UNIVERSITY OF MANITOBA

AVAILABILITY OF COPPER TO PLANTS AND METHODS OF EVALUATING PLANT AVAILABLE COPPER IN ORGANIC SOILS

ΒY

JAMES MICHAEL TOKARCHUK

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ABSTRACT

Field and greenhouse studies were conducted to examine the response of several crops grown on organic soils to copper fertilizer. In addition, several chemical extractants were evaluated for their ability in predicting the amount of copper available to plants grown on organic soils.

In greenhouse studies dry matter yields of barley, wheat, oats and Canola were significantly increased by copper fertilizer on four, five, three and four of ten soils studied, respectively. Plant concentrations of copper in barley, wheat and oats were increased from deficient to sufficient concentrations by the addition of the 10 Kg Cu/ha. Copper concentrations in Canola plants were increased from deficient to sufficient concentrations by 10 Kg Cu/ha on eight of ten soils studied. The crops varied in their sensitivity to copper supply. Wheat was very sensitive to low copper supply (growth was usually greatly reduced at low copper supply) whereas the other crops were relatively tolerant to low copper supply. The order of sensitivity of the crops to low copper supply was wheat was much more sensitive than Canola, barley and oats.

Field studies were conducted at three locations on organic soils. Barley and Canola grain yields were not significantly increased by the addition of copper fertilizer whereas wheat grain yields were significantly increased at two of three locations. Seed yields were low at all sites. This was most likely due to manganese deficiencies. Copper concentrations in wheat were significantly increased by the addition of five Kg Cu/ha. However, at two of the three sites studied copper concentrations were increased to adequate levels only when 40 Kg Cu/ha were applied. The addition of five Kg Cu/ha increased copper concentrations in barley to sufficient levels at all sites, and in Canola at two of the three locations.

In greenhouse tests, none of the extractants studied provided a good method of assessing plant available soil copper. The r^2 values, calculated for the relationship between extractable soil copper and % yield varied from 0.0002 to 0.20. Relationships between extractable soil copper and copper concentrations in plants grown in the greenhouse on soils not fertilized with copper were also poor.

In field studies, plant copper concentrations in barley, wheat and Canola were related to extractable soil copper when values for both fertilized and nonfertilized soils were used. The best relationships for barley and wheat were obtained when 1 M HCL extractable soil copper was used, $(r^2 = 0.61 \text{ and } r^2 =$ 0.49, respectively), whereas Na₂DP provided the best relationship for Canola $(r^2 = 0.67)$. In the field studies all extractants extracted copper from the soil in proportion to the amount of copper fertilizer applied.

It was concluded that none of the extractants adequately assessed plant available soil copper in organic soils not fertilized with copper. Relationships between extractable soil

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copper and plant copper concentrations were good when both copper fertilized and nonfertilized soils were included in the relationship. This indicated that some of these extractants may be useful in predicting plant available soil copper in organic soils previously fertilized with copper.

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I INTRODUCTION

Previous work conducted on organic soils in Manitoba showed that deficiencies of plant available soil copper are likely to limit yields of many crops. A reliable chemical method of evaluating plant available soil copper is not currently available for organic soils. Thus, several greenhouse experiments were conducted to evaluate the capability of several chemical extractants in predicting the amount of copper available to plants from organic soils.

Barley, wheat, oats and Canola were grown in successive experiments on ten organic soils in the greenhouse. Amounts of plant available copper in the ten soils were estimated by using seven different chemical extractants. Dry matter yields with and without copper fertilizer as well as tissue concentrations of copper in the four crops were determined. The relationships between amounts of copper extracted by the various chemical extractants and yield or tissue concentration of copper were studied.

Field studies were also conducted on three organic soils during the summer of 1979 to evaluate the effectiveness of copper fertilizer in increasing yields and tissue concentrations of copper in barley, wheat and Canola. These field studies were also used to assess the capability of various chemical extractants in predicting plant available soil copper.

II LITERATURE REVIEW

(A) Forms of Copper in Soil

Copper comprises approximately 0.0001% of the earth's crust, occurring primarily as oxides, sulphides, and metallic copper (Sauchelli 1969). The principal naturally occurring sulphide forms are chalcosite (Cu₂S), chalcopyrite (CuFeS₂), and covellite (CuS). The principal naturally occurring copper oxides are cuprite (Cu₂O), malachite (CuCO₃.Cu(OH)₂), and tenoute (CuO) (Sauchelli 1969).

Krauskopf (1972) noted that native copper occurs primarily in the monovalent state (Cu⁺) and the divalent state (Cu⁺⁺). The divalent state of copper is the most common form of copper near the earth's surface and is the most important form in plant nutrition. Possible soluble forms of copper in the soil include CuCl⁺, CuCl⁻₂, and Cu(CO₃)₂⁻².

Forms of copper in the soil were investigated by McLearn and Crawford (1973) who listed the forms of copper as (a) ionic and complexed copper in the soil solution; (b) copper on normal exchange sites of soil colloids; (c) copper adsorbed on special adsorption sites which cannot be removed by reagents normally used for determining exchangeable ions; (d) occluded copper in soil oxide material; (e) copper in the biological residues and living organisms in soil; (d) and copper in the lattice structure of primary and secondary minerals. The dynamics of copper in the soil-water-plant system were illustrated by Nielson (1976) as follows:

non-labile Cu Cu complexes Labile Cu Cu ions Cu in plant roots He also noted that the soil solution concentration depends on (1) the amount of labile copper in the soil, (2) the copper adsorption capacity of the soil, and (3) the proportion of the total copper present as soluble copper complexes in the soil solution.

Norvell and Lindsay (1969) suggested that the concentration of Cu^{+2} in the soil solution is related to the hydrogen ion activity of the soil and could be described by the relationship $(Cu^{+2}) = 10^{3} \cdot 2$ (H⁺)². Lindsay (1972) proposed that the dominant copper species in the Cu-soil complex is pH dependant. Below a pH of 7.3, Cu^{+2} predominates, while above this pH, CuOH⁺ is more abundant. Of secondary importance at a basic pH are $Cu_2(OH)_2^{+2}$ and $Cu(OH)^{-3}$.

(B) Copper as an Essential Nutrient in Plants

Arnon (1950) discussed the criteria for the essentiality of an element to plants. An element can not be considered essential to a plant unless (1) its deficiency makes it impossible for the plant to complete the vegetative or reproductive stage of its life cycle; (2) the deficiency is specific to the element in question and can be prevented or corrected only

by supplying this element; and (3) the element is directly involved in the nutrition of the plant apart from its possible effect in the correcting of some unfavorable biological or chemical condition in the culture medium. The first credible evidence that copper fulfilled these criteria in plants was given by Bortel (1927). Since that time, considerable information has been produced indicating the numerous functions of copper in plants.

The most significant function of copper in plants is its role in the activation of certain enzymes (Price 1972). Lehninger (1975) named copper as one of several metal cations which act as cofactors for certain enzymes. He noted that enzymes which require copper for their activation include tyrosine and cytochrome oxidase. Copper is also found in the blue copper protein plastocyanin which is involved in electron transport from photosystem II to photosystem I of photosynthe-Brown and Clark (1977) found that the activity of tyrosis. sine was reduced in copper deficient sugar beets. Brown and Hendricks (1952) observed that copper concentration in plant tissue and ascorbic acid oxidase activity were directly related.

The importance of copper in plant nutrition can also be observed from the plant symptoms which occur when plants do not obtain sufficient amounts of copper. Brown and Clark (1977) indicated that copper was more closely related to reproductive growth than vegetative growth. These observations are in

agreement with those of Graves and Stucliffe (1974) who found the initiation and development of flowers were delayed by a lack of copper in <u>Chrysanthemum morifolium</u>. McAndrew (1979) also noted that the floral parts of Canola plants were vertically compressed and malformed as a result of copper deficiency. Thus, it is evident that copper is very important for the reproductive growth phase as well as for other plant functions.

(C) Critical Levels of Copper in Plant Tissue

A generally accepted definition of a critical nutrient concentration in plant tissue was not found in the literature. Melsted et al., (1969) defined a critical nutrient concentration of a nutrient in a plant as the nutrient concentration below which a growth stress occurs. Jones (1972) stated that a critical concentration was that concentration of a nutrient below which a deficiency occurs. Ulrich and Hill (1967) proposed that the critical concentration of a nutrient is the level of a nutrient in the plant tissue which produces 90% of maximum yield. McAndrew (1979) defined a marginal range of copper in plant tissue as the copper concentration corresponding to a dry matter yield from 15% below the maximum of dry matter yield up to a copper concentration corresponding to the maximum yield of a crop.

There are relatively large variations in critical concen-

trations reported by various workers for a particular plant species. A comprehensive review of factors affecting nutrient concentrations in plants was presented by Bates (1973). He noted that the actual nutrient concentration in a given plant is a complex function of many factors including environment, species, variety, interactions among other nutrients, plant age, and type of tissue sampled. These factors could in part explain the differences in the critical concentrations of copper given in the literature.

Generally, plant tissue copper concentrations vary from five to 10 ppm, with four ppm Cu being considered the critical concentration for most plants (Reuther and Labanauska 1966, Jones 1972). Melsted et al., (1969) found the critical concentration of copper in wheat at the boot stage of growth to be five ppm. Gupta and McLeod (1970) considered 3.2 to 3.3 ppm Cu to be the critical concentration in wheat at the same stage of growth. McAndrew (1979) suggested that wheat tissue at the boot stage containing 3.0 to 4.9 ppm Cu was marginal with respect to copper nutrition.

Reported values for the critical concentration of copper in barley also vary greatly. Akenyede (1978) suggested that barley shoots at the boot stage containing less than 5.2 ppm Cu were copper deficient. Gupta and McLeod (1970) found that barley at the boot stage containing less than 4.8 ppm Cu was copper deficient. McAndrew (1979) suggested a range of 2.3 to 3.7 ppm Cu as the critical concentration in barley tissue at

the boot stage. Reuther and Labanauskas (1966) considered tissue concentrations of less than 6.2 to 11.9 ppm Cu at harvest to be low in copper. Ward et al., (1973) suggested concentrations of less than five ppm Cu in barley tissue were less than adequate for optimal growth.

Critical concentrations of copper in oats given in the literature, are fairly consistent. Gupta and McLeod (1970) found 3.2 to 3.3 ppm Cu as the critical concentration of copper in oats. Reuther (1957) suggested a deficiency of this element would occur when six to nine week old leaves contained less than 3.0 ppm Cu. Ward et al., (1973) considered oat tissue with less than five ppm Cu to be low in this element.

A critical concentration for copper in Canola was established in the greenhouse using organic soil as a growth medium by McAndrew (1979). Canola plants were found to have sufficient copper for normal growth when tissue concentrations were in excess of 2.7 ppm. When Canola tissue contained 2.7 to 1.7 ppm Cu, the plants were considered to contain marginal quantities of copper.

(D) Deficiency Symptoms in Agronomic Crops

An abnormality referred to as reclamation disease was documented by Hudig and Meyer (1925) as being commonly found in many crops grown on newly drained or newly broken organic soils. The abnormality consisted of dead or white leaf tips in

younger leaves of plants with decreased or nil yields resulting from abnormal head emergence. It was first observed in 1931 that the addition of copper to newly reclaimed organic soils would result in improvement of this condition (Lipman and Mackinney 1931, Sommer 1931). This finding obviated the conclusion that the symptoms of reclamation disease were symptomatic of copper deficiency.

Considerable work has been done in regard to copper deficiency since 1931. The generalization was made by Lucas and Knezek (1965) that copper deficiency symptoms would occur when the total copper content was less than six and 30 ppm Cu in a mineral and an organic soil, respectively.

Copper deficiency symptoms have been described by numerous Nelson et al., (1956) suggested that copper authors. deficiency symptoms appear first in the youngest leaves of plants. Reduced growth, and grayish green to blue-green color Shortening of internodes is may precede die-back of leaves. Pizer et al., (1966) found that marginal and also common. interveinal chlorosis in leaves, leaf bending at right angles, spiral twisting of leaves are indicative of copper and deficiency. Poor color development in onion skins was also found to be related to copper deficiency by Campbell and Gusta (1966). Reuther and Labanauskas (1966) found that copper exhibited chlorosis, necrotic deficient vegetable crops spotting on the leaves, and a frequent lack of turgor.

Reuther (1957) referred to copper deficiency in small

grains as white tip, yellow tip, or reclamation disease. The condition was characterized in cereals by necrosis of older As the conleaves and marginal chlorosis of newer leaves. dition progressed, leaves remained unrolled and tended to wilt Davis and Lucas (1959) made similar observations of easily. copper deficient wheat and added that the symptoms were similar to that of frost damage. Disorders of ripening in oats and barley were linked to copper deficiency by Reith (1968). He found grain did not fill properly, remained bluish green in color and was of inferior quality and weight. Vitosh et al., (1973) also noted that copper deficient grain displayed abnormalities in color. Brown and Clark (1977) observed that in addition to the aforementioned symptoms of copper deficiency the affected plants of wheat contained higher levels of reducing sugars, free amino acids, and NO3-N than copper sufficient plants.

Symptoms resulting from insufficient copper nutrition in Canola were documented by McAndrew (1979). Interveinal chlorosis shortly after seedling emergence was characteristic of this deficiency. Leaves were abnormally large whereas vertical growth remained stunted. Compression of floral parts was also noted.

(E) Factors Affecting the Availability of Copper in Soil

(1) Soil pH. Many workers have suggested that organic soils

with pH values less than five are often deficient in plant available copper (Lucas 1948, Lucas and Davis 1961, Lucas 1963, Steenbjerg and Boken 1963, Hamilton and Bernier 1973). It has also been suggested that the parent material of acid organic soils may be deficient due to inherently low total concentrations of copper. Davis and Lucas (1959) noted that acid organic soils are often low in plant available copper. Hamilton and Bernier (1973) also found that an acid organic soil (pH 3.57) containing 1.83 ppm of 0.1N HCl-extractable copper was low in plant available copper. Both the above authors point out that liming of an acid peat soil to raise the pH did not alleviate the copper deficiency. Work presented by Graves et al., (1978) was in agreement with these findings.

