil with 100 ml of 0.5N $NaHCO_3$ at a pH of 8.5 for 30 minutes in the presence of 1 g charcoal and filtering through Whatman #42 filter paper. Concentration of P in the filtrate was determined by the method of Stainton et al [110]. Sulfate-S as well as exchangeable Ca^{+2}, Mg^{+2} and K^+ were not determined in 1977. Plant available Zn, Cu, Mn and Fe were estimated according to the method described in Section 3.2.1 except that 10 g instead of 2 g of soil were used in the usual 20 ml of extracting solution.

Organic matter was determined by the Walkley-Black method as described by Allison [3] except that the titration was preformed with a automatic titrator potentiometrically.

Carbonates were determined by reacting one g of soil with 40 ml of 0.1N HCl, drying the released gases and collecting the evolved CO_2 in ascarite.

4.2.2 Experimental Design

Barley (*Hordeum vulgare* var Conquest), wheat (*Triticum aestevum* var Neepawa), flax (*Linum usitatissimum* var Dufferin) and rapeseed (*Brassica napus* var Tower) were grown in both 1977 and 1978 and oats (*Avena sativa* var Hudson) were grown in 1978. Each treatment was replicated six times in a randomized complete block design. Each plot was 1.07 m by 6.10 m and contained 6 rows which were 0.18 m apart. There were no untreated areas between plots within crops or blocks although blocks were separated by 1.52 m walkways. Flax and rapeseed were separated from the cereals by 1.07 m wide strips of untreated flax or rapeseed to prevent herbicide damage.

All crops in 1977 and 1978 received 120 kg N/ha, mostly as commercial ammonium nitrate broadcast immediately after seeding although some of the 120 kg N was applied with the ammonium phosphate. Phosphorus was drilled with the seed of cereals at 45 kg P_2O_5/ha as monoammonium phosphate. Rapeseed received 22.5 kg P_2O_5/ha as monoammonium phosphate drilled with the seed whereas flax did not receive fertilizer P. Potassium was applied as K_2SO_4 at 67 kg K_2O/ha in 1977 broadcast immediately after seeding and 107 kg K_2O/ha drilled in before seeding in 1978. Sulfur was suppliedwith the K as K_2SO_4 at rates of 25 kg S/ha in 1977 and 38.5 kg S/ha in 1978.

Treatments are described in Table 36 for 1977 and in Table 37 for 1978. Abbreviations used in Tables 36 and 37 are described in Table 35. Flax treatments are not indicated for the 1977 experiment since the flax was severely damaged by an application of a high rate of Buctril M. Therefore, yield and nutrient concentrations for flax are not reported. Copper treatments were included in 1977 to check for either an induced deficiency of Cu or synergistic effects of Cu and Zn fertilizer additions. Iron treatments were included in 1978 to be sure that high carbonate equivalent and frequent wet conditions of the soil were not causing an Fe deficiency.

Cereal crops were all seeded at a rate of 112 kg/ha, flax at 45 kg/ha and rapeseed at 7.9 kg/ha by using a mixture containing 3.2 kg live seed, 2.3 kg 5% furadan granules and 9.5 kg dead seed applied at a rate of 37 kg/ha.

Barley and wheat were seeded on May 30 and flax and rapeseed on May 31 in 1977. Barley, oats, wheat, flax and rapeseed were seeded on May 12 in 1978. Complete weed control was achieved through the use of herbicides.

TABLE 35

Descriptions of abbreviations for micronutrient carriers and placement methods used in field studies

Carrier	Abbreviation
Ciba-Geigy Sequestrene Copper $Na_2CuEDTA \cdot 3H_2O$ 13% Cu	CuEDTA
Ciba-Geigy Sequestrene Zinc $Na_2ZnEDTA \cdot 2H_2O$ 14.2% Zn	ZnEDTA
Ciba-Geigy Sequestrene Iron 330 NaFeDTPA 10% Fe	FeDTPA
Reagent grade $CuSO_4 \cdot 5H_2O$ 25.4% Cu	$CuSO_4$
Reagent grade $ZnSO_4 \cdot 7H_2O$ 22.7% Zn	$ZnSO_4$
Reagent grade $MnSO_4 \cdot H_2O$ 32.5% Mn	$MnSO_4$
Elephant Brand ZnMNS $(NH_4)_2SO_4, ZnSO_3, MnSO_3$ 15% Zn	ZnMNS
Eagle-Picher ZincGro $ZnSO_4 \cdot H_2O$ 36% Zn	ZincGro

Placement	Abbreviation
Mixed by rototilling into surface 10-15 cm of soil in liquid form for most carriers except for granular form for ZnMNS and ZincGro and crystal form for $ZnSO_4$ and $CuSO_4$ at Piney, Marchand and Stead for experiments with wheat on organic soil.	(M)
Drilled with the seed into the center four rows of the subplots by means of V-belts in powder, granular or crystal form	(D)

Midseason sampling of cereals involved harvesting 10 to 20 entire plant shoots at random from the second and fifth

TABLE 36

Treatments for field experiments at Teulon in 1977

Crops	Carrier	Rate (kg/ha)	Placement	Abbrev.
all	---	---	---	control
barley	ZnEDTA	0.5	(M)	ZnEDTA(M)0.5
all	ZnEDTA	1.5	(M)	ZnEDTA(M)1.5
barley	ZnEDTA	4.0	(M)	ZnEDTA(M)4
barley	ZnEDTA	1.5	(D)	ZnEDTA(D)1.5
barley	ZnEDTA $CuSO_4$	1.5 4	(M) (D)	ZnEDTA(M)1.5 + $CuSO_4$(D)4
barley	$ZnSO_4$	7.5	(M)	$ZnSO_4$(M)7.5
barley	$ZnSO_4$	7.5	(D)	$ZnSO_4$(D)7.5
barley	ZnMNS	7.5	(M)	ZnMNS(M)7.5
barley	ZnMNS	7.5	(D)	ZnMNS(D)7.5
barley	ZincGro	7.5	(M)	ZincGro(M)7.5
barley	ZincGro	7.5	(D)	ZincGro(D)7.5
barley	$CuSO_4$	4	(D)	$CuSO_4$(D)4

rows of each plot at heading. Flax and rapeseed plants were sampled at maturity in 1977 and 56 days after seeding in 1978. The plant samples were placed in plastic bags and frozen until analysis. Recently thawed plant samples were rinsed in deionized water, air dried, and ground through a Wiley mill in 1977. The samples from the 1978 experiment

TABLE 37

Treatments for field experiments at Teulon in 1978

Crops	Carrier	Rate (kg/ha)	Placement	Abbrev.
all	---	---	---	control
barley, flax, rapeseed	ZnEDTA	5	(M)	ZnEDTA(M)5
barley, wheat	ZnEDTA	5	(D)	ZnEDTA(D)5
barley, oats	ZnEDTA FeDTPA	5 1	(D) foliar	ZnEDTA(D)5 + 1kg Fe/ha foliar
flax	ZnEDTA FeDTPA	5 2	(M) foliar	ZnEDTA(M)5 + 2kg Fe/ha foliar
barley	$ZnSO_4$	15	(M)	$ZnSO_4$(M)15
barley	$ZnSO_4$	15	(D)	$ZnSO_4$(D)15
barley	ZnMNS	15	(M)	ZnMNS(M)15
barley	ZnMNS	15	(D)	ZnMNS(D)15
barley	ZincGro	15	(M)	ZincGro(M)15
barley	ZincGro	15	(D)	ZincGro(D)15

were ground in a coffee grinder with plastic and aluminum parts so that the samples could be analyzed for Fe. Plant samples were analyzed for micro and macronutrients according to the procedures discussed in Section 3.2.3 except for S in 1978. In 1978, 0.2 ml of digest solution was diluted to 20 ml and the S level in the diluted digest determined according to the method in Section 3.2.1.

Final harvests were taken in 1977 at 95, 95, 106 and 106 days after seeding for barley, wheat, flax, and rapeseed and in 1978 at 88, 91, 101, 113 and 95 days after seeding for barley, oats, wheat, flax and rapeseed. Each plot was harvested by cutting plant shoots at soil surface from the center 3.05 m of the 3rd and 4th rows of each plot. Samples were then placed in cloth bags and dried at 35 to 40^{o}C until suitable for threshing. Dry weights of the entire sample were taken and after threshing and cleaning of the grain the grain was weighed. Straw weights were calculated and recorded, however, they are not reported here since they followed the same trends as grain yields and did not appear to add to or detract from the conclusions reached for all field sites in both 1977 and 1978.

4.3 RESULTS AND DISCUSSION

4.3.1 Soil Characteristics

Some chemical and physical properties of the soils used in 1977 and 1978 are listed in Table 38. The plot sites were highly calcareous in both years as indicated by both pH and $CaCO_3$ equivalent values. Nitrate-N was very high in both years according to criteria of the Manitoba Provincial Soil Testing Laboratory whereas $NaHCO_3$ extractable P was medium in 1977 and low in 1978. Sulfate-S and NH_4Ac extractable K levels in 1978 were very high and medium, respectively, according to the guidelines of the Manitoba ProvincialSoil Testing Laboratory. DTPA extractable Cu, Mn and

Fe were definitely in excess of the critical levels of 0.2, 1.0 and 4.5 ug/g established by Lindsay and Norvell [62]. The DTPA extractable Zn level in the surface 15 cm of the soil would be considered marginally deficient at the 1977 site by guidelines of Lindsay and Norvell [62]. Soil levels of Zn from 15-30 and 30-60 cm would be considered as very deficient at the 1977 site. DTPA extractable Zn in the surface 15 cm of the 1978 field site would be considered sufficient, however, the 15-30 and 30-60 cm depths would be considered as deficient according to the 1.0 Zn ug/g soil critical level of Lindsay and Norvell [62]. The only possible limiting nutrient at either the 1977 site or the 1978 site would have been Zn since adequate P was added to overcome its low status.

4.3.2 Grain Yields and Nutrient Concentrations

Grain yields and nutrient concentrations in shoots at midseason are given in Tables 39 to 53. Within each vertical column numbers followed by the same letter are not significantly different at the 5% level according to Duncans multiple range test [30].

Flax data from 1977 are not reported due to herbicide damage. Only yield data are reported for rapeseed for 1977 since there was no midseason plant sampling.

TABLE 38

Soil characteristics for field experiments at Teulon

		1977	1978
Classification		Lakeland	Lakeland
texture		clay loam	clay loam
pH		8.2	8.0
O.M. %		4.3	5.1
$CaCO_3$ equivalent %		37	26
cond (mmhos/cm)		0.57	0.62
NO_3-N (kg/ha - 0-60 cm)		117	125
PO_4-P (kg/ha -$NaHCO_3$ 0-15 cm)		22	18
SO_4-S (kg/ha H_2O ext 0-60 cm)		---	146
K (kg/ha NH_4Ac pH=7 ext 0-15 cm)		---	277
Ca (% NH_4Ac pH=7 ext 0-15 cm)		---	0.82
Mg (% NH_4Ac pH=7 ext 0-15 cm)		---	0.21
Cu (DTPA ext ug/g)	0-15cm	1.4	1.1
	15-30cm	1.6	1.3
	30-60cm	1.1	1.2
Zn (DTPA ext ug/g)	0-15cm	0.8	1.8
	15-30cm	0.3	0.6
	30-60cm	0.2	0.5
Mn (DTPA ext ug/g)	0-15cm	7.3	15
Fe (DTPA ext ug/g)	0-15cm	14	16

4.3.2.1 1977 Results

Rapeseed grain yield (Table 39) did not significantly change as a result of Zn fertilizer addition.

TABLE 39

Effect of Zn on rapeseed yield at Teulon in 1977

Treatment	grain yield kg/ha
control	1100 a
ZnEDTA(M)1.5	1390 a

Barley grain yield, Zn concentration and Cu concentration were not affected by addition of fertilizer Zn, regardless of carrier, rate or method of application (Table 40). Manganese concentration did vary significantly in some treatments, however, there was no discernible pattern to the variations. Phosphorus, S, K, Ca and Mg concentrations in barley shoots (Table 41) were also not affected by Zn treatment. Levels of all nutrients in the 1977 barley shoots would be considered sufficient for normal growth according to the literature critical values already mentioned when discussing growth chamber results. The very high yields also suggest that no nutrient was limiting growth. It is not surprising that grain yield did not respond to Zn fertilization since all shoot Zn concentrations were above the critical level of 12.5 ug Zn/g established by Akinyede [2] for barley. In addition, Cu levels were well above the critical concentration suggested by the growth chamber experiment.

TABLE 40

Effect of Zn carrier, placement and rate as well as of Cu on grain yield and micronutrient concentration of barley shoots at Teulon in 1977

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	5264 a	8.0 a	14 a	28 c
ZnEDTA(M)0.5	5364 a	7.7 a	14 a	26 def
ZnEDTA(M)1.5	5336 a	7.2 a	17 a	25 ef
ZnEDTA(M)4	5835 a	7.8 a	26 a	28 c
ZnEDTA(D)1.5	6216 a	8.2 a	20 a	27 cd
$ZnSO_4$(M)7.5	5733 a	7.4 a	19 a	25 ef
$ZnSO_4$(D)7.5	5802 a	8.2 a	20 a	32 a
ZnMNS(M)7.5	5518 a	8.9 a	19 a	27 cde
ZnMNS(D)7.5	6125 a	7.7 a	17 a	28 bc
ZincGro(M)7.5	5402 a	7.4 a	16 a	25 f
ZincGro(D)7.5	5827 a	8.9 a	20 a	30 b
$CuSO_4$(D)4	5416 a	7.8 a	17 a	28 bc
ZnEDTA(M)1.5 +$CuSO_4$(D)4	5301 a	8.1 a	19 a	27 cde

TABLE 41

Effect of Zn carrier, placement and rate as well as Cu on macronutrient concentrations in barley shoots at Teulon in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	3.0 a	2.0 a	24.0 a	3.1 a	3.6 a
ZnEDTA(M)0.5	3.0 a	2.0 a	22.3 a	2.9 a	3.8 a
ZnEDTA(M)1.5	3.0 a	2.0 a	21.1 a	2.6 a	3.4 a
ZnEDTA(M)4	3.2 a	2.2 a	20.6 a	2.7 a	3.6 a
ZnEDTA(D)1.5	3.3 a	2.2 a	21.2 a	2.7 a	3.4 a
$ZnSO_4$(M)7.5	3.1 a	2.2 a	21.9 a	2.9 a	3.6 a
$ZnSO_4$(D)7.5	3.0 a	1.8 a	16.5 a	2.9 a	3.5 a
ZnMNS(M)7.5	3.2 a	2.3 a	19.6 a	2.9 a	3.6 a
ZnMNS(D)7.5	3.3 a	2.1 a	22.4 a	3.0 a	3.7 a
ZincGro(M)7.5	3.1 a	2.1 a	21.9 a	2.7 a	3.6 a
ZincGro(D)7.5	3.5 a	2.5 a	20.8 a	3.1 a	4.1 a
$CuSO_4$(D)4	3.3 a	2.6 a	22.0 a	3.1 a	3.8 a
$ZnSO_4$(M)1.5 +$CuSO_4$(D)4	3.2 a	2.3 a	21.7 a	3.0 a	4.3 a

Wheat grain yield and nutrient concentrations (Tables 42 and 43) were not influenced by the addition of Zn fertilizer. The levels of all nutrients were above suggested critical levels. As with barley high yields tended to confirm that no nutrient deficiencies existed.

TABLE 42

Effect of Zn on grain yield and micronutrient concentrations in wheat shoots at Teulon in 1977

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	4629 a	7.3 a	13 a	38 a
ZnEDTA(M)1.5	4707 a	6.5 a	15 a	34 a

TABLE 43

Effect of Zn on macronutrient concentrations in wheat at Teulon in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	2.8 a	1.4 a	22.2 a	1.9 a	3.0 a
ZnEDTA(M)1.5	3.0 a	1.7 a	21.1 a	1.8 a	3.0 a

4.3.2.2 1978 Results

Barley grain yields and Cu, Mn and Fe concentrations in shoots at heading were not influenced by treatment (Table 44). Lack of response in grain yield to Zn fertilization was not surprising since all plant Zn concentrations are above the 12.5 ug Zn/g critical level and the level of DTPA extractable soil Zn was above the 0.8 ug Zn/g critical level.

TABLE 44

Effect of Zn carrier and placement of Zn as well as Fe on grain yield and micronutrient concentrations in barley shoots at Teulon in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	3391 a	7.0 a	17 cd	30 a	54 a
ZnEDTA(M)5	3168 a	6.9 a	30 a	27 a	48 a
ZnEDTA(D)5	3171 a	6.6 a	22 bc	29 a	54 a
$ZnSO_4$(M)15	3214 a	7.4 a	24 b	29 a	56 a
$ZnSO_4$(D)15	3291 a	7.4 a	24 b	30 a	52 a
ZnMNS(M)15	3442 a	7.0 a	18 cd	28 a	57 a
ZnMNS(D)15	3247 a	6.4 a	17 d	28 a	62 a
ZincGro(M)15	3369 a	6.8 a	16 d	28 a	51 a
ZincGro(D)15	3236 a	6.4 a	17 d	25 a	55 a
ZnEDTA(D)5 +1 kg Fe/ha foliar	3256 a	7.1 a	24 b	29 a	60 a

The 5 kg Zn/ha as ZnEDTA mixed throughout the surface 10 cm was the most effective in increasing barley shoot Zn concentration. Mixing ZnEDTA was much more effective than drilling which is surprising considering the high mobility of ZnEDTA. The 5 kg Zn/ha as ZnEDTA drilled with the seed and the 15 kg Zn/ha as $ZnSO_4$ mixed with the surface 10 cm or drilled with the seed were not significantly different from each other. That result in conjunction with the greater effectiveness of drilling 5 kg Zn as ZnEDTA suggested that the chelated source was more than 3 times as effective as $ZnSO_4$. The two $ZnSO_4$ treatments had higher Zn concentrations than the control although method of application had no influence on Zn uptake which was surprising considering the low mobility of inorganic Zn in soil. The other carriers, ZnMNS and ZincGro, did not influence shoot Zn concentrations indicating that these materials may not be good Zn fertilizers. Results concerning ZnMNS and ZincGro in 1977 were inclusive. Although plant Zn concentrations were sometimes increased by ZnMNS or ZincGro in 1977, the increases were not statistically significant.

The foliar Fe treatment did not influence either barley grain yield or plant nutrient concentrations. There also was no visual response in colour of the barley as a result of the treatment. It is not surprising that Fe did not influence barley yield considering the relatively high DTPA extractable soil Fe and the plant Fe levels. However, foliar application of Fe should have increased plant Fe concentration. Perhaps not enough Fe was applied or the method of application was not effective.

Phosphorus, K, Ca and Mg concentrations were not influenced by Zn fertilization (Table 45). Sulfur concentration in the ZnEDTA mixed and drilled treatments were significantly lower than some of the other treatments. However, the reason for those differences are not known. The plant

TABLE 45

Effect of Zn carrier and placement as well as Fe on macronutrient concentrations of barley shoots at Teulon in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	2.3 a	2.5 abc	8.6 a	3.0 a	2.5 a
ZnEDTA(M)5	2.0 a	2.5 bc	8.3 a	3.0 a	2.3 a
ZnEDTA(D)5	1.8 a	2.2 c	7.8 a	3.3 a	2.3 a
$ZnSO_4$(M)15	2.3 a	2.6 abc	8.5 a	3.3 a	2.5 a
$ZnSO_4$(D)15	2.4 a	2.7 ab	10.1 a	3.6 a	2.9 a
ZnMNS(M)15	2.4 a	2.7 ab	10.8 a	3.6 a	2.9 a
ZnMNS(D)15	2.1 a	2.6 abc	9.8 a	3.7 a	3.0 a
ZincGro(M)15	2.1 a	2.8 ab	10.7 a	3.6 a	2.8 a
ZincGro(D)15	2.1 a	2.9 a	10.2 a	3.5 a	2.9 a
ZnEDTA(D)5 +1 kg Fe/ha foliar	2.3 a	2.7 a	10.7 a	3.6 a	2.9 a

concentrations of all nutrients in barley except K would be considered as sufficient. Potassuim levels in the plant were low and were less than the suggested deficient level proposed by Ward et al [116] of 12.5 mg K/g plant material. Because of the medium soil K level of 277 kg/ha (Table 38) and because fertilizer K was added, there should have been no shortage of K. The reason for the low plant level is not known for certain but in the General Discussion a possible error in analyses for K which would have resulted in erroneously low plant K levels for all field experiments will be discussed. Consequently, it is felt that the K level probably did not limit yield or interfere with the experiment.

Oat grain yield and concentrations of all nutrients except Fe in the shoots were not influenced by the fertilizer treatments (Tables 46 and 47). Grain yield may not have responded to Zn fertilization because of the very small increase in Zn uptake resulting from Zn fertilization. However, large responses to Zn fertilization would not have been expected considering that plant Zn levels were probably adequate when no Zn was applied. Oat shoot Fe concentration at heading stage was increased slightly by the addition of 5 kg Zn/ha as ZnEDTA drilled with the seed plus a foliar application of 1 kg Fe/ha as FeDTPA (Table 46). As with barley, K concentration was likely erroneously low although all other nutrients would be considered sufficient for normal growth.

Wheat grain yield and nutrient concentrations were not influenced by addition of 5 kg Zn/ha as ZnEDTA drilled with the seed (Tables 48 and 49). As with oats, wheat grain yield may not have increased because Zn fertilization was not very effective in increasing Zn uptake. However, plant Zn levels would probably have been adequate without Zn fertilization. Copper concentrations in wheat shoots were in

TABLE 46

Effect of Zn and Fe on grain yield and micronutrient concentrations in oat shoots at Teulon in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	4361 a	4.1 a	15 a	32 a	41 a
ZnEDTA(D)5 +1 kg Fe/ha foliar	4570 a	4.4 a	18 a	32 a	43 b

TABLE 47

Effect of Zn and Fe on macronutrient concentrations in oat shoots at Teulon in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	1.7 a	1.8 a	7.5 a	1.6 a	1.7 a
ZnEDTA(D)5 +1 kg Fe/ha foliar	1.6 a	1.8 a	7.6 a	1.5 a	1.6 a

the upper portion of the low range established in the growth chamber study. Therefore, supply of Cu probably only slightly limited response to Zn. As with the other cereals, K concentrations were likely only erroneously low whereas all other nutrients were sufficient for normal growth.

Flax grain yield and shoot concentrations of all nutrients except Zn in flax shoots were not influenced by treatment (Tables 50 and 51). Flax shoot Zn concentration was increased by the addition of fertilizer Zn (Table 50).