The literature studied showed that the relationship between soil pH and the plant availability of copper is not well defined for organic soils. Work conducted by Campbell and Gusta (1966) showed a slightly acid organic soil (pH 6.4) to be copper deficient for onion production. McAndrew (1979) found several organic soils in Manitoba with a basic pH to be deficient in available copper for several agronomic crops.

The relationship between soil pH and the plant availability of copper in mineral soils is also not clearly defined. Bohn and Husyan (1971) were not able to find a clear relationship between soil pH and the plant availability of soil copper. Blevins and Massey (1959) were not able to find a clear relationship between soil pH and the plant availability

of soil copper in a mineral soil. However, work done by Dolar and Keeney (1971) showed that the inclusion of soil pH in multiple regression equations improved their ability to predict the total uptake of copper by plants.

The availability of copper generally decreases with increasing soil pH. Reuther and Labanauskas (1966) pointed to calcareous soils and alkaline soils as being suspect of copper deficiency especially if the soils are sandy. Work conducted by Brady (1974) was in agreement with this. Cavallaro and McBride (1978) noted that low pH soils are much less effective than high pH soils in removing Cu^{++} from the soil solution. This would imply that an acid soil would not remove Cu⁺⁺ from solution effectively, and that the Cu⁺⁺ remaining in solution can be leached through the soil profile to depths below the root zone. Evidence of Cu⁺⁺ leaching through the soil profile in an acidic and coarse textured soil was given by Udo et al., With time such removal of Cu⁺⁺ from the soil solum (1979). would lead to depletion of total copper reserves and eventually a copper deficiency in plants.

(2) <u>Organic Matter</u>. The relationship between the plant availability of soil copper and the organic matter content of soils has been studied by many workers. Shuman (1979) found that copper in soil was mainly associated with soil organic matter and clay. In fine textured soils copper was mainly associated with the clay and silt fractions, whereas in a coarse textured

soil the copper was mainly associated with the organic frac-The importance of organic matter to copper retention in tion. soils has been demonstrated by several authors. McBride and Blasiak (1979) found that the retention of copper in soils was more dependent on organic complexation mechanisms than on pH dependent retention on clay mineral surfaces. Hodgson et al., (1965) determined that as much as 99% of the copper in soil solution was complexed by the soluble organic fraction of the soil. Copper which is complexed in this manner would be highly plant available. Stevenson and Ardakani (1972) also pointed out that complexing agents in soil solution have the ability to transfer solid phase forms of micronutrients such as copper into soluble metal complexes, thus increasing their plant availability.

Copper can also be held in an exchangeable form with colloidal soil organic matter, as well as in a complexed form with the soluble organic fraction. Lewis and Broadbent (1960b) determined that most of the cation exchange capacity of an organic soil was due to phenolic and carboxylic groups of the organic matter. Previous work done by Lewis and Broadbent (1960a) showed that in an organic soil, the carboxylic groups adsorbed copper as CuOH⁺ and phenolic groups adsorbed the Cu⁺⁺ form. In regards to the availability of these two forms of copper, the above authors determined that the copper adsorbed by carboxyl groups is not released above a pH of 4.52. In most organic soils this form of copper would not be available to

crops. Copper in the Cu⁺⁺ form held in an exchangeable form by the phenolic groups of organic soils was found to be largely plant available (Lewis and Broadbent 1960a).

Specific adsorption of copper by the organic fraction in soil was investigated by Petruzzelli and Guidi (1976). They determined that copper added to an organic soil was, to a large extent, specifically adsorbed by the humic fraction of the soil and copper so adsorbed was largely plant available. McLearn and Crawford (1973) reported that copper which had been specifically adsorbed on soil organic matter was in equilibrium with soil solution copper and would contribute to the plant available pool of copper through this equilibrium. In contrast, Bloom and McBride (1979) reported that copper specifically adsorbed by carboxylate groups was unavailable to plants.

The preceding discussion shows that copper adsorbed by soil organic matter can vary in availability to plants. Portions of both native soil copper and copper added in fertilizers can be adsorbed by high molecular weight humic materials and rendered unavailable to plants. Accordingly to Petruzzelli and Guidi (1976), adsorption of this type predominates until all such sites are saturated with copper. Following this reaction, adsorption of copper by lower molecular weight humic materials occurs. This fraction of soil copper is largely plant available.

The above adsorption reactions of copper are useful in explaining deficiencies of copper in organic soils. Since most

organic soils are low in total and plant available copper, adsorption of copper by high molecular weight humic materials usually dominate the system resulting in low concentrations of plant available soil copper. Copper additions to these soils result initially in saturation of the high molecular weight humic materials with copper. As more copper is applied, the low molecular weight humic materials may adsorb the copper, resulting in formation of organic matter-Cu complexes which provide plant available copper.

(3)The influence of clay and silt on the Other Factors. availability of copper to plants is of little importance in organic soils. However, when these soil fractions are present, micronutrients enter into cation exchange reactions with them. Clay minerals have been noted for their ability to adsorb copper in an exchangeable form. Ellis and Knezeck (1972) found that montmorillonite was particularly effective in the adsorp-They pointed out that clays such as monttion of copper. morillonite were able to adsorb copper in excess of its cation exchange capacity, probably as a result of the adsorption of hydrolized forms of copper, or the precipitation of hydroxides such as Cu(OH)₂. The ability of montmorillonite to adsorb copper in a plant available form was also demonstrated by Banin and Navrot (1976) who utilized a modified form of montmorillonite as a carrier of copper for plant uptake. Shuman (1979) noted that copper adsorbed on the surface of clay minerals in

an exchangeable form was highly plant available. However, it should be noted that copper has a much stronger affinity for soil organic matter when compared to clay minerals. Consequently, most soil copper should be held in association with the soil organic fraction leaving only a small amount of copper to participate in exchange reactions on clay mineral surfaces.

Soil temperature may also affect the plant availability of copper in soils. McMillian and Hamilton (1971) found that an increase in soil temperature from 16C to 20C resulted in an increase in the tissue concentration of copper and copper uptake in carrots. As dry matter yields did not significantly increase in this range of temperature they proposed that an increase in the solubility of copper, or an improvement in the copper uptake mechanism in the plant occurred as a result of an increase in temperature. Since copper uptake by plants may be restricted by lower soil temperature, the low soil temperatures usually encountered in organic soils may be an additional factor resulting in copper deficient plants on organic soils.

(F) Extractants Used for Assessing Available Soil Copper

The main objective of any soil test is to determine the quantity of a nutrient which is plant available. Also, a soil test should be useful in assessing the amount of a nutrient required to alleviate a deficiency. Bray (1948) suggested that a good soil test should meet the following criteria: (1) the

extractant should extract all or a proportionate part of the available form or forms of a nutrient from soils with variable properties, (2) the amount of the nutrient extracted should be measured with reasonable accuracy and speed, and (3) the amount extracted should be correlated with the growth response of each crop to that nutrient under variable conditions.

Chelate Extractants. Chelating agents have shown promise (1)as extractants of plant available soil copper. Chelates combine with free metal ions in solution forming soluble complexes (Lindsay and Norvell 1970). This decreases the activity of the free metal ion in solution which results in desorption from soil surfaces and dissolution of labile solid phases. The amount of free metal that accumulates in solution during the extraction is therefore a function of both the activity of the metal in the soil (intensity factor) and the ability of the soil to replenish those ions (capacity factor). Both factors are important in determining the availability of elements to plants. Chelate extractants such as EDTA, DTPA, and EDDHA have been used to determine the availability of soil copper to Chelating agents have been examined for their suitplants. ability in assessing plant available soil copper primarily in minerals soils.

(a) <u>EDTA</u>. The most commonly used chelating extractant is EDTA. Viets (1962) noted that EDTA provided a measure of

strongly adsorbed copper and chelated forms of copper. He also noted that EDTA dissolved some inorganic precipitates of copper in soils. Dolar and Keeney (1971) indicated that EDTA extracted copper from the soil solution and forms of copper associated with organic matter.

Relatively good relationships between EDTA extractable soil copper and plant growth and/or copper content of plants have been obtained by many workers. Reith (1968) classified soils as being responsive, moderately responsive, and not responsive to copper additions when EDTA extractable copper values were <0.7 ppm, 0.7-1.0 ppm, and >1.0 ppm Cu, respect-McKenzie (1966) found a significant correlation ively. (r=0.80) between amounts of copper extracted by EDTA and the total copper concentrations in 82 Australian soils. He also noted that copper deficient soils could be identified in 90% of instances based on EDTA extractable copper levels. Oien (1966) found that quantities of copper extracted by 0.02M NaEDTA were correlated with yield. Viro (1955) obtained a correlation coefficient of 0.679 between the amount of soil copper extracted with EDTA and the fertility status of the soil as measured by density and height of tree growth. McGregor (1972) obtained R^2 values of 0.91 and 0.90 when EDTA extractable copper, soil pH, and organic matter content were correlated with the copper uptake of flax and wheat, respectively. Martens (1968) found copper uptake by millet plants to be highly correlated (r=0.57) with EDTA-extractable soil copper. Beavington and Wright

(1977) obtained an r value of 0.51 for the relationship between EDTA-extractable soil copper and the level of copper in herbage.

In contrast to the findings noted above Blevins and Massey (1959) suggested that copper extracted with EDTA would not provide a good measure of plant available copper as Al present in soil would compete with copper for chelation by EDTA.

Norvell and Lindsay (1969) showed that the Cu-EDTA complex was most stable at pH values near neutral. In an acid medium, replacement of copper by Fe⁺³ occurred, whereas in strongly basic solutions, Ca-EDTA was the dominant EDTA species. Lindsay and Norvell (1969) developed pH-stability diagrams for the EDTA complexes that demonstrated that Fe^{+3} was the major cation chelated by EDTA below a pH of 6.8. Above this pH Ca⁺² was shown to be the dominant cation complexed by EDTA. Further investigations by Halvarson and Lindsay (1972) provided a pHstability diagram when Fe^{+3} , Ca^{+2} , Zn^{+2} , Mn^{+2} , and Cu^{+2} were present and competing for chelation with EDTA. They found that as pH increased above 6.5, Zn^{+2} , Mn^{+2} , and Cu^{+2} were more able to compete with Fe⁺³ for chelation with EDTA. These results suggest that for soils of about neutral pH, EDTA can extract appreciable guantities of copper and that Fe⁺³ or Al may not sufficiently interfere with the Cu-EDTA chelation process to preclude the use of EDTA as a soil test.

(b) DTPA. A comparison of the stability of Cu-chelates

of EDTA and DTPA in soils suggested similar behavior of these ligands (Norvell and Lindsay 1969; Norvell and Lindsay 1972; Norvell 1972). Thus, Lindsay and Norvell (1978) proposed that DTPA could be used as an extractant for plant available soil copper. Lindsay and Norvell (1969) later showed that EDTA and DTPA metal complexes behaved similarly when Fe^{+3} , Zn^{+2} , Ca^{+2} , and H^+ were all present and competing for chelation with DTPA.

Halvarston and Lindsay (1972) showed that the amount of copper complexed by DTPA in competition with other cations was very consistent and stable beyond a pH of about 6.0. Norvell (1972) suggested that in calcareous soils the stability of Cuchelates should be in the order Cu-DTPA, >Cu-HEDTA, >Cu-CDTA, >Cu-EDTA, >Cu-EDDHA, >Cu-EGTA, >Cu-NTA, >Cu-Cit., >>Cu-P₂O₇, CuP₃O₁₀, Cu-O_x. Norvell and Lindsay (1972) found that Cu-DTPA showed moderate to good stability over a 30 day period in soils with pH values between 6.8 and 7.9. Stability of the complexes increased with increases in pH.

Lindsay and Norvell (1967) proposed a solution consisting of 0.005M DTPA (diethylenetriamine-pentaacetic acid), 0.1M triethanolamine, and 0.01M CaCl₂ adjusted to pH 7.3 as an extractant of soil micronutrients. A soil solution ratio of 1 to 2 was used and two hours was selected for extraction time. This extraction procedure is commonly known as the DTPA test. Lindsay and Norvell (1967) suggested that soils containing less than 0.2 ppm DTPA extractable copper may be considered copper deficient. This value has been widely accepted as the

deficient level of copper in soil even though this critical level was determined using only a few data points at or near this level.

Follet and Lindsay (1971) indicated that DTPA was useful availability of native soil in monitoring the copper. Proskovec (1976) identified 34 Colorado soils with DTPA extractable copper concentrations below 0.2 ppm. He obtained a significant correlation between DTPA-extractable soil copper and plant available copper where copper fertilizer was added to the Dolar and Keeney (1971, 1971a) extracted soil copper soil. using DTPA and found DTPA extractable copper to be highly correlated (r=0.78) with copper extracted by a Mg solution. They also found that DTPA complexed some organically bound metals as well as copper, zinc and manganese in oxides, hydroxides or salts.

Reviews of factors affecting the amount of copper extracted by DTPA were presented by Soltanpour et al. (1976, 1979). These studies emphasized the need for maintaining standardized conditions during extraction in order to obtain consistent results.

Several modifications were made recently to the DTPA extraction procedure outlined by Lindsay and Norvell (1967). These modifications were proposed in order to increase the rapidity with which soils can be analyzed and to use the DTPA solution for extraction of nutrients other than copper. Lopez and Graham (1972) used an extraction solution consisting of

0.005M DTPA, 0.01M CaCl₂ and 0.1M NaOAc to extract copper and other micronutrients for spectrographic analysis. Soltanpour and Schwab (1977) and Soltanpour and Workman (1979) used a solution consisting of 1M NH₄HCO₃ and 0.005M DTPA at a pH of 7.6 to extract P and K as well as other micronutrients. The coefficient of determination between the standard DTPA test and the above modified method was 0.745 for copper. Khan (1979) also modified the DTPA soil test by decreasing shaking or equilibration time from 2 hours to 60 seconds with sonic dispersion. Copper extracted during 60 seconds with sonic dispersion did not differ significantly from copper extracted during 2 hours of shaking without sonic dispersion.