TABLE 48

Effect of Zn on grain yield and micronutrient concentrations in wheat shoots at Teulon in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	2805 a	4.8 a	15 a	28 a	42 a
ZnEDTA(D)5	2814 a	4.8 a	19 a	24 a	42 a

TABLE 49

Effect of Zn on macronutrient concentrations in wheat shoots at Teulon in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	1.8 a	2.6 a	8.6 a	1.3 a	1.7 a
ZnEDTA(D)5	1.6 a	2.5 a	8.8 a	1.3 a	1.7 a

Perhaps increases in plant Zn concentration were greater than in oats or wheat because the chelated source was mixed throughout the surface soil for flax in order to avoid seedling injury whereas it was drilled with the seed of oats and wheat. However, responses to Zn fertilization would not be expected since plant Zn levels were above the critical level of 13 ug Zn/g established by McGregor [68]. All nutrients except K would be considered sufficient for normal growth.

TABLE 50

Effect of Zn and Fe on grain yield and micronutrient concentrations in flax at Teulon in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	1273 a	3.8 a	13 b	125 a	37 a
ZnEDTA(M)5	1240 a	4.3 a	20 a	160 a	36 a
ZnEDTA(M)5 +Fe foliar	1414 a	4.7 a	22 a	147 a	39 a

TABLE 51

Effect of Zn and Fe on macronutrient concentrations in flax shoots at Teulon in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	1.8 a	2.2 a	10.7 a	6.5 a	4.2 a
ZnEDTA(M)5	1.8 a	2.4 a	11.1 a	6.3 a	4.1 a
ZnEDTA(M)5 +Fe foliar	1.7 a	2.6 a	10.1 a	6.4 a	4.1 a

Grain yield and nutrient concentrations in rapeseed shoots were not influenced by treatment (Tables 52 and 53). The plant levels of all nutrients except K were sufficient. Since plant Zn levels were not particularily low, substantial yield increases would not have been expected. Unfortunately, however, plant Zn critical levels have not been established for rapeseed.

TABLE 52

Effect of Zn on grain yield and micronutrient concentrations in rapeseed shoots at Teulon in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	1369 a	2.9 a	16 a	38 a	43 a
ZnEDTA(M)5	1606 a	2.9 a	20 a	37 a	37 b

TABLE 53

Effect of Zn on macronutrient concentrations in rapeseed shoots at Teulon in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	3.0 a	6.9 a	11.1 a	7.7 a	6.2 a
ZnEDTA(M)5	2.8 a	5.3 a	8.6 a	7.7 a	5.8 a

Chapter V

STUDY III: EFFECT OF CU CARRIER, PLACEMENT AND RATE ON GROWTH AND CU UPTAKE OF BARLEY, OATS, WHEAT AND FLAX

5.1 INTRODUCTION

Yield of barley grown in 1976 on Menisino sand near Zhoda, Manitoba was increased by the application of 5 kg Cu/ha as $CuSO_4$ with the seed [63]. However, oats, wheat and flax in the same experiment did not respond to Cu and all yields were very low suggesting that some other factor may have been limiting responses to Cu. McGregor [68] also reported responses in flax in the greenhouse to Cu fertilization on Pine Ridge sand obtained from the Zhoda area. Those experiments, however, did not determine the severity of Cu deficiency on those leached, sandy Brunisolic or gray Luvisolic mineral soils which occur primarily in southeastern Manitoba. The preliminary research and results in the literature would suggest that such soils would be the most likely of any mineral soils to be deficient in Cu. The 1976 field experiment and the greenhouse experiment also did not determine the relative effectiveness of various Cu carriers and methods of application. The present study was conducted to clear up existing uncertainties about the need for Cu fertilization and to determine the most efficient method of supplying Cu if indeed the need for Cu fertilization was confirmed. The experiments were conducted on sandy soils near Zhoda, because it was felt that if responses to Cu fertilization were not obtained on those soils, they probably would not be obtained on any mineral soil in Manitoba.

5.2 METHODS AND MATERIALS

5.2.1 Soil Properties

The field site in 1977 was located at NW 1/4 16-4-7E near Zhoda on an imperfectly drained associate in the Menisino association (Ehrlich et al [35]). The soil texture was loamy sand and it was classified as a Gleyed Eluviated Eutric Brunisol. The field site in 1978 was located at NW 1/4 18-4-7E on a poorly drained associate of the Pine Ridge association (Ehrlich et al [35]). The soil texture was loamy sand and it was classified as a Rego Humic Gleysol, Carbonated phase.

Soil levels of NO_3-N, SO_4-S in 1978 and exchangeable Ca^{+2}, Mg^{+2} and K^+ were determined by the methods described in Section 3.2.1. All other soil analyses were identical to those described in section 4.2.1. Sulfate-S as well as exchangeable Ca^{+2}, Mg^{+2} and K^+ were not determined in soil from the 1977 field site.

5.2.2 Experimental Design

Barley (*Hordeum vulgare* var Conquest), oats (*Avena sativa* var Harmon in 1977 and var Hudson in 1978), wheat (*Triticum aestevum* var Neepawa) and flax (*Linum usitatissimum* var Dufferin) were grown. Plot size, replication and arrangement were the same as those at Teulon.

All treatments received the same macronutrient levels as those at Teulon. The treatments used in 1977 and 1978 are described in Table 54. Meanings for the terms "mixed" and "drilled" are given in Table 35.

Seeding rates, midseason plant sampling and analyses, weed control and final harvest procedures were the same as those for Teulon. Barley, oats, and flax were seeded on May 20 in 1977 and on May 5 in 1978, whereas the seeding dates for wheat were May 19 and May 4 in 1977 and 1978, respectively. Barley, oats and flax were havested 83 days after seeding in 1977 and 87, 96, and 109 days after seeding, respectively in 1978. Wheat was harvested 99 and 97 days after seeding in 1977 and 1978, respectively.

5.3 RESULTS AND DISCUSSION

5.3.1 Soil Characteristics

Chemical and physical characteristics of the soils at the 1977 and 1978 sites are given in Table 55. In 1977, the site was slightly acidic with a pH of 6.8 whereas in 1978

TABLE 54

Treatments for field experiments near Zhoda

Year	Crops	Carrier	Rate (kg/ha)	Placement	Abbrev.
1977	all	---	---	---	control
1977	barley, flax	CuEDTA	1	(M)	CuEDTA(M)1
1977	barley	CuEDTA	1	(D)	CuEDTA(D)1
1977	barley, flax	ZnEDTA	1.5	(M)	ZnEDTA(M)1.5
1977	barley, flax	$CuSO_4$	1.5	(D)	$CuSO_4$(D)1.5
1977	all	$CuSO_4$	4	(D)	$CuSO_4$(D)4
1977	barley, flax	$CuSO_4$	10	(D)	$CuSO_4$(D)10
1977	barley, flax	$CuSO_4$	4	(M)	$CuSO_4$(M)4
1977	barley, flax	$CuSO_4$ ZnEDTA	4 1.5	(D) (M)	$CuSO_4$(D)4 + ZnEDTA(M)1.5
1978	all	---	---	---	control
1978	barley, flax	CuEDTA	2	(M)	CuEDTA(M)2
1978	barley, oats, wheat	CuEDTA	2	(D)	CuEDTA(D)2
1978	barley, oats, wheat	CuEDTA ZnEDTA	2 5	(D) (D)	CuEDTA(D)2 + ZnEDTA(D)5
1978	flax	CuEDTA ZnEDTA	2 5	(M) (M)	CuEDTA(M)2 + ZnEDTA(M)5
1978	barley	$CuSO_4$	10	(M)	$CuSO_4$(M)10
1978	barley	$CuSO_4$	10	(D)	$CuSO_4$(D)10

the site was calcareous having a $CaCO_3$ equivalent of 7.5% and a pH of 7.9. Nitrate-N was very high at the 1977 site and medium at the 1978 site according to the Manitoba Provincial Soil Testing Laboratory guidelines. Sodium bicarbonate extractable P was high in 1977 and low in 1978. The levels of SO_4-S and NH_4Ac extractable K were medium in 1978. The DTPA extractable soil Cu level in both 1977 and 1978 was 0.3 ug Cu/g soil which was 0.1 ug Cu/g in excess of the soil Cu critical level suggested by Lindsay and Norvell [62]. The DTPA extractable soil Zn level was marginal in 1977 and just adequate in 1978 according to Lindsay and Norvell's [62] guidelines. Levels of DTPA extractable Mn and Fe were above suggested critical levels in both 1977 and 1978.

The addition of macronutrients in both years should have eliminated any shortage of N, P, K or S. Of those nutrients determined only Cu and Zn may have been deficient.

5.3.2 Grain Yields and Nutrient Concentrations

5.3.2.1 1977 Results

The field site in 1977 suffered from a severe infestation of armyworms shortly after barley, oats and wheat headed. This resulted in nearly all leaves being stripped from cereal plants and was felt to be a major contributor to the low cereal crop yields. Although armyworms did not damage the flax, it was harvested before maturity. Unfortunately, flax was harvested at the same time as the cereals, only 83

TABLE 55

Soil characteristics for field experiments at Zhoda in 1977 and 1978

		1977	1978
Classification		Menisino	Pine Ridge
texture		loamy sand	loamy sand
pH		6.8	7.9
O.M. %		2.6	6.3
$CaCO_3$ equivalent %		1.0	7.5
cond (mmhos/cm)		0.75	0.30
NO_3-N (kg/ha 0 -60 cm)		70	48
PO_4-P (kg/ha $NaHCO_3$ 0 - 15 cm)		32	16
SO_4-S (kg/ha H_2O ext 0-60 cm)		---	32
K (kg/ha NH_4Ac pH=7 ext 0-15cm)		---	162
Ca (% NH_4Ac pH=7 ext 0-15)		---	0.82
Mg (% NH_4Ac pH=7 ext 0-15)		---	0.53
Cu (DTPA ext ug/g)	0-15cm	0.3	0.3
	15-30cm	0.2	0.4
	30-60cm	0.3	0.1
Zn (DTPA ext ug/g)	0-15cm	0.7	1.3
	15-30cm	0.2	0.8
	30-60cm	0.1	0.2
Mn (DTPA ext ug/g)	0-15cm	8.2	9.7
Fe (DTPA ext ug/g)	0-15cm	56	32

days after planting. Since no midseason samples were taken for flax no dataare presented here for flax. It is possible that the flax would have matured if harvest had been delayed. However, it is interesting to note that failure to set seed is one of the symptoms of Cu deficiency and the growth chamber study indicated that flax is very susceptible to Cu deficiency.

Barley grain yield and nutrient concentrations in shoots were not influenced significantly by Cu fertilization (Tables 56 and 57). However, it is interesting to note that mixing 4 kg Cu/ha as $CuSO_4$ with the surface soil resulted in the highest plant Cu concentration. Sulfur concentrations in the midseason samples were all below the low level suggested by Ward et al [116] for all treatments other than the control. The combined effect of armyworms infestation and low S concentrations in the shoots were felt to be responsible for the low yields and perhaps partially responsible for the lack of response in yield and plant Cu concentration to Cu fertilization, although large yield responses to Cu fertilization would not be expected since plant Cu concentrations were slightly above the critical level established in the growth chamber study. Plant levels of all nutrients other than S were above suggested critical levels (Tables 56 and 57). It is surprising that plant Zn concentrations were so high in barley as well as oats and wheat when it is considered that the DTPA extractable soil Zn level was about the same as that at Teulon in 1977 and lower than at Teulon in 1978.