(c) <u>EDDHA</u>. The chelating agent, Na₂EDDHA [ethylenediamine-di (-0-hydroxyphenol acetic acid) disodium salt], was also used as an extractant of soil micronutrient cations (Wallace and Heimadin 1962; Ravikovitch 1968; McGregor 1972). However, this chelating agent was not commonly used as an extractant of available soil copper. Halvarston and Lindsay (1972) found that Fe^{+3} was very strongly held by EDDHA at pH values of 4.0 to 9.0. Copper, at concentrations of 0.315 uM did not compete strongly with the Fe^{+3} . However, the formation constants given by these authors indicate that Cu-EDDHA should be a stable species when the Cu⁺² concentration is sufficiently high.

McGregor (1972) showed that soil copper extracted by a solution consisting of 0.01M EDDHA and 1.0M NH₄OAc at pH 7.0

was closely related to both copper concentration and uptake by flax. The r_2 values were 0.93 and 0.75, respectively. He also found that soils with extractable copper concentrations of less than 1.3 ppm did not supply sufficient quantities of copper for maximum growth of flax.

(2) <u>Acid Extractants</u>. Various acids and concentrations of acids were evaluated as extractants of plant available soil copper. Of the acid extractants, HCl was one of the most suitable extractants of plant available micronutrients (Viets and Lindsay 1973). Andersson (1975) found that 2M HCl extracted the total amount of heavy metals contained in a clay soil, including any copper that was of biological importance. Lucas (1948) found that 0.2M HCL was an effective extractant for removing copper which had been adsorbed by an organic soil.

MacLean and Langille (1976) found that the copper extracted by 0.1M HCl was highly correlated with the organic matter content and clay content of soils. Dolar and Keeney (1971) used 0.1M HCl to extract copper from both organic and inorganic complexes in mineral soils.

McGregor (1972) found that the quantity of copper extracted by 0.1M HCL was not closely correlated with copper concentration and uptake by flax and wheat on mineral soils. However, R^2 values of 0.91 and 0.89 were obtained when copper concentration in the tissue of flax and wheat, respectively, were related to soil pH, organic matter, and <0.1M HCL-extract-

able copper. Dolar and Keeney (1971b) found that copper extracted by a mixture of 0.1M HCl and EDTA was closely related to the copper uptake by oats grown on a mineral soil. Nelson et al., (1956) found that 0.1 M HCL extractable copper had little value in predicting response in yield and copper tissue concentration of oats grown on an organic soil with and without fertilizer.

Martens (1968) found an R value of 0.847 when pH, organic matter, percent clay, and 1.0 M HCL extractable copper were correlated with the uptake of copper by corn. Organic matter content and 1.0 M HCL-extractable soil copper accounted for most of the relationship (r=0.761). Whitney (1975) advocated the use of 1.0 M HCL as an extractant of plant available soil copper on organic soils. This author noted that 1.0 M HCL was routinely used as a soil test for plant available soil copper in Michigan for organic soils. Vitosh et al., (1973) reported that organic soils in Michigan with less than nine ppm of 1.0 M HCL-extractable copper did not supply sufficient quantities of copper for optimal growth of plants. Fiskell and Leonard (1967) observed that 1.0 M HCL could be used to evaluate the plant availability of varying amounts of copper fertilizer applied to a sandy soil. These authors also noted that 1.0 M HCL extractable copper was highly correlated (r=0.936) with the NH₄-Ac-extractable copper content of the same soil.

(3) Salt Extractants. Dolar and Keeney (1971a) suspected that

a particular chemical fraction of a nutrient may not be the only source of available nutrient for plant uptake. However, since the exchangeable fraction of soil copper represents a fraction that is readily available to plant uptake and is in equilibrium with other fractions of soil copper, a measure of this form of soil copper may provide an index of availability to plants. Dolar and Keeney (1971a) found that forms of copper that were exchangeable with Mg^{+2} , NH_4+ , or Ca^{+2} ions were readily available to plants. They also found that copper extracted by a Mg salt solution was highly correlated with quantities of organically and inorganically precipitated copper in soil. Since these forms of copper are in a rapid equilibrium with exchangeable forms of copper, it was postulated that a measure of exchangeable soil copper may be of value in evaluating plant available soil copper. However, it was later noted by Dolar and Keeney (1971b) that 1.0 M Mg(NO₃)₂-extractable copper was not as well correlated with plant uptake of copper by oats as was 0.1 M HCl-, 0.001 M EDTA, or 0.005 M DTPAextractable copper.

One-tenth molar NH_4OAc at pH 4.8 was also used as an extractant of plant available soil copper in both Florida (Mokma et al. 1979) and Michigan (Andersson 1975). Andersson (1975) noted that NH_4OAc was particularly effective in extracting copper from soil, and that this method was effective in determining the plant available pool of copper from exchangeable and easily soluble fractions in near neutral to slightly acid
soils. Viets (1962) also noted that the common use of 1 M NH_4OAc as an extractant was useful in measuring the exchangeable pools of cations such as copper, zinc, and manganese.

Neelkanta (1961) found that 0.1M NH4OAc extractable copper correlated better with the amount of copper taken up by Jowar plants than 0.1M HCL, 0.5M HNO3, 0.01 M EDTA, and 1 M HCLextractable copper. Fiskell and Leonard (1967) noted that NH4OAc extractable copper reflected the quantities of copper fertilizer added to soils. However, McKenzie (1966) reported that 0.02M NH4OAc was not as well suited as EDTA for the separation of copper deficient and sufficient soils.

Other salt solutions such as NH4NO3 and CaCl2 were also used to assess plant available soil copper. McGregor (1972) found that NH4NO3 did not extract sufficient quantities of copper from Manitoba soils to allow for accurate measurement. McLaren and Crawford (1973) used 0.05 M CaCl2 to determine soil solution and exchangeable copper. However, CaCl2 did not extract sufficient copper for accurate analysis.

The extractants which have proven most useful in the evaluation of plant available soil copper were discussed in the preceding section. Many studies were conducted to evaluate the various extractants for estimating plant available soil copper; yet no single extractant can be recommended as being universally acceptable for this purpose on mineral or organic soils. The DTPA soil test developed by Lindsay and Norvell (1967) is the most widely accepted extractant for estimating plant avail-

able soil copper on mineral soils. Some soil testing laboratories prefer the use of 1M HCL on organic soils and 1M NH4OAc on mineral soils as extractants for plant available soil copper. The differences in preference of extractant used are undoubtedly due to the nature of copper in soil which varies with location and soil properties. For example, different extractants are recommended for determining plant available soil copper in mineral and organic soils by Whitney (1975). It is therefore essential to evaluate extractants on a regional basis to determine the most suitable extractant for a particular climate and soil type.

III METHODS AND MATERIALS

(A) <u>An Evaluation of Chemical Methods for Determining Plant</u> Available Soil Copper in Organic Soils-Greenhouse Study

(1) <u>Soils</u>. Locations from which the ten organic soils were obtained for use in this study and some chemical and physical characteristics of the soils are shown in Tables 1 and 2, respectively.

(2) <u>Greenhouse Procedures</u>. Barley (<u>Hordeum vulgare</u> var Conquest), wheat (<u>Triticum aestivum</u> var Neepawa), and oats (<u>Avena</u> <u>sativa</u> var Hudson) were grown on ten organic soils in a greenhouse environmnent using a 16-hour photoperiod, and a temperature of 21°C. Canola (<u>Brassica campestris</u> var Torch) was grown on the 10 organic soils in a Conviron Model PGW 36 environmental growth chamber. A 15-hour photoperiod with a light intensity of 550-500 micro-Einsteins/m²/sec and a day/night temperature regime of 21/17°C were maintained. All crops were grown in polyethylene pots.

(3) <u>Fertilizers</u>. To evaluate the sensitivity of the four crops to low levels of soil copper and their relative response to fertilizer copper, a control treatment (no copper added) and a treatment consisting of 10 Kg Cu/ha as CuSO₄.5H₂O (calculated on an area basis) were applied to each soil. The treatments

Soil	Legal	Soil				
No.	Location	Type				
1	NW 1/4 of 24-1-11E	Typic Mesisol				
2	NE 1/4 of 21-17-9E	Terric Mesisol				
3	NE 1/4 of 19-17-9E	Terric Mesisol				
4	SW 1/4 of 24-1-11E	Typic Mesisol				
5	SE 1/4 of 25-5-8E	Terric Mesisol				
6	NW 1/4 of 10-5-8E	Terric Mesisol				
7	SE 1/4 of 2-5-8E	Terric Mesisol				
8	SW 1/4 of 32-17-9E	Terric Mesisol				
9	SE 1/4 of 12-5-8E	Terric Mesisol				
10	NW 1/4 of 6-2-10E	Terric Mesisol				

Table 1. Location and description of soils used in greenhouse studies.

Table 2. Some physical and chemical characteristics of soils used in greenhouse studies.

Soil No.	1	2	3	4	5	6	7	8	9	10
Organic Matter (%)	87.3	86.2	84.0	89.1	75.8	99.5	80.5	91.4	86.1	91.7
Bulk Density (g/cc)	0.14	0.15	0.12	0.12	0.19	0.16	0.18	0.11	0.18	0.15
Soil pH	6.3	5.1	5.9	5.8	6.9	7.3	6.6	6.2	7.2	6.4
Conductivity (mmhos/cm ²)	0.4	2.0	1.0	0.4	0.5	0.6	0	0.4	0.3	0.1
Inorganic Carbonates (%CaCO ₃)	0.6	0.7	0.7	0.1	1.2	1.3	1.0	0.8	1.9	0.7
NO3-N (ppm)	257	53.4	532	27.2	347	311	83.9	54.9	418	3.7
NaHCO3 Ext. P (ppm)	14.7	17.1	153	22.2	21.9	39.7	16.2	27.5	24.3	8.5
NH4Ac Ext. K (ppm)	276	54.8	196	47.5	150	138	77	334	150	79.3
SO4-S (ppm)	9.4	+*	+	+	20.0	+	+	+	+	3.0
Field Capacity (%H ₂ O)	388	503	306	418	233	354	461	533	384	592

* SO_4 -S concentrations were greater than 50 ppm.

were replicated three times and soils and treatments arranged in a randomized block design. The weights of soil used per pot for each soil are given in Table 3.

Every pot received 100 Kg N/ha as NH_4NO_3 , 50 Kg P/ha as $(NH_4)_2HPO_3$, 100 Kg K/ha as K_2SO_4 and 50 Kg S/ha as K_2SO_4 and $CuSO_4$ 5H₂O. All fertilizer materials were dissolved in deionized water, and sprayed onto the entire thinly spread soil mass which was then thoroughly mixed.

Twelve cereal seeds or 20 Canola seeds were planted 2.5 cm below the soil surface of each pot. The cereals were thinned to eight plants and Canola to four plants per pot one week after emergence. The pots were watered daily to field capacity.

(4) <u>Harvest Procedures</u>. Barley, wheat, oats and Canola were harvested 72, 62, 82 and 46 days after seeding, respectively. The crops were grown on growth benches and large variations in the air temperature occurred during the growth period of the various crops. Undoubtedly, days to heading was affected by the variations in temperature. The cereals were harvested at heading and the Canola at the early flowering stage. Plants were cut near the soil surface, washed with deionized water to remove adhering soil particles, placed in paper bags, and dried for 48 hours in a forced air oven at 85°C. The plant samples were weighed and then milled to a fine powder in a domestic coffee grinder.

Soil No.	Weight of oven dried soil (g/pot)
1	385.6
2	409.8
3	608.6
4	422.4
5	534.9
6	437.4
7	507.4
8	324.4
9	498.1
10	405.6

Table 3. Weight of each soil used in the greenhouse study (g/pot).

(B) <u>An Evaluation of Chemical Methods for Determining Plant</u> Available Soil Copper in Organic Soils-Field Studies

(1) <u>Soils</u>. Field studies were conducted at three locations in southeastern Manitoba in 1979. One site was located near Piney on the NW 1/4 of 24-1-11E on a Typic Mesisol of the Stead series (Mills et al, 1977). A second site was located near Stead on the SW 1/4 of 2-17-19E on a Terric Mesisol. A third site near Marchand was located on the NW 1/4 of 10-5-8E, also a Terric Mesisol. Some physical and chemical characteristics of these soils are shown in Table 4.

Field Procedures. Barley (Hordeum vulgare var Conquest) (2)and wheat (Triticum aestivum var. Neepawa) were seeded at 110 kg/ha and Canola (Brassica campestris var. Torch) at seven kg/ha at each of the three field sites. Seeding dates for each crop and site are shown in Table 5. Due to wet conditions in the spring of 1979 all crops were seeded late. The Canola seed was treated with furadan prior to seeding. The field plots were arranged in a randomized block design with five treatments per crop replicated six times (Figure 1). Individual treatment plots were six 0.18-m rows wide and 6.10 m in length, providing 6.53x10⁻⁴ ha of land area per treatment plot. Replicate blocks were separated by a 1.52 m roadway. A 5.4 m buffer strip of barley separated the cereals and the Canola crop to avoid herbicide damage during spraying operations. The entire

Table 4. Some physical and chemical characteristics of soils used in field experiments.

	Location					
	Piney	Stead	Marchand			
Organic Matter (%)	76.9	79.2	70.6			
Bulk Density (g/cm ³)	0.14	0.12	0.16			
Soil pH	6.6	6.2	7.2			
Conductivity (m mhos/cm)	0.7	0.8	2.2			
NO3-N (Kg/ha)*	50.3	30.3	66.1			
Bray I Ext. P (Kg/ha)	0.19	2.40	0.14			
NH4Ac Ext. K (Kg/ha)	47.5	83.7	70.6			
SO ₄ -S (Kg/ha)*	165	300	375			
Inorganic Carbonates (%)	.14	.06	.74			
Field Capacity (% H ₂ O)	403	366				

* Determined on the 0 to 60-cm depth, all other analyses were conducted on the 0 to 15-cm depth.

Table 5. Seeding dates for barley, wheat and Canola in 1979.

	Crop						
Location	Barley	Wheat	Canola				
Piney	June 4	June 5	June 4				
Marchand	June l	June 2	June l				
Stead	June 12	June 12	June 11				

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Figure 1. 1979 Field plot design.

- 20.3 m -

site was enclosed by six guard rows seeded to barley.

Each field site was sprayed with Round-up 10 days prior to seeding. Broadleaf weeds in the cereal crops were controlled by the use of Banvel-3 applied at recommended rates. Control of sow thistle and other broadleaf weeds in the Canola plots was achieved by repeated hand weedings.