TABLE 56

Effect of carrier, placement and rate as well as Zn on grain yield and micronutrient concentrations in barley shoots near Zhoda in 1977

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	2033 a	4.4 a	33 a	34 a
$CuSO_4$(D)1.5	2108 a	3.7 a	30 a	36 a
$CuSO_4$(D)4	2012 a	5.1 a	29 a	34 a
$CuSO_4$(D)10	2072 a	4.2 a	29 a	38 a
$CuSO_4$(M)4	2176 a	7.4 a	37 a	40 a
CuEDTA(M)1	1882 a	5.0 a	30 a	36 a
CuEDTA(D)1	1952 a	3.6 a	37 a	34 a
ZnEDTA(M)1.5	1970 a	4.9 a	32 a	34 a
ZnEDTA(M)1.5 +$CuSO_4$(D)4	2182 a	3.9 a	34 a	40 a

Oat grain yield and plant nutrient concentrations were not influenced by the addition of $CuSO_4$ (Tables 58 and 59). As with barley, the shoot S concentrations were below the low level suggested by Ward et al [116]. The low S and armyworm damage were felt to be major factors in the low

TABLE 57

Effect of Cu carrier, placement and rate as well as Zn on macronutrient concentrations in barley shoots near Zhoda in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	3.8 a	1.5 a	17.2 a	6.1 a	2.7 a
$CuSO_4$(D)1.5	3.6 a	1.4 a	17.5 a	5.4 a	2.5 a
$CuSO_4$(D)4	3.4 a	1.4 a	16.8 a	6.7 a	2.9 a
$CuSO_4$(D)10	3.5 a	1.2 a	17.4 a	5.9 a	2.7 a
$CuSO_4$(M)4	3.9 a	1.4 a	18.7 a	7.0 a	3.2 a
CuEDTA(M)1	3.6 a	1.3 a	19.5 a	6.4 a	2.7 a
CuEDTA(D)1	3.9 a	1.2 a	17.1 a	6.5 a	2.8 a
ZnEDTA(M)1.5	3.9 a	1.3 a	19.7 a	6.1 a	2.6 a
ZnEDTA(M)1.5 +$CuSO_4$(D)4	3.7 a	1.3 a	19.7 a	6.4 a	2.7 a

grain yields. All other nutrients including Cu were above their respective critical levels (Tables 58 and 59) consequently responses to Cu fertilization would not be expected, especially since Cu fertilization did not increase plant Cu concentration.

Wheat grain yield was increased by the addition of 4 kg Cu/ha as $CuSO_4$ drilled with the seed. The yield level was very low due to armyworm damage and a suspected S deficiency. Sulfur concentration in the shoots at midseason har-

TABLE 58

Effect of Cu on grain yield and micronutrient concentrations in oat shoots near Zhoda in 1977

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	1266 a	5.6 a	39 a	60 a
$CuSO_4$(D)4	1430 a	5.4 a	34 a	62 a

TABLE 59

Effect of Cu on macronutrient concentrations in oat shoots near Zhoda in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	3.7 a	1.3 a	18.3 a	5.4 a	2.5 a
$CuSO_4$(D)4	3.8 a	1.3 a	20.2 a	5.2 a	2.4 a

vest for the control was lower than the low levels suggested by Ward et al [116]. Nutrient concentrations were not influenced significantly by the addition of Cu. However, a yield response to Cu fertilization would be expected since Cu concentration increased nonsignificantly from 3.7 ug Cu/g which is in the low range established in the growth chamber study to 5.2 ug Cu/g which is in the sufficiency range. Plant concentrations of all nutrients other than Cu and S were above suggested critical levels.

TABLE 60

Effect of Cu on grain yield and micronutrient concentrations in wheat shoots near Zhoda in 1977

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	1200 a	3.7 a	36 a	34 a
$CuSO_4$(D)4	1352 b	5.2 a	38 a	39 a

TABLE 61

Effect of Cu on macronutrient concentration of wheat at Zhoda in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	3.8 a	1.2 a	19.3 a	4.3 a	2.3 a
$CuSO_4$(D)4	3.9 a	1.5 a	21.1 a	4.3 a	2.4 a

5.3.2.2 1978 Results

All crops experienced very severe hail damage on July 17, 1978 at the soft dough stage of the cereals. The hail damage was at least partially responsible for the low yields and may have contributed to the lack of response in yield to Cu fertilization in all crops.

Copper concentration in barley shoots at midseason was increased by the addition of supplemental Cu to barley (Table 62). Placement of the Cu also had a significant influence. Mixing either CuEDTA or $CuSO_4$ was better at sup-

TABLE 62

Effect of Cu carrier and placement as well as Zn on grain yield and micronutrient concentration in barley shoots near Zhoda in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	2318 a	4.3 d	25 b	20 a	125 ab
CuEDTA(M)2	2067 a	5.5 a	27 b	18 bc	107 b
CuEDTA(D)2	2371 a	5.0 bc	28 b	18 c	110 b
$CuSO_4$(M)10	2135 a	5.2 ab	24 b	18 bc	104 b
$CuSO_4$(D)10	2138 a	4.6 cd	26 b	18 bc	112 b
CuEDTA(D)2 +ZnEDTA(D)5	2245 a	5.2 ab	32 a	19 ab	146 a

plying available Cu to barley than drilling with the seed suggesting that for optimum Cu uptake even CuEDTA should be mixed rather than banded. This result suggested that Cu fertilization might have increased oat and wheat yields more in 1977 if $CuSO_4$ had been mixed with the surface soil instead of drilled with the seed. Copper carriers also influenced plant Cu uptake. Ten kg of Cu as $CuSO_4$ was approximately as effective as 2 kg of Cu as CuEDTA, suggesting that the chelated source was 5 times as effective as $CuSO_4$. Addition of CuEDTA along with ZnEDTA increased both Cu and Zn concentrations. It is not surprising that there was no yield response to Zn fertilization since plant Zn

TABLE 63

Effect of Cu carrier and placement as well as Zn on macronutrient concentrations in barley shoots near Zhoda in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	2.4 a	1.7 a	6.7 a	3.5 a	1.9 a
CuEDTA(M)2	2.5 a	1.6 a	7.3 a	3.4 a	1.9 a
CuEDTA(D)2	2.6 a	1.5 a	6.4 a	3.3 a	1.9 a
$CuSO_4$(M)10	2.5 a	1.5 a	6.9 a	3.3 a	1.8 a
$CuSO_4$(D)10	2.5 a	1.5 a	6.6 a	3.2 a	1.8 a
CuEDTA(D)2 + ZnEDTA(D)5	2.6 a	1.6 a	7.0 a	3.7 a	2.0 a

concentrations were well above the critical level of 12.5 ug Zn/g established for barley by Akinyede [2]. In addition all treatments had shoot Cu concentrations within the sufficiency range established in the growth chamber study. Consequently, even without the hail damage there probably would not have been yield responses to Cu fertilization.

Manganese and Fe concentrations in barley shoots were affected only slightly by treatment. All other nutrients analyzed were not influenced by treatment (Table 63). Shoot concentrations of all nutrients except Mn and K were above suggested critical levels. Manganese concentrations in barley were just in the low range suggested by Ward *et al*

[116]. Therefore, the Mn deficiency was likely only slight and probably did not influence responses to Cu or Zn. Potassium levels in barley shoots were very low which was not expected considering the high soil test results and the fact that 107 kg K_2O/ha was added to ensure sufficient K supply. It will be seen later that the low K levels may have resulted from errors in analysis so that K deficiency probably did not occur and was not limiting the response to Cu or Zn.

Concentration of Fe in oat shoots (Table 64) was decreased by the addition of either CuEDTA or CuEDTA plus ZnEDTA. The cause of that decrease is not known. It probably did not result from dilution since yield was not influenced by Cu fertilization. Plant concentrations of all other nutrients including Cu were not influenced by treatment. Perhaps more Cu and Zn should have been applied or the more efficient mixed application method used. As with barley, the plant concentrations of Mn and K were low. However, for the same reasons given for barley Mn and K deficiencies probably did not limit response to Cu. Plant concentrations of all other nutrients, including Cu were above suggested critical levels (Tables 64 and 65). As with barley, oats suffered from hail damage which definitely decreased yields and may have influenced responses although large responses to Cu would not have occurred since plant Cu levels were just within the sufficiency range and increased only slightly as the result of Cu fertilization.

TABLE 64

Effect of Cu and Zn on grain yield and micronutrient concentrations in oat shoots near Zhoda in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	1773 a	2.7 a	20 a	19 a	93 a
CuEDTA(D)2	1778 a	3.2 a	21 a	18 a	74 b
CuEDTA(D)2 + ZnEDTA(D)5	1664 a	3.5 a	22 a	17 a	73 b

TABLE 65

Effect of Cu and Zn on macronutrient concentrations in oat shoots near Zhoda in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	2.4 a	1.8 a	8.0 a	3.0 a	2.5 a
CuEDTA(D)2	2.5 a	1.9 a	8.7 a	3.5 a	2.8 a
CuEDTA(D)2 + ZnEDTA(D)5	2.3 a	1.7 a	7.6 a	3.0 a	2.5 a

Nutrient concentrations other than Cu in wheat shoots were not influenced by treatment (Tables 66 and 67). Two kg Cu as CuEDTA drilled with the seed increased Cu concentrations in wheat shoots from 3.3 ug Cu/g, in the low range as established in the growth chamber, to 5.2 ug Cu/g, which was in the sufficiency range. The addition of CuEDTA plus ZnEDTA increased shoot Cu concentration to 4.6 ug Cu/g, however, this concentration would still be considered as low. Grain yields were very low, likely as a result of hail damage. The lack of response to Cu may have resulted from hail damage. As with barley and oats, both Mn and K shoot concentrations were low. However, it is felt that deficiencies in Mn and K were not limiting response to Cu. All other nutrients were in sufficient supply for normal growth.

TABLE 66

Effect of Cu and Zn on grain yield and micronutrient concentrations in wheat shoots near Zhoda in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	1550 a	3.3 c	27 a	21 a	173 a
CuEDTA(D)2	1702 a	5.2 a	28 a	20 a	172 a
CuEDTA(D)2 ZnEDTA(D)5	1809 a	4.6 b	31 a	20 a	204 a

TABLE 67

Effect of Cu and Zn on macronutrient concentrations in wheat shoots near Zhoda in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	3.0 a	1.9 a	8.4 a	3.4 a	2.2 a
CuEDTA(D)2	2.9 a	1.9 a	8.8 a	4.0 a	2.6 a
CuEDTA(D)2 ZnEDTA(D)5	2.9 a	1.9 a	7.9 a	4.1 a	2.6 a

Copper concentrations in flax shoots were not influenced significantly by Cu fertilization (Table 68). However, it should be mentioned that the 2.3 ug Cu/g concentration when no Cu was applied would be considered deficient as established in the growth chamber study whereas 3.7 or 4.3 ug Cu/g would be considered sufficient. Flax Zn concentration (Table 68) was increased by the addition of ZnEDTA. However, a large yield increase would not have been expected since plant Zn concentrations were slightly above the critical level suggested by McGregor [68]. Calcium and Mg concentrations were decreased slightly by the CuEDTA plus ZnEDTA treatment (Table 69). However, the causes of those decreases are not known. No other plant nutrient levels were influenced by treatment. Potassium concentrations in flax shoots (Table 69) were very low but for reasons previously mentioned in this section are felt to have no effect on the results. Plant concentrations of all nutrients other than Cu and K were adequate for good growth.