(3)The fertilizer treatments applied to the Fertilizers. field plots are outlined in Table 6. All crops received 120 Kg N/ha mostly as commercial grade ammonium nitrate banded into the soil prior to seeding. Wheat and barley received commercial grade ammonium phosphate at 50 Kg P_2O_5 /ha applied with the seed. Twenty-five Kg P205/ha were applied with the Canola seed at time of seeding. All crops received 200 Kg K₂O/ha as KCL broadcast prior to seeding. Additional sulphur as gypsum (CaSO₄.H₂O) was applied to treatments 1, 2, 3, and 4 of wheat, 6, 7, 8 and 9 of barley and 11, 12, 13, and 14 of Canola in amounts such that all treatments received equal amounts of sulphur (equal to the amount applied with the CuSO4.5H20 at 40 Kg Cu/ha). Copper as $CuSO_4.5H_2O$ was applied at 0, 5, 10, 20 and 40 Kg Cu/ha. The CuSO₄.5H₂O was dissolved in deionized water and sprayed onto the soil surface. All plots were then rototilled to a depth of 15 cm and the copper fertilizer well mixed with the soil.

Gron	Treatment	Nutrient Applied (Kg/ha)						
Crop	No.	N P205		K	S	Cu		
wheat """ barley """ canola	1 2 3 4 5 6 7 8 9 10 11 12	120 120 120 120 120 120 120 120 120 120	50 50 50 50 50 50 50 50 50 50 25 25	200 200 200 200 200 200 200 200 200 200	20 17.5 15 10 20 17.5 15 10 0 20 17.5	0 5 10 20 80 0 5 10 20 40 0 5		
н н н н	13 14 15	120 120 120	25 25 25	200 200 200	15 10 0	10 20 40		

Table 6. Fertilizer treatments applied to field plots.

(4) Midseason Harvest.

(a) <u>Plant Sampling</u>. Entire wheat, barley and Canola shoots were sampled about midway through the growing season when the cereals were at the boot stage of growth and the Canola was at the early flowering stage. Dates of sampling are shown in Table 7. Samples were taken from the 2nd and 5th rows of each treatment plot at a minimum distance of 1.52 m from the roadways. Plants were cut as close to the soil surface as possible, placed in sealed plastic bags and frozen as soon as possible. Prior to analysis, the samples were thawed, washed in deionized water, air dried and then ground to a fine powder in a domestic coffee grinder.

(b) <u>Soil Sampling</u>. Soil samples were taken to a depth of 15 cm from each treatment and crop at time of sampling for plant tissue analysis. The samples were taken from the area from which the plants had been cut. The soil samples were placed in plastic bags and frozen as soon as possible. Prior to analysis, the samples were thawed, air dried, and milled to a fine powder in a domestic coffee grinder. The samples were then analyzed for copper using several extractants.

(5) <u>Final Harvest</u>. Final grain harvest dates are shown in Table 8. Grain and straw yields were obtained on a 3.05-m strip of crop taken from the centre two rows of each treatment

	Crop						
Location	Barley	Wheat	Canola				
Piney	August 1	August l	July 20				
Stead	August 8	August 8	July 27				
Marchand	August l	August l	July 17				

Table 8. Final harvest dates for barley, wheat and Canola in 1979.

	Crop					
Location	Barley	Wheat	Canola			
Piney	Sept. 1	Sept. 15	Aug. 10			
Stead	Sept. 6	Sept. 24	Aug. 27			
Marchand	Aug. 29	Sept. 14	Aug. 17			

plot 1.52 m from the roadway. The plants were cut by hand approximately five cm above the soil surface and placed in cloth bags. The samples were dried and then threshed. Weights of straw and grain were obtained and yields calculated.

(C) Analytical Procedures

(1) <u>Plant Tissue Analysis</u>. A two-gram sample of ground plant tissue was placed in a micro-Kjeldhal flask, 10.0 ml concentrated HNO₃ and 15 ml 70% HClO₃ added, and the mixture digested until clear using a micro-Kjeldhal unit. The plant digest was filtered through Whatman No. 42 filter paper into a 25-ml volumetric flask and diluted to volume with deionized water. The copper, zinc, iron and manganese concentrations in the solutions were determined using a Perkin-Elmer 303 Atomic Adsorption Spectrophotometer.

Concentrations of Ca, Mg and K were determined on a one-ml aliquot of the above digest diluted to 25 ml using 2.5 ml of a 2500 ppm Li NO₃ solution and 21.5 ml deionized water. The concentrations of Ca, Mg and K were determined using a Perkin-Elmer 303 Atomic Adsorption Spectrophotometer.

Phosphorus concentrations in the plant digest were determined as described by Stainton et al., (1974). A 0.5-ml aliquot of the original digest was diluted to 10.5 ml using deionized water. A 0.5-ml aliquot of the dilute digest was then diluted again to 10.5 ml and reacted with 2.0 ml of a

solution containing 250 g/l ascorbic acid and 7.5 g/l ammonium molybdate. Phosphorus concentrations were then measured using a Spectronic 100 UV-visible spectrophotometer set at 885 nm.

Concentrations of sulphur in the plant digest were determined as described by Lazrus et al., (1966). A 0.2 ml aliquot of the original plant digest was diluted to 30 ml and reacted with a solution containing 1.576 g/l BaCl₂ and 0.236 g/l methylthymol blue at a pH of 2.5-3.0. Excess BaCl₂ reacted with the methylthymol blue which formed a colored chelate at a pH of 12.5 to 13.0. Since the methylthymol blue and the BaCl₂ were initially equimolar, the amount of uncomplexed methylthymol blue as measured on a Auto Analyzer II at 460 nm reflected the amount of sulphur in the sample.

(2) <u>Soil Analysis</u>. Organic matter was determined on the field and greenhouse soils by the Walkley-Black method as described by Allison (1965). Titrations were conducted using an automated potentiometer.

Soil pH was determined on a 3:1 soil to water paste using a standard glass-calomel pH electrode. Conductivity was determined on the same paste using a standard conductivity cell.

The inorganic carbonate content of the soil samples was determined by reacting a 0.5-g sample of soil with 40 ml. of 0.1M HCL. The CO₂ evolved was collected on ascarite and the change in weight of the ascarite was taken to be the weight of CO₂ evolved.

The field capacity moisture content and bulk density of each soil were estimated by filling a plastic cylinder of known volume with a known weight of soil. Since the moisture content of each soil had been determined, its oven dry weight and the bulk density could be calculated. The full cylinder was then saturated with water and allowed to drain through Whatman No. 42 filter paper for 24 hours. A subsample was removed from the centre of the tube and the moisture content (field capacity) determined.

Nitrate-nitrogen was determined by Harper's modified phenoldisulphonic acid method (Harper, 1924). Five g of air dried soil were extracted with 50.0 ml of a solution containing AgSO4. Nitrate measured 0.02 Μ CuS04 and 0.06% was colorimetrically as the nitrate form of phenoldisuphonic acid alkaline solution using a Cecil Instruments in an 202 Ultraviolet Spectrophotometer at 415 nm.

Exchangeable K was extracted by shaking a five-gram sample of soil in 100 ml of solution containing 1.0 M NH4OAc and 250 ppm LiNO₃ for one hour. The solution was filtered through Whatman No. 42 filter paper into a 125 ml Erlnmyer flask. Potassium concentration in the filtrate was determined using a Perkin-Elmer 303 Atomic Adsorption Spectrophotometer.

Sulphate sulphur was extracted by shaking 25 grams of soil in 50 ml of distilled water for 30 minutes. The suspension was filtered and the sulphate sulphur concentration in the filtrate determined as described previously.

Extraction of Plant Available Copper From Soil. (3) Several different extracting solutions were evaluated. However, extraction procedures were the same for all extractants. Ά two-gram sample of soil was shaken for one hour in 20 ml of extracting solution. The suspensions were then centrifuged at 1800 rpm for 15 minutes and the supernatants filtered through Whatman No. 42 filter paper into 50 ml Erlnmyer flasks. The copper concentrations in the filtrates were determined using a Perkin-Elmer 303 Atomic Adsorption Spectrophotometer. The various extracting solutions used for the greenhouse studies are listed below.

1. 1 M NH4NO3

2. 1 M KCL

3. 0.1 M HCL

 1% Na₂EDTA (ethylenediaminetetraacetic acid, disodium salt)

5. 2% Na₂EDTA + 1 M NH₄OAc adjusted to a pH of 7.3

6. 0.1 M Na₂DP + 1 M NH₄OAc adjusted to a pH of 7.3. Na₂DP could not be purchased and was prepared from ethylenediamine di (o-hydroyphenyl acetic acid) (EDDHA) which was 90% pure. The EDDHA was purified by grinding the EDDHA to a fine powder using a mortar and pestle, shaking in methanol (ACS Reagent Grade, glass distilled) for 15 minutes, and then centrifuging for 20 minutes at 500 rpm. The supernatant was decanted and discarded and the remaining compound dried and ground. One hundred ml of deionized water containing 3.6 g of the purified

EDDHA, 0.8 g. NaOH and 0.77 g. NH4OAc were shaken for one hour. Any undissolved materials were considered as impurities and were removed by filtration, weighed after drying and then discarded. Additional EDDHA equivalent to the weight of the amount discarded above was then added. The resulting solution was adjusted to a pH of 7.3 with HCL and diluted to a final volume of one litre.

7. 0.005 M DTPA (diethylemetriamine pentaacetic acid) + + 0.01 M $CaCl_2$ + 0.1M TEA (triethanolamine) adjusted to a pH of 7.3.

Solutions used for extracting copper from the soils obtained from the field plots were:

1. 1 M HCL

2. 0.005M DTPA + 0.01 M CaCl₂ + 0.1M TEA, adjusted to a pH of 7.3

3. 1% Na₂ EDTA

4. 2% Na₂ EDTA, and

5. Na₂DP.

IV RESULTS AND DISCUSSION

Greenhouse experiments were conducted to evaluate various chemicals as extractants of plant available copper from organic soils. Barley, wheat, oats and Canola were grown with and without fertilizer copper. Relationships between extractable soil copper and percent yield or plant copper concentration were investigated.

(A) Greenhouse

(1)Yields. Yields of barley receiving no copper varied from 2.8 to 17.9 g/pot whereas yields of barley receiving copper varied from 3.4 to 22.0 g/pot (Table 9). Yields of barley were significantly increased by copper fertilization on only four of 10 soils studied. It is interesting to note that copper fertilization actually decreased yields on three soils. The extremely low yields on soil no. 9 and the negative yield response to copper fertilizer on soil no. 6 were most likely due to low levels of Mn in the barley tissue when fertilizer copper was applied (Appendix 1A). The manganese concentrations in barley grown on these soils were about 12 to 14 ppm when treated with copper fertilizer. The critical concentrations of manganese in barley tissue at the boot stage has been shown to be about 25 ppm (Ward, et al., 1973). The negative response to soil no. 2 may have been related low copper on to

Soil No.	Yield (g/pot)					
	no Cu	10 Kg Cu/ha				
1 2 3 4 5 6 7 8 9 10	17.9 13.3 11.5 13.2 4.6 7.9 9.1 10.8 2.8 16.9	22.0 $11.4 * (-)$ 12.6 $16.3 *$ $15.1 *$ $6.7 * (-)$ $16.5 *$ $16.8 *$ 3.4 $14.3 * (-)$				
Average	10.8	13.5				

Table 9. Effect of copper fertilizer on yield of barley (g/pot) - greenhouse study.

- * Yield with copper significantly greater than without copper (P=.05)
- *(-) Yield with copper significantly less than without copper (P=.05)

Table	10.	Effect	of	copper	fertilizer	on	yield	of	wheat	(g/	'pot)	í.
		- green	nhou	ise stud	dy.							-

Soil No.	Yield (g/pot)					
	no Cu	10 Kg Cu/ha				
1 2 3 4 5 6 7 8 9 10	11.7 7.4 16.5 7.9 2.9 2.0 1.0 2.5 0.9 2.2	20.4 24.4 * 18.6 19.7 13.7 * 12.6 * 12.6 * 22.7 * 3.5 5.9				
Average	5.5	15.4				

* Yield with copper significantly greater than without copper (P=.05)

concentrations of iron in the plant (Appendix 1A) (Ward et al., 1973).

In contrast to the results obtained for barley, applications of copper appeared to increase yields of wheat in all instances (Table 10) although the increases were significant in only five of ten soils studied. The lack of statistical significance in instances where there were relatively large yield increases was likely due to extreme replicate variability and insufficient number of replicates. The extremely low yields on soils 9 and 10, even with copper fertilizer, were related to the extremely low concentrations of manganese (approximately 5 ppm) in the wheat plants (Appendix 2A). Yields of wheat were less than yields of barley when copper was not applied. This indicates that barley was more tolerant to low levels of soil McAndrew (1979) also noted that barley was not as copper. susceptible to copper deficiency as was wheat. Average yields of wheat were similar to those of barley when copper was applied.

Dry matter yields obtained for oats (Table 11) were similar to those obtained for barley. The average yield of oats from the 10 soils was 10.8 and 13.5 g/pot without copper and with 10 Kg Cu/ha, respectively. Oat yields appeared to respond positively to copper on all except soil no. 1 where a slight decrease in yield with copper occurred. However, the yield increases were statistically significant on only three of ten soils indicating that oats were relatively tolerant to low

Soil No.	Yield (g/pot)			
	no Cu	10 Kg Cu/ha		
1 2 3 4 5 6 7 8 9 10	18.3 12.2 11.0 14.3 7.2 8.3 10.9 12.5 8.5 4.4	17.6 14.2 11.1 16.4 * 8.6 9.1 14.6 * 18.3 * 9.2 5.9		
Average	10.7	12.5		

Table 11. Effect of copper fertilizer on yield of oats (g/pot) - greenhouse study.

* Yields with copper significantly greater than without copper (P=.05)

Table	12.	Effect	of	copper	fertilizer	on	yield	of	Canola
		(g/pot)	– gi	reenhous	e study.				

Soil No.	Yield	(g/pot)
	no Cu	10 Kg Cu/ha
1 2 3 4 5 6 7 8 9 10	12.7 11.3 11.7 12.2 7.7 6.0 15.4 10.4 2.6 12.7	13.2 12.8 12.9 * 13.8 17.3 * 10.4 * 15.2 13.2 15.3 * 12.3
Average	10.3	13.6

*Yields with copper significantly greater than without copper (P=.05)

copper supply. As noted for barley and wheat, oat yields were low on soils no. 9 and 10. Manganese concentrations in oat tissue grown on these soils were about 8 ppm (Appendix 3A), well below the critical concentration of 25 ppm suggested by Ward et al., (1973).

Supplementary copper increased Canola yields significantly on four of ten soils (Table 12). The negative yield response to added copper on soil no. 10 was probably due to low manganese concentrations in the Canola tissue (10-14 ppm Mn) (Appendix 4A). The yield decrease when copper was added to soil no. 7 however, was not related to low nutrient concentrations in the plant. Canola, barley and oat dry matter yields obtained without copper fertilizer were similar indicating that these crops were similar in their tolerance to low copper supply.

(2) <u>Percent Yield</u>. Percent yield ((Yield without copper/yield with copper)x100) was calculated to further illustrate the response of various crops to copper fertilizer. The most responsive crop to copper fertilizer was wheat which had an average percent yield for the ten soils of 32% (Table 13). Percent yield values for barley, oats and Canola were similar and were 83%, 87% and 77% respectively.

Sensitivity of the crops to low copper supply was wheat was much more sensitive than Canola, barley and oats. McAndrew (1979) found the sensitivity of crops to low copper supply was wheat>oats>barley>Canola. The relative sensitivity of the

Table 13.	Percent	yield*	of	crops		greenhouse	studies.
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Soil No.	Barley	Wheat	Oats	Canola
1 2 3 4 5 6 7 8 9	81 117 91 81 31 118 55 64 75	57 30 89 25 21 16 8 11 27 38	104 87 99 87 84 92 76 68 93 75	96 92 91 88 45 58 101 79 17
Average	83	32	87	77

* % yield = (yield without copper fertilizer/yield with copper fertilizer) x 100 crops to low copper given by McAndrew (1979) was established on only one organic soil whereas 10 organic soils were used in this study.

(3) <u>Plant Copper Concentrations</u>. Copper concentrations in barley shoots varied from 0.7 to 2.7 ppm when no copper was added (Table 14). On five of the ten soils studied barley shoot copper concentrations were below the low range of 2.3-3.7 ppm established by McAndrew (1979). None of the soils produced plants with copper concentrations in excess of this range. Addition of copper increased copper concentrations in the plants to adequate levels in all instances. Copper concentrations in barley shoots varied from 6.3 to 10.6 ppm when 10 Kg Cu/ha were added to the soil.

The copper concentrations in wheat shoots varied from 1.0 to 1.6 ppm, when copper was not applied. In all instances the concentration of copper in wheat grown without copper fertilizer was below the level required for proper plant growth (McAndrew 1979). Copper fertilization increased copper concentrations in wheat to adequate levels except on soil no. 6 where the copper concentration in wheat receiving copper was only 3.8 ppm. The manganese concentration in wheat grown on this soil was 4.9 ppm when 10 Kg Cu/ha were added. Thus, the severe manganese deficiency may have impaired the plants ability to take up copper. Excluding plants grown on soil no. 6, copper concentrations in wheat shoots varied from 4.2 to 8.7 ppm when

Table	able 14. Concentration		of	copper	in	barley,	wheat,	oats	and	
		Canola	shoots	as	affecte	d by	copper	fertil	izatio	on –
		greenho	ouse stu	Idie	<u>s</u> .					

Soil	Treatment	#1	#2	#1	#1
No.		Barley	Wheat	Oats	Canola
1	no Cu	2.5	1.2	2.5	2.6
	10 Kg Cu/ha	8.8	6.0	5.7	3.4
2	no Cu	1.5	1.3	1.1	4.1
	10 Kg Cu/ha	6.3	4.8	5.8	10.1
3	no Cu	2.5	1.6	3.0	4.9
	10 Kg Cu/ha	7.5	6.4	6.5	6.7
4	no Cu	1.3	1.1	1.8	5.2
	10 Kg Cu/ha	6.3	5.3	4.8	6.5
5	no Cu	0.7	1.3	1.0	1.7
	10 Kg Cu/ha	6.5	5.6	3.2	4.9
6	no Cu	2.5	1.6	2.5	4.4
	10 Kg Cu/ha	10.0	3.8	3.3	4.1
7	no Cu	1.3	1.6	2.5	2.5
	10 Kg Cu/ha	6.9	4.2	3.3	4.4
8	no Cu	2.7	1.0	1.0	3.6
	10 Kg Cu/ha	8.1	4.8	3.4	4.6
9	no Cu	2.5	2.0	1.0	1.9
	10 Kg Cu/ha	10.6	7.6	5.2	4.2
10	no Cu	1.1	1.4	2.9	3.7
	10 Kg Cu/ha	6.3	8.7	5.6	2.1

*1 Average of one analysis on each of three replicates

*2 Plant material from all three replicates was bulked and analysis was conducted in duplicate

copper was added.

Oat plants receiving no fertilizer copper contained 1.0 to 3.0 ppm Cu. Only four of the ten soils (soil no. 2, 5, 8 and 9) produced plants with copper concentrations below the low range of 1.7 to 2.5 ppm Cu (McAndrew 1979). Copper concentrations in oat plants on soil no. 3 and 10 were in excess of 2.5 ppm and not considered low in copper (McAndrew 1979). Copper concentrations in oats grown on the remaining four soils were within the low range (McAndrew 1979). Copper fertilization increased copper concentrations in oat plants in all instances. Copper concentrations in oat shoots varied from 3.2 to 6.5 ppm when 10 Kg Cu/ha were added.

Canola plants grown on soils without copper contained 1.7 to 5.2 ppm Cu. None of the Canola plants had concentrations of copper less than the low range of 1.7 to 2.5 ppm Cu given by Copper concentrations in Canola grown on McAndrew (1979). three soils were within the low range whereas seven soils produced Canola which contained sufficient copper. Copper concentrations in the plants varied from 2.1 to 10.1 ppm when copper On Soil no. 10 and 6, addition of 10 Kg/ha dewas added. creased the concentration of copper in Canola shoots. This was probably due to the manganese deficiency encountered on these Except for Canola grown on soils 6 and 10, copper soils. levels in Canola shoots varied from 4.2 to 10.1 ppm where 10 Kg Cu/ha were added.

(4) Amounts of Soil Copper Extracted - Greenhouse Study.

The average total copper concentration in the 10 soils studied was 13.1 ppm, but the total copper concentration varied from 9.1 to 28.3 ppm (Table 15). The extractants in all cases extracted only a portion of the total soil copper. Amounts of copper extracted from the soil by the various methods varied from 0.1 to 2.4 ppm. Much less copper was extracted by 1 M NH4NO3 and 0.1 M HCL than by the other extractants. Degree of variation among the soils in the amount of copper extracted was dependent on the extraction method used. One M KCL extracted approximately the same amount of copper from all soils. Ammonium nitrate extracted very small amounts of copper from the soils, with the amount extracted being very similar for all In contrast, the amount of copper extracted by the soils. other reagents varied among the soils. For example, 1% Na2 EDTA extractable soil copper varied from 1.1 to 2.4 ppm with a standard deviation from the mean of 0.45 ppm Cu. This represented the greatest variation in extractable copper for the methods used. Amounts of copper extracted by 2% Na₂EDTA, 0.01 M Na₂DP and DTPA were similar and varied less among soils than amounts of copper extracted by 1% Na₂ EDTA. In no case was the amount of extractable soil copper related to the total concentration of copper in the 10 soils studied.

Extrac- tants Soil No.	Total CU	1 M NH4NO3	1 M KCL	0.1M HCL	1% Na ₂ EDTA	2% Na ₂ EDTA	0.01M Na ₂ DP	DTPA.
1 2 3 4 5 6 7 8 9 10	13.6 28.3 11.4 9.6 10.9 10.7 11.9 9.1 11.2 14.4	0.1 0.4 0.3 0.3 0.4 0.3 0.4 0.4 0.4	1.5 1.5 1.6 1.5 1.6 1.6 1.6 1.5 1.7	$\begin{array}{c} 0.4 \\ 1.3 \\ 0.4 \\ 0.1 \\ 0.4 \\ 0.5 \\ 0.6 \\ 0.4 \\ 0.4 \\ 0.4 \end{array}$	2.4 1.9 2.3 1.4 1.3 2.1 1.6 1.1 1.6	2.2 1.9 2.1 1.4 1.8 1.9 2.1 1.5 1.6 1.9	1.7 1.3 1.7 1.4 1.8 1.7 1.7 1.3 1.3 1.1	1.2 1.1 1.0 0.8 0.9 0.9 0.9 0.9 0.9 0.9 0.9 0.8 0.3
Ave. St. Dev.	13.11 5.6	0.3 0.1	1.6 0.7	0.5 0.31	1.7 0.45	1.8 0.27	1.5 0.25	0.9 0.24

Table 15. Total and extractable copper in the soils used in the greenhouse studies (ppm).

(5) <u>Relationships Between Extractable Soil Copper and % Yield</u> or Plant Copper Concentration - Greenhouse Study

(a) <u>Relationship Between Extractable Soil Copper and &</u> <u>Yield</u>. Linear regression analysis was used to describe the relationship between percent yield and the amount of copper extracted by each of the extractants in order to assess each extractant's ability to estimate plant available soil copper. A summary of equations derived from each crop and extractant are shown in Tables 16 to 19.

None of the extractants adequately estimated plant available soil copper for the ten soils and four crops used in this study. The r^2 values for the relationships between % yield and extractable soil copper varied from 0.0002 to 0.44. Twentyfour of the 28 r^2 values were below 0.20, indicating that most of the relationships were very poor. In addition, negative slopes were obtained for those relationships which were statistically significant (P=.05). The extremely poor relationships obtained in this study may have been due to the manganese deficiencies encountered on some of the soils, and the small range of extractable soil copper values encountered. However, despite the limitations noted above, it is apparent from the nature of the relationships obtained that these extractants would be of little value in estimating degree of response to applied soil copper.

(b) Relationships Between Extractable Soil Copper and

Table 16. Relationships between % yield of barley and the amount of extractable soil copper as determined by several methods - greenhouse study.

Extractant	Regression Equation	r ²	S.E.
1 M NH ₄ NO ₃	Y = 125.9 - 125.5 X $Y = 327.3 - 156.5 X$ $Y = 92.4 - 19.0 X$ $Y = 74.1 + 5.32 X$ $Y = 147.4 - 34.9 X$ $Y = 155.8 - 48.4 X$ $Y = 77.5 + 6.47 X$	0.17	28.0
1 M KCL		0.14	28.6
0.1 M HCL		0.004	30.2
1% Na ₂ EDTA		0.007	30.7
2% Na ₂ EDTA		0.10	29.2
0.01 M Na ₂ DP		0.17	28.2
DTPA		0.003	30.8

Y =% Yield

X = Extractable Soil Copper (ppm)
* statistically significant at the 5% level of probability ** statistically significant at the 1% level of probability

Table	17.	Relationships betwee	n % yield	of wheat and	the amount
		of extractable soil	copper as	s determined	by several
		methods - greenhouse	study.	· · · · · · · ·	

Extractant	Regression Equation	r ²	S.E.
1 M NH $_4$ NO $_3$	Y = 10.6 + 63.5 X $Y = (-20.3) + 150.8 X$ $Y = 26.0 + 12.6 X$ $Y = 42.2 - 5.9 X$ $Y = 89.8 - 31.3 X$ $Y = 131.0 - 65.9 X$ $Y = 57.8 - 29.4 X$	0.06	25.1
1 M KCL		0.19	23.4
0.1 M HCL		0.26	25.6
1% Na $_3$ EDTA		0.01	25.8
2% Na $_2$ EDTA		0.12	24.4
0.01 M Na $_2$ DP		0.44*	19.5
DTPA		0.08	53.9

Y =% Yield

X = Extractable Soil Copper (ppm)

* statistically significant at the 5% level of probability ** statistically significant at the 1% level of probability

Table 18. Relationships between % yield of oats and the amount of extractable soil copper as determined by several methods - greenhouse study.

Extractant	Regression Equation	r ²	S.E.
1 M NH4NO3	Y = 84.3 + 6.55 X $Y = -12.1 + 6.32 X$ $Y = 82.5 + 8.14 X$ $Y = 88.4 - 1.14 X$ $Y = 106 - 10.6 X$ $Y = 132 - 30.4 X$ $Y = 102 - 17.9 X$	0.003	11.8
1 M KCL		0.16	10.9
0.1 M HCL		0.05	11.5
1% Na3 EDTA		0.002	11.8
2% Na2 EDTA		0.06	11.5
0.01 M Na2DP		0.44*	8.8
DTPA		0.15	10.9

Y =% Yield

X = Extractable Soil Copper (ppm)

* statistically significant at the 5% level of probability ** statistically significant at the 1% level of probability

Table	19.	Relatio	nsh	ips	bet	ween	물	yi	eld	of	Ca	inola	and	t]	he
		amount	of	extr	act	able	soi	1	copp	er	as	deter	mine	d	by
		several	me	thod	s -	gree	nhou	se	stu	dy.					

Extractant	Regression Equation	r ²	S.E.
1 M NH $_4$ NO $_3$	Y = 102 - 73.7 X $Y = (-38.8) + 74.3 X$ $Y = 36.0 + 105.1 X$ $Y = 82.2 - 3.1 X$ $Y = 74.0 + 1.7 X$ $Y = 64.0 + 8.7 X$ $Y = 113.6 - 42.0 X$	0.06	29.1
1 M KCL		0.03	29.5
0.1 M HCL		0.23	26.4
1% Na $_3$ EDTA		0.002	30.0
2% Na $_2$ EDTA		0.0002	30.0
0.01 M Na $_2$ DP		0.006	30.0
DTPA		0.13	28.1

Y = % Yield

X = Extractable Soil Copper (ppm)

* statistically significant at the 5% level of probability ** statistically significant at the 1% level of probability

Table 20. Relationships between the copper concentration in barley shoots and amounts of extractable soil copper as determined by several extractants - greenhouse study.