TABLE 68

Effect of Cu and Zn on grain yield and micronutrient concentrations in flax shoots near Zhoda in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	1073 a	2.3 a	13 c	52 a	116 a
CuEDTA(M)2	1106 a	3.7 a	16 b	59 a	129 a
CuEDTA(M)2 + ZnEDTA(D)5	914 a	4.3 a	25 a	49 a	116 a

TABLE 69

Effect of Cu and Zn on macronutrient concentrations of flax shoots near Zhoda in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	2.7 a	2.0 a	7.4 a	11.9 a	4.9 a
CuEDTA(M)2	2.5 a	2.1 a	6.4 a	11.4 a	4.8 a
CuEDTA(M)2 ZnEDTA(M)5	2.1 a	1.9 a	6.3 a	9.6 b	4.0 b

Chapter VI

STUDY IV: THE INFLUENCE OF CU CARRIER, RATE AND PLACEMENT UPON YIELD AND NUTRIENT UPTAKE OF CEREALS AND FLAX ON ORGANIC SOILS

6.1 INTRODUCTION

Organic soils have historically been the most likely of any group of soils to be severely deficient in Cu. Gusta [44] reported a significant increase in wheat yield as a result of Cu fertilization of a shallow organic soil near Stead in 1964. Workers in Minnesota established the need for Cu fertilization of cereal crops in Roseau County, Minnesota about 40 km from Piney. This study was initiated to determine if Cu deficiency in cereal crops and flax also occur on organic soils in Manitoba and to evaluate the relative effectiveness of various Cu fertilizers and placement methods. In 1977, barley, oats, wheat and flax were grown on organic soil near Piney, Manitoba. In 1978, those crops were again grown near the 1977 Piney site. Also in 1978, micronutrients were added to wheat on organic soils near Marchand and Stead.

6.2 METHODS AND MATERIALS

6.2.1 Soil Properties

The field sites at Piney in 1977 and 1978 were on the farm of S. Goodman located at NW 24-1-11E. The soil at the 1977 site was mapped by Mills et al [71] in the Murry Hill series which is a Terric Mesisol. The soil at the 1978 site was placed by Mills et al [71] in the Stead series which is classified as a Typic Mesisol. The field sites at Marchand and Stead in 1978 were located at NW 10-5-8E and SW 32-17-9E, respectively, and were mapped as bog soils but would both be classified as Terric Mesisols.

Analyses of the soils for pH, conductivity, NO_3-N, SO_4-S, NH_4Ac extractable Ca, Mg and K as well as available Cu, Zn, Mn and Fe were all as described in Section 3.2.1. Plant available soil P was estimated in 1977 by the $NaHCO_3$ method described in Section 4.2.1 and in 1978 by the Bray #1 method described in Section 3.2.1. Soil organic matter and carbonate levels were analyzed as described in Section 4.2.1.

6.2.2 Experimental Design

Barley (*Hordeum vulgare* var Conquest), oats (*Avena sativa* var Harmon), wheat (*Triticum aestivum* var Neepawa) and flax (*Linum usitatissimum* var Dufferin) were seeded at Piney on May 24 in 1977. Barley was seeded on May 15 in 1978 whereas oats (*Avena sativa* var Hudson) and flax were seeded on May 16 near Piney. Flax was killed by frost on June 10th, 1978, so that no experimental results were obtained. Barley, oats and wheat were severely set back by that frost but totally recovered so that final yields were not affected. Wheat was seeded in separate experiments near Piney as well as Marchand and Stead on May 16, May 22 and 23 and May 29, 1978, respectively.

All crops except wheat in 1978 at Piney received the same macronutrient treatments as outlined in Section 4.2.2. The wheat experiments in 1978 at Piney, Marchand and Stead received 120 kg N/ha mostly as NH_4NO_3. The remaining N was applied with the phosphate as $NH_4H_2PO_4$ at a rate of 50 kg P_2O_5/ha. Sulfur was applied to wheat in 1978 as elemental sulfur (90% S) at a rate of 50 kg S/ha and K as KCl at a rate of 180 kg K_2O/ha. The P fertilizer was drilled with the seed whereas the other macronutrients were broadcast immediately after seeding.

The treatments used for all crops in 1977 and for barley and oats in 1978 are given in Table 70. Treatments for the wheat experiments at Piney, Marchand and Stead in 1978 are listed in Table 71. Method of application of Cu and $ZnSO_4$ in the wheat experiment differed from that in other field experiments. They were broadcast in fine crystalline form and mixed with surface 10 cm by rototilling prior to seeding. Plot size, arrangement and replication as well as seeding rates and weed control were the same as those at Teulon and Zhoda.

TABLE 70

Treatments for field experiments at Piney in 1977 and 1978

Year	Crops	Carrier	Rate (kg/ha)	Placement	Abbrev.
1977	barley, wheat	---	---	---	control
1977	barley	CuEDTA	1.5	(M)	CuEDTA(M)1.5
1977	barley	CuEDTA	1.5	(D)	CuEDTA(D)1.5
1977	barley	$CuSO_4$	2.5	(D)	$CuSO_4$(D)2.5
1977	barley, wheat	$CuSO_4$	7	(D)	$CuSO_4$(D)7
1977	barley	$CuSO_4$	17	(D)	$CuSO_4$(D)17
1977	barley	$CuSO_4$	7	(M)	$CuSO_4$(M)7
1978	barley, oats	---	---	---	control
1978	barley	CuEDTA	2	(M)	CuEDTA(M)2
1978	barley, oats	CuEDTA	2	(D)	CuEDTA(D)2
1978	barley, oats	CuEDTA $MnSO_4$	2 1	(D) foliar	CuEDTA(D)2 + 1kg Mn/ha foliar
1978	barley	$CuSO_4$	10	(M)	$CuSO_4$(M)10
1978	barley	$CuSO_4$	10	(D)	$CuSO_4$(D)10

Midseason samples of all crops were taken when cereals were at the heading stage or about 50 days after seeding. Sampling and analytical procedures were identical to those for studies at Zhoda and Teulon. Barley, wheat and flax were harvested 93 days after seeding in 1977 and 98, 109 and 108 days after seeding in 1978 for barley, oats and wheat,

TABLE 71

Treatments used for wheat grown on organic soil at Piney, Marchand and Stead in 1978

Treatment number	broadcast Cu kg/ha (as $CuSO_4$)	broadcast Zn kg/ha (as $ZnSO_4$)	foliar Mn kg/ha (as $MnSO_4$)
1	0	0	0
2	10	20	1
3	10	20	0
4	10	0	1
5	0	20	1

respectively. Harvesting procedures were identical to those for the other field studies.

6.3 RESULTS AND DISCUSSION

6.3.1 Soil Characteristics

Some soil characteristics and available nutrients are listed in Table 72 for Piney in 1977 and 1978 and in Table 73 for Marchand and Stead in 1978. Bulk densities of all soils were very low being approximately one tenth the bulk density of a typical mineral soil. Soil pH at the Piney site in 1977 and 1978 was slightly above neutral. Soil at the Marchand site in 1978 had a pH of 7.7 which likely resulted from the 4.4% $CaCO_3$ equivalent in that soil. Soil at the Stead site had a pH which was slightly acid. Soil at the Piney site was high in NO_3-N in 1977 and low in NO_3-N in 1978 according to Manitoba Provincial Soil Testing Laboratory guidelines. Phosphate-P in 1977 was determined by $NaHCO_3$ extraction and would be considered as very low. Soil PO_4-P in 1978 at all sites was determined by the Bray #1 method and was very low. Levels of SO_4-S were not determined in 1977 at Piney, but in 1978 the soil SO_4-S level at Piney was medium and the levels at Marchand and Stead were very high. Soil K availability was not estimated in 1977 but was very low at Piney, Marchand and Stead in 1978. Macronutrient deficiencies should not have occurred, however, since macronutrient fertilizer levels were high. Availability of Cu, Zn, Mn and Fe were estimated by DTPA extraction with a 1 to 10 instead of 1 to 2 soil to solution ratio. Because of the different ratio and because the bulk densities of the soils were also approximately one tenth that of a typical mineral soil, comparison to suggested critical levels for mineral soils is virtually impossible.

6.3.2 Yields and Nutrient Concentration

6.3.2.1 1977 Results

Barley grain yields were very high and were not influenced by treatment (Table 74). Although shoot Mn concentrations were just in the upper portion of the low range according to the guidelines of Ward *et al* [116], plant levels of all other nutrients including Cu were adequate for

TABLE 72

Soil characteristics and available nutrients for field studies at Piney in 1977 and 1978

		1977	1978
Classification		Terric mesisol	typic mesisol
bulk density (g/cm^3)		0.14	0.14
pH		7.3	7.1
O.M. %		---	77
cond (mmhos/cm)		0.21	0.28
NO_3-N (kg/ha 0-60 cm)		66	15
PO_4-P (kg/ha $NaHCO_3$ 0-15 cm)		7.2	---
PO_4-P (kg/ha Bray #1 0-15 cm)		---	1.1
SO_4-S (kg/ha H_2O ext 0-60 cm)		---	25
K (Kg/ha NH_4Ac pH=7 ext 0-15 cm)		---	46
Ca (% NH_4Ac pH=7 ext 0-15 cm)		---	0.67
Mg (% NH_4Ac pH=7 ext 0-15 cm)		---	0.28
Cu (DTPA ext ug/g)	0-15cm	1.6	0.6
	15-30cm	2.0	0.8
	30-60cm	1.7	0.5
Zn (DTPA ext ug/g)	0-15cm	4.1	15
	15-30cm	1.5	1.9
	30-60cm	1.8	1.1
Mn (DTPA ext ug/g)	0-15cm	24	102
Fe (DTPA ext ug/g)	0-15cm	195	384

TABLE 73

Soil characteristics and available nutrients for field studies at Marchand and Stead in 1978

		Marchand	Stead
Classification		Terric mesisol	Terric mesisol
bulk densities (g/cm^3)		0.16	0.13
pH		7.7	6.5
O.M. %		64	82
cond (mmhos/cm)		1.1	0.8
$CaCO_3$ equivalent %		4.4	---
NO_3-N (kg/ha 0-60 cm)		100	41
PO_4-P (kg/ha Bray #1 0-15 cm)		0.4	3.7
SO_4-S (kg/ha H_2O ext 0-60 cm)		381	898
K (kg/ha NH_4Ac pH=7 ext 0-15 cm)		19	77
Ca (% NH_4Ac pH=7 ext 0-15 cm)		1.3	0.67
Mg (% NH_4Ac pH=7 ext 0-15 cm)		0.34	0.38
Cu (DTPA ext ug/g)	0-15cm	1.0	1.0
	15-30cm	1.3	1.0
	30-60cm	0.3	1.6
Zn (DTPA ext ug/g)	0-15cm	3.6	9.7
	15-30cm	2.3	7.3
	30-60cm	0.2	3.3
Mn (DTPA ext ug/g)	0-15cm	30	129
Fe (DTPA ext ug/g)	0-15cm	470	253

good plant growth. Therefore, it is not surprising that there were no responses to Cu fertilization. This points out once again that barley is relatively resistant to Cu deficiency. The very high barley yields suggest that Mn deficiency was only very slight. Although plant Cu levels were influenced by treatment, Cu fertilization had no influence on plant levels of other nutrients. Mixing $CuSO_4$ or CuEDTA with the soil was much more effective in increasing plant Cu concentration than drilling those carriers with the seed which was totally ineffective in increasing Cu uptake. Those results would be expected for $CuSO_4$ but not for CuEDTA which is usually much more mobile in soil than $CuSO_4$. Perhaps the CuEDTA was not as stable in the organic soil as in mineral soil. This would not be surprising considering that Cu readily forms insoluble complexes with organic matter. The chelated form of Cu appeared to be about 5 times as effective as $CuSO_4$ considering that plant Cu concentrations were the same when 7 kg Cu/ha as $CuSO_4$ or 1.5 kg Cu/ha as CuEDTA were mixed with the surface soil.

Wheat grain yield and nutrient concentrations were not influenced by the addition of 7.0 kg Cu/ha as $CuSO_4$ drilled with the seed (Tables 76 and 77). The grain yield was quite low and definitely not near potential yield. Copper concentration in wheat shoots were in the low range of 3.0 to 4.9 ug Cu/g as suggested in the growth chamber study. Manganese concentrations in wheat shoots were just in the upper por-

TABLE 74

Effect of placement, carrier and rate of Cu on grain yield and micronutrient concentrations in barley shoots at Piney in 1977

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	4721 a	4.1 b	33.2 a	24.6 a
$CuSO_4$(D)2.5	5199 a	4.4 b	35.7 a	25.5 a
$CuSO_4$(D)7	5195 a	5.0 b	33.1 a	21.3 a
$CuSO_4$(D)17	5241 a	5.3 b	32.4 a	20.0 a
$CuSO_4$(M)7	5001 a	8.4 a	33.3 a	20.9 a
CuEDTA(M)1.5	4732 a	8.9 a	43.4 a	19.6 a
CuEDTA(D)1.5	5135 a	5.9 b	34.0 a	21.0 a

tion of the low range of 5-24 ug Mn/g as suggested by Ward et al [116]. Thus, the ineffectiveness of the drilled application of $CuSO_4$ and perhaps a slight Mn deficiency were probably responsible for the low yields. Frost injury also occurred but since barley yielded extremely well and flax was not destroyed by the frost, frost was probably not the major contributor to the low yield of wheat.

Flax was unfortunately harvested before maturity at the Piney site in 1977 and therefore total dry matter yield at the end of the growing season instead of grain yield is reported in Table 78. Neither dry matter yield nor plant

TABLE 75

Effect of placement, carrier and rate of Cu on macronutrient concentrations in barley shoots at Piney in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	4.7 a	2.0 a	20.2 a	9.3 a	3.8 a
$CuSO_4$(D)2.5	4.9 a	1.9 a	18.8 a	8.9 a	3.8 a
$CuSO_4$(D)7	4.5 a	1.9 a	17.2 a	8.4 a	3.5 a
$CuSO_4$(D)17	4.5 a	2.1 a	18.1 a	8.6 a	3.5 a
$CuSO_4$(M)7	4.7 a	2.0 a	18.6 a	8.4 a	3.5 a
CuEDTA(M)1.5	4.7 a	1.9 a	18.2 a	8.2 a	3.4 a
CuEDTA(D)1.5	4.2 a	1.8 a	18.7 a	7.5 a	3.19 a

concentrations of nutrients were influenced significantly by treatment (Tables 78 and 79). All nutrient concentrations, including Cu, would be considered sufficient for normal growth.

No grain yield is reported for oats at Piney in 1977 because they were destroyed by rust. However, midseason samples were taken and nutrient concentrations are reported in Tables 80 and 81. Addition of Cu as $CuSO_4$ drilled with the seed did not influence nutrient concentrations. Plant concentrations of all nutrients other than Mn were sufficient for normal growth. Plant Mn levels were just slightly below the sifficiency level established by Ward <u>et al</u> [116].

TABLE 76

Effect of Cu on grain yield and micronutrient concentrations in wheat shoots at Piney in 1977

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	1284 a	3.8 a	38.3 a	23.2 a
$CuSO_4$(D)7	1417 a	3.1 a	39.3 a	22.6 a

TABLE 77

Effect of Cu on macronutrient concentrations in wheat shoots at Piney in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	4.6 a	1.6 a	22.5 a	5.0 a	3.2 a
$CuSO_4$(D)7	5.0 a	1.8 a	18.6 a	4.7 a	3.3 a

However, it is unlikely that a deficiency in Mn or any other nutrient contributed significantly to the failure of the oats to yield.

6.3.2.2 1978 Results

Barley grain yield and plant concentrations of Mn, Fe, P, S and K were not influenced by treatment (Tables 82 and 83). Zinc, Ca and Mg concentrations were increased slightly by all Cu treatments except CuEDTA(M). The cause of those

TABLE 78

Effect of placement and carrier of Cu on dry matter yield and micronutrient concentrations in flax shoots at Piney in 1977

Treatment	dry matter yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	7126 a	3.5 a	31.2 a	54.7 a
$CuSO_4$(D)7	8117 a	5.0 a	36.2 a	49.7 a
$CuSO_4$(M)7	9917 a	5.7 a	33.9 a	58.6 a
CuEDTA(M)1.5	9213 a	6.3 a	35.7 a	41.7 a

TABLE 79

Effect of placement and carrier of Cu on macronutrient concentrations in flax shoots at Piney in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	4.6 a	2.3 a	19.7 a	10.0 a	4.9 a
$CuSO_4$(D)7	4.6 a	2.0 a	18.6 a	9.2 a	4.3 a
$CuSO_4$(M)7	4.3 a	2.1 a	18.4 a	9.4 a	4.5 a
CuEDTA(M)1.5	4.5 a	2.1 a	20.3 a	9.4 a	4.4 a

increases is not known. It may have been a synergistic effect, but that would not explain increases in Zn, Ca and Mg concentrations in treatment $CuSO_4$(D)10 when there was no increase in plant Cu concentration. Shoot concentrations of Cu were influenced by both Cu carrier and placement method.

TABLE 80

Effect of Cu on grain yield and micronutrient concentrations in oat shoots at Piney in 1977

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g
control	no	3.6 a	37.7 a	23.7 a
$CuSO_4$(D)7	yield	4.0 a	38.8 a	23.1 a

TABLE 81

Effect of Cu on macronutrient concentrations in oat shoots at Piney in 1977

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	4.5 a	2.3 a	14.8 a	4.3 a	3.8 a
$CuSO_4$(D)7	4.2 a	2.3 a	17.9 a	3.6 a	3.7 a

Plant Cu concentration in the control treatment was in the low range according to guidelines established in the growth chamber experiment whereas plant Cu concentrations in all treatment which included supplemental Cu were in the sufficient range. However, the corresponding increases in grain yield were not statistically significant because of non-treatment variation. The influence of Cu fertilizer placement on Cu uptake was similar to that at Zhoda in 1978 and Piney in 1977. Mixing CuEDTA or $CuSO_4$ with the surface 10 cm was superior to drilling either source with the seed although the difference was much greater for $CuSO_4$ than for CuEDTA. Mixing 2 kg Cu/ha as CuEDTA was the most effective treatment, significantly better than mixing 10 kg Cu/ha as $CuSO_4$. This indicated that CuEDTA was at least 5 times more efficient than $CuSO_4$. When both sources were drilled with the seed, CuEDTA was considerably more than 5 times as effective as $CuSO_4$ since drilling $CuSO_4$ was almost totally ineffective. Manganese concentrations were lower than in any other experiments and may have slightly limited response to Cu fertilization. The low K concentration likely resulted from errors in analysis which will be discussed later. The application of Mn as a foliar spray of $MnSO_4$ did not significantly increase grain yield. This may have resulted from applying Mn after heading or perhaps the Mn deficiency was only slight. Since Mn was applied after the midseason harvest, plant Mn concentration at heading was not increased by foliar application.

Oat grain yields and shoot nutrient concentrations other than Cu were not influenced by treatment (Tables 84 and 85). The addition of 2 kg Cu/ha as CuEDTA drilled with the seed increased oat shoot Cu concentration from 1.8 ug Cu/g for the control to either 3.6 or 3.4 ug Cu/g for treatments including Cu. The control treatment shoot concentration was the same as the upper limit of the deficiency range that was established in the growth chamber study whereas plant Cu concentrations in oats receiving Cu were in the sufficiency

TABLE 82

Effect of Cu placement and carrier as well as Mn on grain yield and micronutrient concentrations in barley shoots at Piney in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	2747 a	3.3 e	33 d	16 a	55 a
CuEDTA(M)2	3170 a	6.8 a	35 cd	15 a	49 a
CuEDTA(D)2	3100 a	5.7 c	37 bc	16 a	51 a
$CuSO_4$(M)10	2922 a	6.2 b	36 bcd	14 a	50 a
$CuSO_4$(D)10	3211 a	3.7 d	38 ab	16 a	56 a
CuEDTA(D)2 +foliar Mn	3277 a	5.4 c	40 a	16 a	51 a

range. The nonsignificant yield increase likely resulted at least partially from the relatively high field variability. However, a slight Mn deficiency may have also limited response in yield to Cu fertilization. Although oat shoot concentrations of Mn and K were low, Mn concentration likely resulted in only a slight restriction in response whereas low K concentration was likely a result of an error in analysis.

TABLE 83

Effect of Cu placement and carrier as well as Mn on macronutrient concentrations in barley shoots at Piney in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	3.5 a	2.1 a	8.2 a	4.4 b	2.0 b
CuEDTA(M)2	3.6 a	2.3 a	8.0 a	4.3 b	2.0 b
CuEDTA(D)2	3.2 a	2.2 a	8.0 a	5.4 a	2.9 a
$CuSO_4$(M)10	3.4 a	2.2 a	8.0 a	5.3 a	2.9 a
$CuSO_4$(D)10	3.2 a	2.2 a	7.8 a	5.3 a	2.9 a
CuEDTA(D)2 +foliar Mn	3.1 a	2.1 a	7.7 a	5.2 a	2.9 a

6.3.2.3 1978 Wheat Experiment Results

Copper fertilization increased wheat grain yield at Piney (Table 86), but Zn and Mn fertilization did not influence yields. Those results emphasized again the extreme sensitivity of wheat to Cu deficiency. Although yield was increased by Cu, all yields were very low. Apparently not enough Cu was applied to correct Cu deficiency, since all plant Cu concentrations were in the deficiency range as established in the growth chamber study. Lack of response in grain yield to Zn was not surprising since all plant Zn concentrations were adequate. Manganese concentrations were low although not as low as in barley or oats at Piney.

TABLE 84

Effect of Cu and Mn on grain yield and micronutrient concentrations in oat shoots at Piney in 1978

Treatment	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
control	2113 a	1.8 b	25 a	16 a	50 a
CuEDTA(D)2	3184 a	3.6 a	28 a	19 a	48 a
CuEDTA(D)2 +foliar Mn	2793 a	3.4 a	28 a	18 a	50 a

TABLE 85

Effect of Cu and Mn on macronutrient concentrations in oat shoots at Piney in 1978

Treatment	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
control	2.7 a	2.7 a	9.0 a	3.0 a	2.1 a
CuEDTA(D)2	2.6 a	2.4 a	8.1 a	2.7 a	1.9 a
CuEDTA(D)2 +foliar Mn	2.8 a	2.8 a	8.8 a	2.9 a	2.0 a

Plant manganese concentrations were not influenced by Mn fertilization because the midseason harvest occurred before Mn was applied. Manganese may have limited yields, however that seems unlikely since yields were no higher when Mn was applied with Cu than when Cu was applied alone. On the other hand, yield may not have been increased by Mn because it was applied rather late in the season. As with other crops, the low plant K levels likely resulted from an analytical error. Plant concentrations of nutrients other than Cu, Mn and K were adequate for good plant growth (Tables 86 and 87). Plant concentrations of all nutrients except K varied significantly among treatments. Variation in Cu concentration was consistently related to Cu treatment. Zinc concentration was significantly increased in every treatment which received added Zn. Iron, P, S, Ca and Mg concentrations were often lower in treatments which included added Cu, likely as a result of dilution caused by increased yields.