Extractant	Regression Equation	r ²	S.E.
1 M NH4NO3	Y = 1.24 + 1.82 X $Y = (-1.76) + 2.3 X$ $Y = 1.59 + 0.52 X$ $Y = 0.93 + 0.54 X$ $Y = 2.85 - 0.54 X$ $Y = 4.22 - 1.57 X$ $Y = 2.21 - 0.41 X$	0.05	0.78
1 M KCL		0.11	0.78
0.1 M HCL		0.05	0.78
1% Na3 EDTA		0.11	0.76
2% Na2 EDTA		0.04	0.79
0.01 M Na2DP		0.26	0.69
DTPA		0.02	0.79

Y = Copper concentration in barley shoots

X = Extractable Soil Copper (ppm)

* statistically significant at the 5% level of probability

** statistically significant at the 1% level of probability

Table	21.	Relati	onship	s be	tween	the	copper	concei	ntration	in
		wheat	shoots	and	amoui	nt ext	ractable	e soil	copper	as
		detern	ined b	y sev	eral	extrac	ctants -	greenh	ouse st	udy.

Extractant	Reg	gression	Equation	r ²	S.E.
1 M NH ₄ NO ₃ 1 M KCL 0.1 M HCL 1% Na ₃ EDTA 2% Na ₂ EDTA 0.01 M Na ₂ DP DTPA	Y = Y = Y = Y = Y = Y = Y = Y =	1.30 + 5.20 - 1.10 + 1.79 - 2.45 - 2.02 - 1.19 +	0.31X 24.1 X 0.66X 0.22 X 0.57 X 0.41 X 0.26 X	0.10 0.36 0.25 0.12 0.26 0.0009 0.04	0.31 0.26 0.27 0.30 0.27 0.30 0.31

Y = Copper concentration in wheat shoots

X = Extractable Soil Copper (ppm)

* statistically significant at the 5% level of probability

** statistically significant at the 1% level of probability

Table 22. Relationships between the copper concentration in oat shoots and amount of extractable soil copper as determined by several extractants - greenhouse study.

Extractant	Regression Equation	r ²	S.E.
1 M NH4NO3 1 M KCL 0.1 M HCL 1% Na3 EDTA 2% Na2 EDTA 0.01 M Na2DP DTPA	Y = 1.33 + 1.76 X $Y = 1.15 + 0.50 X$ $Y = 2.39 + (-0.93)X$ $Y = 3.92 + (-1.17)X$ $Y = 6.28 + (-2.36)X$ $Y = 4.43 + (-1.67)X$ $Y = 3.94 + (-2.07)X$	0.04 0.0003 0.12 0.40* 0.57* 0.24 0.35	

Y = Copper concentration in oats shoots

X = Extractable Soil Copper (ppm)

* statistically significant at the 5% level of probability

** statistically significant at the 1% level of probability

Table	23.	Relatio	onships	bety	ween	the	copper	c	oncen	tratio	n in
		Canola	shoots	and	amour	t ext	tractab	le	soil	copper	as
		determ	ined by	seve	ral e	xtrac	tants -	- gr	eenho	ouse st	udy.

Extractant	Reg	gression	r ²	S.E.	
1 M NH4NO3 1 M KCL 0.1 M HCL 1% Na3 EDTA 2% Na2 EDTA 0.01 M Na2DP DTPA	Y = Y = Y = Y = Y = Y = Y = Y =	4.93 + 4.03 + 2.58 + 2.06 + 4.76 + 3.21 + 2.81 +	(-4.33)X (-0.36)X 2.26 X 0.83 X (-0.70)X 0.17 X 0.74 X	0.12 0.0004 0.06 0.09 0.02 0.001 0.02	1.23 1.31 1.27 1.25 1.29 1.31 1.29

Y = Copper concentration in Canola shoots

X = Extractable Soil Copper (ppm)

* statistically significant at the 5% level of probability ** statistically significant at the 1% level of probability

Plant Copper Concentration. The r² values for relationships between extractable soil copper concentrations and plant copper concentration (Tables 20 to 23) varied from 0.0003 to 0.57. Negative slopes were obtained for those relationships which were statistically significant (P=.05). Na₂DP resulted in best relationship (r²=0.26) between shoot copper concentration in barley and extractable soil copper. For wheat the highest r^2 (0.26) occurred when 2% Na² EDTA was used to estimate plant available soil copper. Extracting with 2% Na2EDTA also provided a good relationship between copper concentration in oat shoots and extractable soil copper $(r^2=0.57)$. Relationships between copper concentration in Canola shoots and extractable soil copper were best when 1 M NH_4NO_3 was used ($r^2=0.12$). Apart from the above few exceptions all other relationships were very poor. In all cases, the standard errors of estimates were large. Because of the large standard errors and low r^2 values, it was concluded that none of the extractants was useful in predicting copper concentration in barley, wheat, oat and Canola shoots.

(B) Field Studies

Production of annual crops on organic soils presents a unique set of problems. Not only is the management of organic soils difficult in terms of drainage and proper cultivation, but the nutritional management of these soils is equally

challenging. Previous nutritional studies conducted on organic soils in Manitoba revealed that deficiencies of nitrogen, phosphorus, potassium and copper were likely to limit yields of annual crops (Campbell and Gusta 1966, Loewen-Rudgers et al., 1978, Racz et al., 1978, McAndrew 1979).

To achieve a better understanding of the problems of copper nutrition of cereals and oil seeds grown on organic soils, field studies were conducted at three locations in southeastern Manitoba during the summer of 1979. The influence of varying amounts of copper fertilizer upon seed and straw yields of barley, wheat and Canola and upon shoot nutrient concentrations at midseason was determined. In addition, several extractants were evaluated for their ability in assessing plant available soil copper.

(1) <u>Yields</u>. Yields of seed were low for all crops with the exception of barley at Stead. However, straw yields for all three crops were high and did not vary greatly with treatment.

(a) <u>Barley</u>. Barley straw yields varied from 4007 Kg/ha to 5254 Kg/ha (Table 24). Although there were some significant differences among treatments, the differences did not appear to be related to the amount of copper applied. Straw yields were also quite consistent among experimental sites. There were some small differences in barley grain yields among treatments but those differences were either statistically non-significant or were not consistently related to treatment (Table 25).
Table 24. Yields of barley straw as affected by copper fertilization - field experiments (Kg/ha).

	Location					
Treatment	Marchand	Piney	Stead			
Control	4007 ab ¹	4972 a	4643 ab			
5 Kg Cu/ha	4205 ab	4659 a	4963 a			
10 Kg Cu/ha	4436 a	4596 a	4290 b			
20 Kg Cu/ha	3775 ъ	4719 a	49 40 a			
40 Kg Cu/ha	4094 ab	5260 a	4385 b			

¹ Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level.

Table	25.	Yields	of	bar	ley g	grain	as	affected	by	copper
		fertili	zatic	on –	field	experi	iment	(Kg/ha).		

	Location					
Treatment	Marchand	Piney	Stead			
Control	2443 a ^l	1612 a	3 131 ab			
5 Kg Cu/ha	2722 a	1590 a	3469 a b			
10 Kg Cu/ha	2689 a	1760 a	3067 b			
20 Kg Cu/ha	2361 a	1282 a	3698 a			
40 Kg Cu/ha	2686 a	1731 a	3227 a b			

Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level.

(b) Yields of wheat straw at Marchand increased Wheat. when 5 Kg Cu/ha were applied but did not increase further when 10 Kg Cu/ha were applied and decreased to the level of the control when more than 10 Kg Cu/ha were applied. A similar trend at Piney was not statistically significant. Addition of 5 Kg Cu/ha at Stead increased straw yield by about 2000 Kg/ha. Increasing amounts of copper fertilizer above 5 Kg Cu/ha did not increase straw yields above that obtained with 5 Kg Cu/ha. Yields of wheat grain at Marchand and Stead (Table 27) were significantly increased by the addition of 5 Kg Cu/ha, but more than 5 Kg Cu/ha did not increase grain yields of wheat above that obtained with 5 Kg Cu/ha. Copper fertilization had no significant influence upon wheat grain yields at Piney. Even with the addition of copper wheat grain yields were very low at all three sites.

(c) <u>Canola</u>. Canola straw yields at Piney and Stead were not affected by copper fertilization (Table 28). Straw yields of Canola at Marchand followed the same trend as wheat straw yields at that site, increasing when 5 Kg Cu/ha were added, but decreasing to the level of the control when more than 10 Kg Cu/ha were added. Yields of Canola straw were high at all locations. Seed yields of Canola were low at all three locations varying from 650 Kg/ha to 1079 Kg/ha (Table 29). Seed yields followed the trend noted for straw yields. Yields of seed at Piney and Marchand were not significantly increased

Table 26. Yields of wheat straw as affected by copper fertilization - field experiments (Kg/ha).

	Location					
Treatment	Marchand	Piney	Stead			
Control	2808 bl	4448 a	4 717 b			
5 Kg Cu/ha	3791 a	4732 a	6658 a			
10 Kg Cu/ha	3609 ab	4335 a	6622 a			
20 Kg Cu/ha	3045 ab	4594 a	6586 a			
4 0 Kg Cu/ha	29 26 b	4443 a	6781 a			

Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level.

Table 27. Yields of wheat grain as affected by copper fertilization - field experiments (Kg/ha).

	Location					
Treatment	Marchand	Piney	Stead			
Control	26 c ¹	185 a	94 b			
5 Kg Cu/ha	39 1 b	219 a	371 a			
10 Kg Cu/ha	502 a	236 a	4 28 a			
20 Kg Cu/ha	384 b	232 a	445 a			
40 Kg Cu/ha	313 b	243 a	334 a			

Duncan's Multiple Range Test. Values followed by the same letter are not signififcantly different at the 5% proability level.

Table 28. Yields of Canola straw as affected by copper fertilization - field experiments (Kg/ha).

	Location					
Treatment	Marchand	Piney	Stead			
Control	4894 bcl	3104 a	4339 a			
5 Kg Cu/ha	6439 a	3177 a	464 2 a			
10 Kg Cu/ha	5660 ab	2937 a	4 563 a			
20 Kg Cu/ha	4225 d	3149 a	5037 a			
4 0 Kg Cu/ha	4857 cd	3144 a	4 577 a			

- Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level.
- Table 29. <u>Yields of Canola seed as affected by copper</u> fertilization - field experiments (Kg/ha).

	Location					
Treatment	Marchand	Piney	Stead			
Control	793 c ¹	652 a	704 a			
5 Kg Cu/ha	1359 a	650 a	840 a			
10 Kg Cu/ha	1079 b	632 a	853 a			
20 Kg Cu/ha	747 c	679 a	909 a			
40 Kg Cu/ha	927 bc	639 a	804 a			

Duncan's Multiple Range Test. Values followed by the same letter are not signififcantly different at the 5% proability level.

by copper fertilization. Yield of Canola at Marchand was highest when 5 Kg Cu/ha was applied.

(2) Chemical Composition

(a) Barley. Copper fertilization increased the concentration of copper in barley shoots at all three locations (Table 30). Copper concentrations in barley shoots were increased significantly by the application of only 5 Kg Cu/ha while application of 20 and 40 Kg Cu/ha increased shoot copper concentrations three, two and two fold at Marchand, Piney and Stead, respectively. Copper concentrations in barley shoots in the range of 2.3 to 3.7 ppm Cu were considered to be low by McAndrew (1979). Copper concentrations in barley grown without copper were below, or just above the low end of this range. Ten Kg Cu/ha increased copper concentrations to nearly sufficient or sufficient levels, while copper in barley grown with 20 and 40 Kg Cu/ha were well above 3.7 ppm Cu. Despite the fact that copper concentrations in the tissue were increased to levels considered to be sufficient, yields were quite low, particularly at Marchand and Piney, and were influenced very little by copper fertilization.

The low yields of barley grain may have been due to a manganese deficiency at Marchand and Piney (Table 31). Yields of barley grain were highest at Stead when the manganese concentrations were above the suggested critical level of 24 ppm

	Location				
Treatment	Marchand	Piney	Stead		
Control	1.8 c ¹	2.4 d	2.1 c		
5 Kg Cu/ha	3.6 b	3.6 c	3.2 b		
10 Kg Cu/ha	3.8 ab	4.0 bc	3.7 ba		
20 Kg Cu/ha	4.6 a	4.4 ab	4. 2 a		
40 Kg Cu/ha	4.5 a	5.0 a	4.1 a		

Table 30. Copper concentration in barley shoots as affected by copper fertilization - field experiments (ppm).

¹ Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level.

Table 31. Mn, Zn, Fe, Ca, Mg, K, S and P concentrations in barley shoots as affected by copper fertilization field experiments (ppm).

	Marchand							
Treatment	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (%)	K (%)	S (%)	P (%)
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	12.2 a ¹ 11.3 ab 10.2 ab 10.2 b 10.7 b	13.4 a 13.6 a 13.1 a 12.7 a 12.1 a	104 a 84.0 b 76.2 bc 68.8 c 67.8 c	0.64 a 0.56 a 0.55 a 0.59 a 0.58 a	0.22 a 0.22 a 0.21 a 0.22 a 0.21 a	0.54 a 0.65 a 0.63 a 0.43 a 0.48 a	0.18 a 0.18 a 0.13 b 0.13 b 0.13 b 0.17 ab	0.18 ab 0.19 a 0.17 bc 0.18 ab 0.15 c
				Pine	∋y			
	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (%)	K (%)	S (%)	P (%)
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	11.1 ab 8.2 b 12.6 a 11.2 ab 12.1 a	20.5 b 21.7 b 23.8 ba 22.7 ba 25.7 a	32.7 a 29.2 a 31.7 a 31.1 a 34.5 a	0.30abc 0.29 ab 0.33abc 0.36 a 0.35 ab	0.18 a 0.18 a 0.18 a 0.20 a 0.20 a	0.80 ab 0.87 ab 0.90 a 0.77 b 0.75 b	0.10 a 0.09 a 0.09 a 0.12 a 0.13 a	0.15 b 0.25 a 0.26 a 0.28 a 0.24 a
	Stead							
	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (%)	K (%)	S (%)	P (%)
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	37.7 a 36.7 a 33.4 ab 35.4 a 31.0 b	24.2 ab 20.9 b 25.2 ab 27.7 a 24.9 ab	56.5 a 49.0 a 47.2 bc 48.3 bc 44.3 c	0.35 ab 0.40 a 0.33 ab 0.30 b 0.28 b	0.21 a 0.22 a 0.22 a 0.22 a 0.22 a	0.58 a 0.63 a 0.57 a 0.88 b 0.77 ab	0.20 ab 0.26 a 0.16 b 0.18 b 0.16 b	0.18 c 0.17 c 0.21 b 0.24 a 0.22 b

¹ Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level.

by copper (Ward et al., 1973). In contrast, the low grain yields obtained at Marchand and Piney were associated with plant manganese concentrations between 12.6 and 8.2 ppm. Manganeseconcentrations in barley were not influenced by copper fertilization at Piney whereas at Marchand and Stead the manganese concentrations tended to decrease with increasing levels of applied copper.