Experimental results at Marchand and Stead were similar to those at Piney with a few notable exceptions. Both yields and plant Cu concentrations were lower at Marchand (Table 88) and particularily at Stead (Table 90) than at Piney. Yields at Stead where no Cu was applied were zero, whereas where Cu was applied there was some yield both of dry matter and grain. However, the small amount of grain which was produced was certainly not viable and therefore no values are listed in the Table 90 for treatments 2, 3 and 4. For the most part, plant concentrations of nutrients did not vary as much at Marchand (Tables 88 and 89) and Stead (Tables 90 and 91) as they did at Piney. Foliar application of Mn at Marchand and Stead increased plant Mn concentrations (Tables 88 and 90) because Mn was applied before the midseason sampling. At Marchand application of both Zn and Mn without Cu accentuated Cu deficiency. No visual Cu

TABLE 86

Effect of micronutrients on grain yield and micronutrient concentrations in wheat shoots at Piney in 1978

Treatment number	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
1	847 b	1.7 b	29 c	22 a	58 a
2	1770 a	2.8 a	42 b	17 b	45 c
3	2084 a	2.6 a	41 b	16 b	48 bc
4	1656 a	2.9 a	27 c	21 a	52 abc
5	944 b	1.9 b	48 a	19 ab	55 ab

TABLE 87

Effect of micronutrients on macronutrient concentrations in wheat shoots at Piney in 1978

Treatment number	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
1	3.2 a	2.0 ab	8.4 a	2.4 abc	1.8 ab
2	2.6 b	1.8 b	9.1 a	2.4 abc	1.7 abc
3	2.7 b	1.8 b	8.8 a	2.2 bc	1.6 bc
4	2.6 b	2.0 ab	9.4 a	2.1 c	1.5 c
5	3.2 a	2.3 a	8.9 a	2.6 a	1.9 a

deficiency symptoms occurred when no micronutrients were added (treatment #1) although yield was lower than when Cu was applied. Application of Mn and Zn without Cu resulted in visual Cu deficiency symptoms and the lowest grain yield.

TABLE 88

Effect of micronutrients on grain yield and micronutrient concentrations in wheat shoots at Marchand in 1978

Treatment number	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
1	341 bc	1.4 a	28 a	14 b	103 a
2	655 a	1.5 a	33 a	152 a	86 a
3	614 ab	1.3 a	36 a	15 b	110 a
4	917 a	1.4 a	31 a	160 a	100 a
5	75 c	1.3 a	35 a	163 a	115 a

TABLE 89

Effect of micronutrients on macronutrient concentrations in wheat shoots at Marchand in 1978

Treatment number	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
1	3.0 a	2.1 a	7.0 a	2.0 a	2.2 a
2	2.7 a	2.0 a	8.0 a	2.1 a	2.1 a
3	2.8 a	2.1 a	7.4 a	2.3 a	2.3 a
4	2.9 a	2.2 a	7.4 a	2.1 a	2.1 a
5	3.1 a	2.3 a	8.0 a	2.3 a	2.3 a

TABLE 90

Effect of micronutrient treatments on grain yield and micronutrient concentrations in wheat shoots at Stead in 1978

Treatment number	grain yield kg/ha	Cu conc. ug/g	Zn conc. ug/g	Mn conc. ug/g	Fe conc. ug/g
1	0	1.3 a	32 b	47 c	87 a
2	---	1.5 a	42 a	119 b	82 a
3	---	1.3 a	37 a	38 c	74 a
4	---	1.5 a	28 b	124 b	81 a
5	0	1.0 a	42 a	148 a	91 a

TABLE 91

Effect of micronutrients on macronutrient concentrations in wheat shoots at Stead in 1978

Treatment number	P conc. mg/g	S conc. mg/g	K conc. mg/g	Ca conc. mg/g	Mg conc. mg/g
1	5.6 a	2.1 a	7.0 a	2.0 a	2.2 a
2	3.9 b	1.9 a	8.0 a	2.1 a	2.1 a
3	4.1 b	1.8 a	7.4 a	2.3 a	2.3 a
4	3.7 b	1.8 a	7.4 a	2.1 a	2.1 a
5	5.5 a	2.1 a	8.0 a	2.3 a	2.3 a

Chapter VII

GENERAL DISCUSSION

7.1 GROWTH CHAMBER STUDY

The growth chamber study was conducted to determine Cu nutritional ranges for barley, oats, wheat, flax and rapeseed. The soil used in that experiment was known to be severely Cu deficient from field work near Stead in 1978 which is reported in Study IV. Thus, it was quite certain that Cu deficiency would occur when no Cu was added and it was hoped that complete Cu growth reponse curves from severely deficient to totally sufficient could be obtained. That was the case with the possible exception of wheat which may not have received quite enough Cu to achieve maximum yield.

The concentration ranges corresponding to low nutritional status were 2.3 to 3.7, 1.7 to 2.5, 3.0 to 4.9, 2.4 to 3.5 and 1.7 to 2.7 ug Cu/g plant material for barley, oats, wheat, flax and rapeseed, respectively. Shoot concentrations below those ranges were considered Cu deficient and concentrations above those ranges were considered Cu sufficient. The low ranges for barley and oats were lower than those given by Ward et al [116]. In addition, the low range for barley was considerably lower than the critical level suggested by Akinyede [2] of 5.2 ug Cu/g. However, the Cu nutritional ranges for oats would be in fair agreement with Gupta and MacLeod's [43] optimal level of 3.2 - 3.3 ug Cu/g. The low range for wheat agreed very well with the critical level of Melsted et al [70] and Ward et al [116] of 5 ug Cu/g plant material. The critical level suggested by McGregor [68] for flax shoots of 3.0 ug Cu/g was in good agreement with the low range established in the growth chamber study. It is not surprising that the Cu nutritional levels established in this study did not always agree with those in the literature since critical concentrations vary with crop variety and environmental conditions.

The ranking of the crops in the growth chamber study from most to least tolerant to Cu deficiency was rapeseed > barley > oats > wheat > flax. This ranking should help farmers decide which crops to grow on soils suspected of being low in available Cu and give them some idea as to which crops would be expected to respond the most to Cu fertilization. Rapeseed, barley and oats would likely grow fairly well on soils low in available Cu but would probably respond to Cu fertilization on soils extremely deficient in Cu. Wheat and flax are very intolerant of Cu stress and should not be grown on soils low in available Cu without supplemental Cu fertilization.

The visual symptoms of Cu deficiency in cereals were typical of Cu deficiency symptoms reported by other workers

[94]. Copper deficiency symptoms in flax included interveinal chlorosis followed by necrosis of lower leaves of the older stems. These symptoms were completely alleviated by addition of Cu. Moraghan and coworkers [73,74] observed virtually identical symptoms in flax in the greenhouse. Those symptoms were eliminated by the addition of 2 ug Fe/g soil as FeEDDHA. However, the application of Fe resulted in only a 0.43 g/pot dry matter yield increase, considerably lower than the yield increases obtained in the growth chamber study. Volumes of soil and number of plants per pot were similiar in both experiments. It is possible that the FeEDDHA increased the availability of soil Cu or that increased uptake of Fe encouraged the plant to take up more Cu. If Moraghan's flax was suffering from Cu deficiency, it is evident that the deficiency was not totally corrected. Unfortunately plant Cu levels were not reported in Moraghan's papers [73,74] and the symptoms were attributed to a Mn toxicity which was alleviated by the increase in the availability of Fe.

Concentrations of P and K in the shoots of most crops in the growth chamber were often slightly below critical levels reported in the literature and may have limited responses to Cu fertilization. However, since yields in the growth chamber experiments were very high and responses to Cu fertilization followed typical response curves it is felt that low P and K levels did not interfere significantly with the study.

7.2 FIELD STUDIES

The objectives of the field studies were to evaluate the need for Cu and Zn fertilization on Manitoba soils and to determine the most efficient carriers and placement methods for Cu and Zn. The soils chosen for these studies were felt to be typical of the groups of soils upon which deficiencies of Cu or Zn would be most likely to occur and if responses were not obtained on the soils chosen it could be assumed that Cu and Zn deficiencies were not likely in Manitoba.

7.2.1 Zinc Studies

The field studies at Teulon in 1977 and 1978 were designed to evaluate the need for Zn fertilization on a highly calcareous soil, low in available Zn. Yields were not increased by Zn fertilization in either year although plant Zn uptake increased nonsignificantly in 1977 and significantly in 1978. The lack of yield responses was not surprising since plant Zn concentrations in the control treatments were usually above suggested critical levels. The DTPA extractable soil Zn level in 1978 (1.8 ug Zn/g) was above the critical level of 0.8 ug Zn/g soil suggested by Lindsay and Norvell [62]. In 1977, however, the DTPA level (0.8 ug Zn/g soil) was equal to Lindsay and Norvell's critical level. In 1976, Zn was applied to barley, wheat and flax on Lakeland clay loam containing only 0.4 ug DTPA extractable Zn/g [63]. Plant Zn concentrations were increased but yields were not influenced by Zn fertilization. Plant Zn concentrations in the control treatments were above suggested critical levels. It probably can be concluded that Zn deficiency in wheat, oats, barley, flax and rapeseed is not very likely in Manitoba.

MacGregor _et al_ [65] reported that plowed down $ZnSO_4$ increased corn yields more than banding the same amount of $ZnSO_4$. In both growth chamber [47] and field experiments [69] with blackbeans, mixing $ZnSO_4$ was more effective in increasing plant Zn uptake than sidebanding. In the growth chamber, mixing $ZnSO_4$ was more effective in increasing Zn uptake into barley shoots than banding with the seed [2]. However, placement of $ZnSO_4$ had no influence on barley yields or plant Zn uptake in the experiments at Teulon. The reasons for method of $ZnSO_4$ placement not influencing Zn uptake at Teulon is not known. In contrast to the results for $ZnSO_4$, in 1978 mixing ZnEDTA with the surface 10 cm increased Zn concentrations in barley shoots more than banding ZnEDTA with the seed. Although Zn complexed by EDTA is much less subject to reaction with other substances than Zn in $ZnSO_4$, it is apparent that a significant portion of the Zn from ZnEDTA was involved in the same kinds of reactions with soil components as Zn from $ZnSO_4$. Although the results in the field experiments with barley did not suggest that $ZnSO_4$ should be mixed rather than banded, the growth chamber experiment with barley and all experiments with blackbeans suggested that $ZnSO_4$ should be well mixed with the surface soil for optimal efficiency. The field experiment at Teulon with barley suggested that the same recommendation should be made for ZnEDTA. It should be noted that the mixed treatments for both $ZnSO_4$ and $CuSO_4$ involved dissolving the compounds in water, spraying onto the soil followed by thorough mixing. Mixing even fine crystalline $ZnSO_4$ or $CuSO_4$ may not be as effective as will be seen later when results from the organic field trials are discussed.