Zinc concentrations in barley at Marchand were less than 15 ppm and may have limited yields (Ward et al., 1973). Zinc concentrations in barley at Piney and Stead were in the sufficient range and were not affected by copper fertilization.

Iron concentrations in barley were low at Piney and Stead. Ward et al., (1973) considered iron concentrations of less than 50 ppm low and likely to affect yields. Iron concentrations in barley at Piney varied from 29.2 to 34.5 ppm and may have limited yields. Iron concentrations in barley at Stead were below 50 ppm for all treatments which received copper.

Calcium and magnesium concentrations in barley were at adequate levels. Copper fertilization did not influence calcium and magnesium concentrations in barley except at Stead. At Stead, calcium concentration in barley grown with 40 Kg Cu/ha was significantly less than that in barley grown with 5 Kg Cu/ha.

Potassium concentrations in barley were below the critical level of 1.25% (Ward et al., 1973) at all three locations.

Potassium at 200 Kg K₂O/ha was applied to all plots and thus potassium should not have been deficient. The low potassium values in plant tissue were most likely due to the loss of potassium from the plant material during the washing procedures prior to analysis. Reid and Racz (1980) grew barley on sites adjacent to those used in this study and found potassium concentrations to be much higher when plant samples were not washed. Thus, potassium was most likely not limiting to yields.

Sulphur concentrations in barley were adequate at Marchand and Stead, but less than adequate at Piney (Ward et al., 1973). Sulphur concentrations in barley tissue were not affected by the application of copper except at Stead. At Stead sulphur concentrations in barley grown with 5 Kg Cu/ha were significantly higher than sulphur concentrations in barley grown without and with 10, 20 and 40 Kg Cu/ha.

Phosphorus concentrations in barley tissue were within the sufficient range for all locations.

Analysis of barley tissue suggested that several nutrient deficiencies of differing severity were encountered. The soils at Marchand and Piney were deficient in both copper and manganese whereas the soil at Stead was deficient in copper only. In addition to copper and manganese deficiencies, iron deficiencies may also have been encountered at Stead and Piney.

(b) <u>Wheat</u>. Copper concentrations in wheat shoots were

	Location				
Treatment	Marchand	Piney	Stead		
Control	1.0 d ¹	1.9 b	1.3 c		
5 Kg Cu/ha	1.7 bc	3.0 a	2.1 b		
10 Kg Cu/ha	2.1 bc	3.6 a	2.3 b		
20 Kg Cu/ha	2.3 bc	3.5 a	2.6 ba		
4 0 Kg Cu/ha	3.0 a	3.6 a	3.3 a		

Table 32. Copper concentration in wheat shoots as affected by copper fertilization - field experiments (ppm).

¹ Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level. lower than those in barley shoots, but they were increased by copper fertilization (Table 32). Copper additions at 5 Kg Cu/ha significantly increased the copper concentration of wheat above that obtained without copper. Copper concentrations in wheat at Marchand and Stead increased to levels above the critical concentration of about 3 ppm Cu only when more than 20 Kg Cu/ha were added. McAndrew (1979) considered copper concentrations in wheat shoots at heading in the range of 3.0 to 4.9 ppm Cu to be low.

Plant concentrations of several other nutrients also appeared to be deficient. Wheat at Marchand was severely manganese deficient, whereas wheat at Piney was moderately manganese deficient (Table 33). Manganese deficiencies were not encountered in wheat at Stead. Manganese concentrations usually decreased when copper was applied but the decreases were significant only at Marchand and only when large amounts of copper were applied. Part of the cause of low yields at Marchand and Stead when copper was added and the decrease in yield at Marchand at the higher levels of copper was likely manganese deficiency which was likely accentuated at the higher levels of copper at Marchand. However, other nutrient deficiencies and/or unfavorable environmental conditions also depressed yields as evidenced by the low yields at Stead where manganese was not deficient.

Zinc concentrations in wheat at Marchand were less than the critical level of 15 ppm suggested by Ward et al., (1973).

Table 33. Mn, Zn, Fe, Ca, Mg, K, S and P concentrations in wheat shoots as affected by copper fertilization field experiments (ppm).

	Marchand							
Treatment	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (%)	K (%)	S (%)	P (%)
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	7.9 a ¹ 7.7 a 5.5 ab 4.9 b 4.9 b	15.7 a 13.1 b 13.1 b 15.2 ab 14.8 ab	70.9 a 59.0 b 49.9 c 44.3 cd 42.7 d	0.33 a 0.33 a 0.34 a 0.38 a 0.38 a	0.24 a 0.23 a 0.24 a 0.24 a 0.25 a	0.77 bc 0.72 c 0.84 ab 0.90 a 0.86 ab	0.09 c 0.09 c 0.10 bc 0.11 ab 0.12 a	0.20 a 0.19 a 0.19 a 0.19 a 0.20 a
				Pin	ey			
	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (%)	K (%)	S (%)	P (%)
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	17.1 a 15.2 a 13.6 a 16.7 a 13.8 a	23.5 a 21.5 ab 18.9 b 20.9 ab 19.5 b	36.3 a 33.8 ab 33.6 ab 34.2 ab 30.4 b	0.27 a 0.23 a 0.25 a 0.26 a 0.23 a	0.20 a 0.17 b 0.17 b 0.18 b 0.17 b	0.88 ab 0.97 a 0.88 ab 0.82 ab 0.73 b	0.08 a 0.09 a 0.10 a 0.10 a 0.09 a	0.19 b 0.18 a 0.15 b 0.19 a 0.18 a
	Stead							
	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (%)	K (%)	S (%)	P (%)
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	48.0 a 39.3 a 39.6 a 41.6 a 36.1 a	26.3 b 23.9 b 23.6 b 23.4 b 22.5 b	46.0 a 38.4 b 38.4 b 37.6 b 38.6 b	0.30 a 0.29 a 0.28 a 0.28 a 0.28 a	0.19 a 0.20 a 0.18 a 0.19 a 0.15 a	0.83 a 0.87 a 0.74 a 0.77 a 0.81 a	0.12 c 0.14 ab 0.16 ab 0.16 ab 0.18 a	0.22 a 0.21 a 0.20 a 0.20 a 0.19 a

¹ Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level.

Wheat at Piney and Stead contained sufficient quantities of zinc. Zinc concentrations in wheat were usually decreased by copper applications at all sites. However, the decreases were not closely related to the amount of copper added.

Concentrations of iron in wheat at Piney and Stead were below 50 ppm which was considered to be the lower level of sufficiency by Ward et al., (1973). Iron concentrations at Marchand decreased from about 71 ppm to 43 ppm as copper fertilizer was increased from 0 to 40 Kg Cu/ha. Decreases in iron concentration in wheat with copper fertilization were also noted at Piney and Stead.

Moderate deficiencies of sulphur were observed from the analysis of the wheat tissue from Piney and Marchand (Ward et al., 1973). This trend was not noted for barley except at Piney where sulphur was low.

Concentrations of calcium, magnesium and phosphorus in wheat were sufficient at all locations. Potassium concentrations in wheat plants were low. The low concentrations of potassium in wheat were most likely due to the washing of plant material prior to analysis.

(C) <u>Canola</u>. Copper concentrations in Canola shoots (Table 34) from the Marchand site were increased above the critical level of 1.7 ppm (McAndrew 1979) Cu by the addition of 5 Kg Cu/ha. At Piney and Stead, copper concentrations in shoots of control plants were within the low range of 1.7 to 2.7 ppm (McAndrew

	Location				
Treatment	Marchand	Piney	Stead		
Control	1.5 a ^l	2.2 b	2.0 c		
5 Kg Cu/ha	2.3 a	3.0 c	2.9 b		
10 Kg Cu/ha	2.2 a	3.2 bc	3.0 b		
20 Kg Cu/ha	2.8 a	3.5 b	3.1 b		
40 Kg Cu/ha	2.8 a	4.0 a	3.7 a		

Table 34. Copper concentration in Canola shoots as affected by copper fertilization - field experiments (ppm)

¹ Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level. 1979) and copper fertilization at 5 Kg Cu/ha increased plant copper concentrations into the sufficient range above 2.7 ppm.

Critical concentrations of manganese, zinc, iron, calcium, magnesium, potassium, phosphorus and sulphur in Canola were not found in the literature. However, nutrient concentrations in Canola shoots from this study were compared with shoot nutrient concentrations in other studies to assist in identifying possible deficiencies. Table 35 shows the results of plant analysis conducted by McAndrew (1979) on Canola which yielded about 1600 Kg/ha. The site used by McAndrew (1971) was slightly zinc deficient and thus it was assumed that the zinc concentration found in this study was lower than that normally found in Canada.

Manganese concentrations in Canola grown at Marchand (Table 36) suggest that an acute manganese deficiency was encountered. Manganese concentrations in Canola grown at Piney were also quite low and thus manganese deficiencies may have limited yields. Plant concentrations of iron at Piney also were quite low. Thus, low yields of Canola at Marchand may have been the result of manganese deficiency while at Piney low yields may have been related to low plant concentrations of both manganese and iron. Other environmental conditions must have also limited Canola yields as yields at Stead were low despite adequate concentrations of nutrients in the shoots. All other nutrients were present in adequate concentrations in Canola shoots and were not influenced by copper applications.

Table	35.	Cor	lcent	rat	ions	of	Cu,	Zn,	Mn,	Fe,	P,	S,	Κ,	Ca	and	Mq
		in	Cano	la	(ppm)	(N	lcAnd	lrew	1979).						

		— ppi	n		&					
Element	Cu	Zn	Mn	Fe	Р	S	K	Ca	Mg	
Concentration	2.9	16	38	43	0.3	0.7	1.1	0.8	0.6	

Table 36. Mn, Zn, Fe, Ca, Mg, K, S and P concentrations in Canola shoots as affected by copper fertilization field experiments (ppm).

	Marchand										
Treatment	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (웅)	K (%)	S (%)	P (%)			
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	7.8 a ¹ 7.3 a 7.3 a 10.5 a 7.6 a	18.0 a 19.1 a 19.1 a 17.4 a 19.3 a	57.2 a 45.7 a 42.3 a 48.1 a 47.6 a	2.6 a 1.9 a 2.9 a 2.5 a 2.5 a	0.64 a 0.58 a 0.58 a 0.56 a 0.54 a	0.71 a 0.69 a 0.68 a 0.70 a 0.69 a	0.58 a 0.60 a 0.58 a 0.49 a 0.51 a	0.29 0.28 0.25 0.30 0.28			
Piney											
	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (%)	K (%)	S (%)	P (%)			
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	22.6 a 22.8 a 21.7 a 22.3 a 21.2 a	44.2 a 43.3 a 45.4 a 42.4 a 44.2 a	26.6 a 31.1 a 34.2 a 27.9 a 28.1 a	1.9 a 2.1 b 2.0 ab 1.9 ab 2.0 ab	0.51 a 0.56 a 0.52 a 0.51 a 0.53 a	0.84 a 0.88 a 0.87 a 0.83 a 0.87 a	0.38 a 0.40 a 0.41 a 0.44 a 0.42 a	0.15 0.19 0.16 0.15 0.16			
				Stea	ad						
	Mn (ppm)	Zn(ppm)	Fe(ppm)	Ca (%)	Mg (%)	K (%)	S (%)	P (%)			
Control 5 Kg Cu/ha 10 Kg Cu/ha 20 Kg Cu/ha 40 Kg Cu/ha	34.2 a 46.7 a 43.3 a 45.4 a 52.5 a	45.9 a 40.2 a 37.8 a 38.0 a 35.2 a	37.5 a 37.9 a 37.9 a 37.5 a 40.8 a	2.3 a 2.2 a 2.1 a 2.2 a 2.1 a	0.79 a 0.79 a 0.76 a 0.77 a 0.78 a	0.69 a 0.82 a 0.74 a 0.79 a 0.73 a	0.58 a 0.55 a 0.55 a 0.53 a 0.53 a	0.30 ab 0.29 ab 0.28 b 2.27 b 0.33 a			

1 Duncan's Multiple Range Test. Values followed by the same letter are not significantly different at the 5% probability level.

(3) <u>Relationships Between Extractable Soil Copper and Amounts</u> of Copper Fertilizer Applied or Plant Copper Concentrations - Field Studies

The field experiments conducted in 1979 were also used to evaluate several chemical extractants for their ability in assessing plant available soil copper. Soil samples were taken from every replicate of every treatment at each experimental site at the time of the midseason harvest and analyzed for extractable copper using the extractants previously described in the Methods and Materials section. The amounts of copper extracted by the various reagents (Appendix 5A to 13A) were then related to amounts of copper applied and (b) midseason plant copper concentrations. The above relationships were calculated for each crop and extractant used. Relationships between amounts of copper extracted by the various extractants and response of the crop to copper fertilizer were not calculated as only three experimental sites were used.

(a) <u>Relationships between extractable soil copper and</u> <u>amounts of copper fertilizer applied</u>. The ability of each extractant to reflect the rate of copper fertilizer applied was examined by plotting the average level of extractable soil copper (average of all six replicates and three crops) versus the rate of copper applied in Kg/ha. Generally, the relationships between extractable soil copper and amount of copper

fertilizer added were linear. An example of the type of relationship obtained is shown in Figure (2) in which 1 M HCL extractable copper (ppm) was plotted versus the rate of copper added. Extractable copper levels were compared by linear regression analysis to the rate of copper added. A summary of these relationships are shown in Table 37. All extractants appeared to extract copper from soils in proportion to the amount of copper fertilizer applied. The r^2 values were all high and varied from 0.65 to 0.97. The values of r^2 varied from 0.83 to 0.97 except at Stead where the r^2 values for Na₂DP was 0.65. Except for Na₂DP extractable copper at Stead r^2 values were not greatly affected by location or extractant.