The superiority of ZnEDTA over inorganic sources has been well documented in the literature. Schnappinger _et al_ [101] reported that ZnEDTA was approximately 1.6 times more effective than $ZnSO_4 \cdot H_2O$ when both source were broadcast and worked into the surface 8 cm of Zn deficient soil. Boawn [11] indicated that ZnEDTA was approximately 2 to 2.5 times as effective as $ZnSO_4$, regardless of placement. ZnEDTA was more efficient than $ZnSO_4$ in several blackbean field experiments conducted in Manitoba during 1976 [64] and 1977 [69]. The barley experiment at Teulon also indicated that ZnEDTA when mixed with the surface 10 cm of soil or banded with the seed was more than 3 times as effective as $ZnSO_4 \cdot 7H_2O$ at increasing concentration of Zn in barley shoots at the heading stage.

Potassium levels in all crops from all field sites in 1978 were low, suggesting that all crops were deficient in K. This may not in fact have been the case. All field samples in 1978 were analyzed for Cu, Zn, Mn and Fe in October and November of 1978 and 10 ml aliquots of the diluted perchloric acid digests stored until assayed for K, Ca, Mg, P and S in January of 1979. More recently it has been found that after more than 3 weeks storage, K in plant sample digests is precipitated or coprecipitated out of solution. The amount of K taken out of solution in this manner can be very substantial, possibly 50% of that originally present. Since plant sample digests from the 1978 field studies were stored for 1 to 2 months, it is believed that the reported K levels were erroneously low. Since this error was discovered only recently the field samples have not been re-analyzed.

The DTPA extractable Zn levels in the surface 15 cm at Teulon in 1976, 1977, and 1978 were 0.4, 0.8 and 1.8 ug Zn/g soil, respectively. In none of those years were there yield responses to Zn fertilization in wheat, oats, barley, flax and rapeseed although according to Lindsay and Norvell's [62] guidelines the Zn levels were deficient, marginal and adequate in 1976, 1977, and 1978, respectively. Hedayat [47] reported that Zn fertilization in the growth chamber increased grain yields of fababeans and blackbeans grown on soils containing 0.8 and 0.4 ug DTPA extractable Zn/g soil, respectively. Akinyede [2] reported increases in both dry matter production and Zn concentration in shoots of six week old barley in a growth chamber study on Lakeland clay loam containing 1.0 ug DTPA extractable Zn/g soil. Zinc fertilization increased grain yield of blackbeans grown in 1976 on Hordean clay loam containing 1.0 ug DTPA extractable Zn/g soil but did not significantly increase yields in two other experiments in which the soils contained 1 and 1.4 ug DTPA extractable Zn/g soil [64]. In 1977, however Zn fertilization did not increase blackbean grain yields on soils containing 0.58 and 0.51 ug DTPA extractable Zn/g soil, well below Lindsay and Norvell's 0.8 ug Zn/g soil critical level [69]. In most of the aforementioned experiments Zn fertilization did increase plant Zn concentrations. However, when there were no responses to Zn fertilization, plant Zn levels in the control treatments were usually above suggested critical levels. Thus, it would appear that Lindsay and Norvell's critical level may be valid for crops grown in the environmental chamber. However, it would appear that the critical level in the field is lower than 0.8 ug Zn/g soil, even for crops such as blackbeans which are very susceptible to Zn deficiency.

7.2.2 Copper Studies on Mineral Soils

Field studies near Zhoda on mineral soils most likely to be deficient in Cu were conducted to determine the extent and severity of Cu deficiency in Manitoba. However, results to the studies were inconclusive. Barley appeared to respond in yield to Cu fertilization in field studies in 1976 on soil containing 0.6 ug DTPA extractable Cu/g soil [63].

However, in that experiment wind erosion shortly after seeding was possibly responsible for blowing away a broadcast application of K_2SO_4. The apparent response to Cu may have been a response to the S in $CuSO_4$. Unfortunately, plant S levels were not determined in 1976. Also, drought severely restricted growth in 1976. The field study at Zhoda in 1977 suffered from an infestation of armyworms as well as slight S deficiency both of which may have limited response in yield to Cu fertilization. The field experiment at Zhoda in 1978 suffered severe hail damage, again decreasing yields. Greenhouse and growth chamber results with sandy soils from these areas have been more conclusive. McGregor [68] reported increases in both yield and Cu concentrations in flax shoots as a result of addition of 1.0 ug Cu/g soil in a pot experiment with a Pine Ridge soil which had DTPA (pH=7, 1 hour shaking) extractable Cu level of 0.2 ug Cu/g soil. Akinyede [2] working with barley in the growth chamber on Pine Ridge sand containing 0.56 ug DTPA extractable Cu/g soil found that Cu fertilization increased dry matter yields of six week old shoots slightly but resulted in substantial increases in shoot Cu concentration. The yield increase was surprising since the DTPA extractable soil Cu level was well above the critical level suggested by Lindsay and Norvell [62]. However, further field experimentation would have to be conducted in order to accurately determine the extent and severity of Cu deficiency on mineral soils in Manitoba.

The field sites in both 1977 and 1978 had DTPA extractable Cu levels of 0.3 ug Cu/g soil which were slightly in excess of the soil critical level of 0.2 ug Cu/g soil suggested by Lindsay and Norvell [62]. Barley shoot Cu concentrations in 1977 were generally higher than the control for those treatments in which the Cu source was mixed throughout the soil surface although those differences were not significant. The experiments in 1978 were slightly more successful since shoot Cu concentrations of barley and wheat were significantly increased by Cu fertilization. Placement methods and carrier also influenced response of barley shoot Cu concentrations to Cu fertilization. Mixing either CuEDTA or $CuSO_4$ with the surface 10 cm of soil was more effective in increasing barley shoot Cu concentrations than drilling either source with the seed. This difference was more pronounced for $CuSO_4$ than for CuEDTA. Copper EDTA was approximately five times as effective as $CuSO_4$ in increasing barley shoot Cu concentrations. Akinyede [2] had shown in his growth chamber studies that mixing $CuSO_4$ with soil was superior to banding with seed of barley. This finding was confirmed in the field experiments at Zhoda.

The experiments at Zhoda also included addition of Zn along with Cu in both 1977 and 1978. This treatment significantly increased barley shoot Zn concentrations in 1978 but had no influence on plant Zn concentrations in 1977. There were no yield response to Zn fertilization in either year although DTPA extractable soil Zn levels were 0.7 ug Zn/g soil in 1977 and 1.3 ug Zn/g soil in 1978. In addition, in both 1977 and 1978 the shoot Zn concentrations in barley receiving no Zn would have been considered sufficient for normal growth. Those results illustrated again that the DTPA extractable soil Zn critical level is likely less than the 0.8 ug Zn/g soil suggested by Lindsay and Norvell [62]. On the other hand, although further experimentation on sandy soils in the field are needed, it could very well be that the DTPA extractable Cu critical level on mineral soils is higher than the 0.2 ug Cu/g soil suggested by Lindsay and Norvell [62].

7.2.3 Copper Studies on Organic Soils

The field experiments on organic soils in 1977 and 1978 were designed to determine the extent and severity of Cu deficiency on organic soils and to find optimal combinations of carrier, rate and placement of fertilizer Cu. In 1977, wheat and flax at Piney were harvested before maturity whereas oats were destroyed by rust. Only barley reached maturity and barley grain yield did not respond to Cu fertilization. The soil at Piney in 1977 contained 1.6 DTPA extractable Cu/g soil. It may have been marginally deficient in Cu, but because barley was the only crop which reached maturity and it is quite tolerant of Cu deficiency, it is not surprising that there were no responses to Cu fertilization. The soils in 1978 contained 0.6, 1.0 and 1.0 DTPA extractable Cu/g soil at Piney, Marchand and Stead, respectively. Wheat, a crop which is quite susceptible to Cu deficiency responded in yield to Cu fertilization at all three sites. Flax, barley and oats were grown only at Piney. Flax was killed by frost early in the growing season. The yield increases for both barley and oats were not statistically significant. Yield responses for barley and oats should not have been as large as for wheat or flax since barley and oats are more tolerant of Cu deficiency. The field experiments on organic soils suggested that Cu is likely to be deficient on organic soils, particularly in crops such as wheat which is very susceptible to Cu deficiency. Further experimentation is needed in order to determine the DTPA extractable Cu critical level on organic soils. However, the value is likely greater than 1 ug Cu/g soil and may be as high as 2 ug Cu/g soil.

Mixing either $CuSO_4$ or CuEDTA with the surface 10 cm of soil was far more effective in increasing Cu uptake of barley than drilling either sources with the seed. The differences between the two methods of application were larger than on mineral soils, particularily in the case of CuEDTA. Copper EDTA was slightly more than five times as effective as $CuSO_4$ in increasing Cu uptake by barley.

It should be noted that although wheat yields were increased by Cu fertilization in 1978 at all three sites, wheat yields were very low. The low shoot Cu concentrations in wheat which received supplemental Cu suggest that mixing 10 kg Cu/ha as finely ground $CuSO_4$ with the surface 10 cm of soil did not supply enough Cu to totally correct Cu deficiency. More Cu should have been applied. However, it is possible that the same amount of Cu as $CuSO_4$ sprayed in solution onto soil before rototilling would have been more effective.

7.3 CONCLUSION

Results of field studies suggested that Zn deficiency in barley, oats, wheat, flax and rapeseed is not very likely to occur in Manitoba even on high lime soils relatively low in plant available Zn. Conclusions concerning the extent and severity of Cu deficiency on mineral soils can not be made until further research is conducted. However, results indicated that Cu is likely to be deficient on organic soils, particularly in crops such as wheat which are very susceptible to Cu deficiency.

Low shoot Cu concentration ranges in the growth chamber for 6 week old barley, oats, wheat, flax and rapeseed plants were estimated at 2.3 to 3.7, 1.7 to 2.5, 3.0 to 4.9, 2.4 to 3.5, and 1.7 to 2.7 ug Cu/g plant material, respectively. A shoot Cu concentration below the lowest value for each range was considered deficient whereas a value above the highest Cu concentration was considered sufficient. The order of tolerance to Cu deficiency was rapeseed > barley > oats > wheat > flax.

Copper or Zn EDTA broadcast in solution form and thoroughly mixed with the surface soil was the most efficient method of supplying Cu or Zn. The next most efficient method of supplying Cu or Zn was Cu or Zn SO_4 applied in a similar fashion at rates 3 to 5 times those which would be for the chelated forms. Drilling Cu or Zn EDTA with the seed was effective on mineral soils but the mixed throughout treatment is much preferred on organic soils. Drilling Cu or Zn SO_4 was very seldom effective, regardless of soil type. The commercial Zn fertilizers, ZnMNS by Elephant Brand and ZincGro by Eagle-Picher were not acceptable at increasing either grain yield or shoot Zn concentrations in the year of application, there may have been residual benifits.

Estimating plant available soil Cu and Zn levels by extracting with DTPA may be acceptable, but Zn critical levels should perhaps be lower and Cu critical levels on mineral soils higher than the values of 0.8 ug Zn/g soil and 0.2 ug Cu/g soil suggested by Lindsay and Norvell [62]. The DTPA extractable Cu critical level on organic soil is likely greater than 1 ug Cu/g soil and may be as high as 2 ug Cu/g soil. However, more research is needed to develop reliable

DTPA Zn and Cu critical levels on both organic and mineral soils.

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