(b) <u>Relationships Between Extractable Soil Copper and</u> <u>Plant Copper Concentrations</u>. The relationship between plant copper concentration in a particular crop and extractable soil copper was calculated using the data from all three sites and all rates of copper applied. Individual data for plant tissue concentrations of copper and extractable soil copper were used.

Several mathematical functions were examined to determine which best described the various relationships between soil and plant copper. An equation in the form [Plant] = EXT/a+b EXT + c EXT² where [Plant] = the midseason plant copper concentration (ppm) and Ext = concentration of extractable soil copper (ppm) was selected and regression analysis performed using [Plant] obs/Ext as the dependent variable and Ext and Ext² as





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Table 37. Relationships between the amount of copper fertilizer applied and the amount of extractable soil copper as determined by several extractants - field experiments.

Extractant	Location	Equation	r ²	S.E.	F
INHCL	Piney Stead Marchand	*1 *2 y = 6.2 + 2.0X y = 10.9 + 2.4X y = 3.5 + 1.8X	0.96 0.89 0.85	6.0 12.8 11.4	336.9 105.8 73.3
DTPA	Piney	y = 3.5 + 2.4X	0.88	13.6	97.5
	Stead	y = 15.9 + 2.4X	0.83	16.0	65.2
	Marchand	y = 3.3 + 1.7X	0.90	8.6	121.2
1%Na ₂ EDTA	Piney	y = 10.0 + 3.2X	0.96	10.1	293.3
	Stead	y = 18.9 + 3.0X	0.84	20.0	65.7
	Marchand	y = 4.3 + 2.0X	0.92	8.9	143.9
2%Na ₂ DTPA	Piney	y = 11.4 + 3.6X	0.97	10.4	357.5
	Stead	y = 17.7 + 3.4X	0.83	25.8	63.2
	Marchand	y = 5.6 + 3.0X	0.90	15.5	115.9
Na ₂ DP	Piney Stead Marchand	y = 13.1 + 2.2X y = 20.5 + 1.7X y = 3.3 + 2.2X	0.92 0.65 0.85	9.5 18.9 14.2	158.8 24.4 73.1

*1 y = amount of copper fertilizer applied (Kg Cu/ha)
*2 X = extractable soil copper (ppm)

* statistically significant at the 5% level of probability ** statistically significant at the 1% level of probability

independent variables to calculate the values of a, b and c for each extractant and crop. Equations for the various extractants for barley, wheat and Canola appear in Tables 38, 39 and 40, respectively. Shoot copper concentrations were then calculated for various extractable soil copper levels using the equations in Tables 38, 39 and 40 and measured plant copper concentrations related by linear regression analysis to those predicted by the equations. The r^2 and standard error of estimate values for those linear regression analyses also appear in Tables 38, 39 and 40. Values of r^2 varied from 0.41 to 0.67. One M HCL provided the best relationship between the observed and calculated tissue concentrations of copper in barley $(r^2=0.61)$ and wheat $(r^2=0.49)$ whereas Na₂DP gave the best relationship for Canola $(r^2=0.67)$.

The r² values were generally low while the standard error of estimates accounted for large portions of the estimates. Consequently, the accuracy of prediction of plant copper concentrations was poor particularly at low concentrations. Actual plant copper concentrations at or near the critical level would be difficult to predict using these equations.

Actual (individual points) and predicted (solid line) copper concentration in barley shoots versus soil copper extracted with 1 M HCL appear in Figure 3. The predicted curve was divided into three regions. Region one was near the origin where the curve was nearly linear. Region two was curvilinear and included the plant copper concentrations at or near the

Table	38.	Relationship	between		the		calculate	ed and	ob	observed	
		concentration	of	copp	er	in	barley	shoots	-	field	
		experiments.									

Extractant	Equation	r ²	S.E.
1 M HCL	$ \begin{array}{r} *1 & *2 \\ y = X/1.64 + 0.23X - 0.00017X^2 \\ y = X/1.14 + 0.22X - 0.000052X^2 \\ y = X/3.90 + 0.19X + 0.000036X^2 \\ y = X/3.63 + 0.21X + 0.000031X^2 \\ y = X/0.74 + 0.26X + 0.00026X^2 \end{array} $	0.61**	0.70
DTPA		0.48**	0.84
1%Na2EDTA		0.56**	0.93
2%Na2EDTA		0.46**	0.79
Na2DP		0.53**	0.42

*1 copper concentration in barley tissue (ppm)

*2 extractable soil copper (ppm)

* statistically significant at the 5% level of probability ** statistically significant at the 1% level of probability

Table	39.	Relationship	betw	een	the	Ca	alculate	d and	ob	served
		concentration	of	copp	er	in	wheat	shoots	-	field
		experiments.								

Extractant	Equation	r ²	S.E.
1 M HCL	$ \begin{array}{c} *1 & *2 \\ y = X/1.17 + 0.38X - 0.00075X^2 \\ y = X/1.39 + 0.36X - 0.00057X^2 \\ y = X/2.80 + 0.38X - 0.00054X^2 \\ y = X/7.70 + 0.27X - 0.0001X^2 \\ y = X/2.18 + 0.35X - 0.00051X^2 \end{array} $	0.49**	0.46
DTPA		0.46**	0.49
1%Na2EDTA		0.41**	0.35
2%Na2EDTA		0.48**	0.59
Na2DP		0.44**	0.48

*1 copper concentration in wheat tissue (ppm)

*2 extractable soil copper (ppm)

* statistically significant at the 5% level of probability

** statistically significant at the 1% level of probability

Table 40.	Relationship	betw	veen tl	the		alculate	d and	ob	served
	concentration	of	copper	· i	n	Canola	shoots	-	field
	experiments.								

Extractant	Equation	r ²	S.E.
1 M HCL	$ \begin{array}{c} *1 & *2 \\ y = x/0.80 + 0.30X - 0.00029X^2 \\ y = x/1.39 + 0.28X - 0.000025X^2 \\ y = x/1.50 + 0.30X - 0.00016X^2 \\ y = x/0.82 + 0.36X - 0.00028X^2 \\ y = x/1.33 + 0.32X - 0.00049X^2 \end{array} $	0.56**	0.49
DTPA		0.50**	0.59
1%Na2EDTA		0.56**	0.49
2%Na2EDTA		0.62**	0.28
Na2DP		0.67**	0.39

*1 copper concentration in Canola tissue (ppm)

*2 extractable soil copper (ppm)

* statistically significant at the 5% level of probability ** statistically significant at the 1% level of probability



Figure 3 Relationships between the copper concentration in barley plants and the amount of copper extracted from soil with IMHCL.

critical level. In region three the level of plant copper was only slightly affected by increasing the level of extractable soil copper.

Multiple regression techniques have been used often to allow for the influence of soil characteristics such as pH and organic matter and interactions of other nutrients on the ability of an extractant to predict the copper status of a soil. However, in this study pH values of the three soils were similar. Also, organic matter contents of the soils were all high and did not vary greatly. Thus, regression equations using soil characteristics as well as extractable soil copper were not calculated due to an insufficient number of sites or variations in soil characteristics.

Martens (1968) found an \mathbb{R}^2 value of 0.847 when pH, organic matter and 1 M HCL extractable copper were correlated with copper uptake by corn grown on 16 mineral soils. In the study reported here, the best relationships between the observed and calculated concentrations of copper in barley ($r^2=0.61$) and wheat ($r^2=0.49$) were obtained with 1M HCL extractable copper but not for Canola. Marten (1968) also found that organic matter contents of soils and 1 M HCL extractable soil copper correlated well ($r^2=0.748$) which may imply that 1 M HCL is a good extractant for estimating plant available soil copper on organic soils. Whitney (1975) and Vitosh et al., (1973) both recommended the use of 1 M HCl to determine the plant available soil copper on organic soils.

Lindsay and Norvell (1967) proposed that on mineral soils the critical concentration for DTPA extractable soil copper was less than 0.2 ppm. From work reported here it is apparent that this level is far below that necessary for good plant growth on organic soils. Calculations using the equations derived in this study indicate that DTPA extractable soil copper concentrations would have to be about 2.25 to 21.0 ppm for barley plants to contain 2.3 to 3.7 ppm copper. According to the relationship established between the amount of DTPA extractable soil copper and the rate of copper added, at least 14.4 Kg Cu/ha would be required on the soils used in this study to ensure adequate concentrations of copper in barley tissue.

It was shown in the greenhouse studies that none of the extractants was a good indicator of plant available soil copper in organic soils not fertilized with copper. However, the relationships obtained between extractable soil copper and tissue copper in the field studies were good when both copper fertilized and nonfertilized soils were included in the relationship. This indicated that these extractants may be useful in predicting plant available soil copper in organic soils treated with copper fertilizer.

V SUMMARY AND CONCLUSIONS

Previous investigations showed that organic soils in Manitoba do not supply copper to plants in sufficient quantities for good growth of many crops. However, the extent and severity of this problem was not known. Thus, greenhouse and field studies were conducted to examine the response of barley, wheat and Canola to copper fertilization. In addition several chemical extractants were evaluated for their ability in predicting the amount of copper available to plants grown on organic soils.

Preliminary work was conducted in the greenhouse using organic soils from 10 locations in Manitoba. Yields of barley, wheat, oats and Canola were significantly increased by copper fertilization on several soils. Levels of copper in the tissue of barley, wheat and oats were increased from deficient to sufficient concentrations by the addition of 10 Kg Cu/ha. Concentrations of copper in Canola tissue were increased from deficient to sufficient levels by 10 Kg Cu/ha in eight of 10 soils studied. These data indicated that many organic soils in Manitoba are deficient in plant available copper, and that under greenhouse conditions levels of copper in plant tissue can be increased to sufficient levels by the addition of copper fertilizer.

The sensitivity of the crops to low copper supply was wheat was much more sensitive than Canola, barley and oats.

Wheat was very sensitive to low copper supply whereas the other crops were relatively tolerant to low copper supply.

Field studies were conducted at three locations on organic soils to determine if barley, wheat, oats and Canola would respond to copper fertilizer. Straw yields were high but grain yields were low for all three crops. Barley grain yields were not significantly increased by copper fertilization whereas wheat grain yields were significantly increased by copper fertilization at two of three locations. Canola yields were not affected by copper fertilization.

Copper concentrations were lower in wheat than in the other crops. Therefore, although five Kg Cu/ha did significantly increase (P=.05) copper concentrations they were still below the critical level. Copper concentrations in wheat were increased to adequate levels on two of three soils when 40 Kg Cu/ha were added. In contrast, copper concentrations in barley were increased to adequate levels by five Kg Cu/ha. Copper fertilization at five Kg Cu/ha increased copper levels in Canola at Piney and Stead above the low range established by McAndrew (1979). However, this range was not exceeded at Marchand even when 40 Kg Cu/ha had been applied.

Yield of grain of all crops at most locations was less than expected even when copper concentrations in the plant were increased to sufficient levels. This was likely due to deficiencies of other nutrients. Plant manganese concentrations indicated the manganese deficiencies were encountered on

two of three locations. Concentrations of zinc, iron, potassium and sulphur in plant tissue of some of the crops grown on some of the soils were also less than needed for optimum growth.

A second major objective of this study was to evaluate several chemical extractants for their ability in estimating plant available soil copper in organic soils. None of the extractants selected provided a good method of estimating plant available soil copper on soils not fertilized within the greenhouse. Relationships calculated between extractable soil copper and % yield generally varied from $r^2=0.0002$ to $r^2=0.20$. Relationships between extractable soil copper and copper content of plants grown in the greenhouse on soils not fertilized with copper were also poor.

Grain yields in the field were not consistently increased by copper fertilization and therefore were not selected as criteria for evaluating extractants in the field. Plant copper concentrations in barley, wheat and Canola were related to extractable soil copper using values from both copper fertilized and nonfertilized soils. An equation of the form: $[TIS]calc = Ext/a+bExt+cExt^2$ was used to describe the relationship between plant copper concentration and the concentration of plant available soil copper. For barley and wheat the best relationships resulted when 1 M HCL was used to extract soil copper, whereas Na₂DP provided the best relationship for Canola. Generally, r^2 values were low for all crops and

extractants.

It was noted in the field study that all extractants extracted copper from the soil in proportion to the amount of copper fertilizer applied. No differences were apparent among the various extractants in their ability to reflect the rate of copper fertilizer applied.

It was concluded that none of the extractants assessed adequately plant available soil copper in organic soils not fertilized with copper. However, the relationships obtained between extractable soil copper and plant copper concentrations were good when both copper fertilized and non fertilized soils were included in the relationships. This indicated that these extractants may be useful in predicting plant available soil copper in organic soils, fertilized previously with copper.

It was also apparent from data obtained that many problems require investigation before organic soils in Manitoba can be fully utilized. The information gained in this study on the effect of fertilizer copper on plant growth will be useful in correcting copper deficiencies on organic soils. However, it several micronutrients, manganese was apparent that in particular, require further study. The studies also showed that plant species vary in their ability to grow on soils low in available copper. Selection of crop species and varieties more suited to organic soils is also required. In addition, negative slopes were obtained for about one-half of the regression equations.

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Appendix Table 1.

	r	T	T	r	·····			<u> </u>
Soil No.	Treatment	Cu ppm	Mn ppm	Zn ppm	Fe ppm	Ca ℁	Mg %	K &
1	No Cu	2.5 2.5 2.5	42.5 43.8 42.5	27.5 25.4 25.4	37.5 37.5 35.0	0.61 0.64 0.56	0.44 0.45 0.44	0.61 0.58 0.95
-	10 Kg Cu/ha	8.8 8.8 8.8	20.0 18.8 18.8	27.5 27.5 27.5	31.3 31.3 31.3	0.50 0.48 0.45	0.36 0.35 0.33	0.88 0.81 0.84
2	No Cu	1.5 1.3 1.6	100 106 106	25.0 22.5 22.5	47.5 45.0 42.5	0.30 0.30 0.30	0.45 0.41 0.44	0.81 0.72 0.66
-	10 Kg Cu/ha	6.1 6.8 5.9	66.3 70.0 51.3	22.5 23.1 22.5	32.5 35.0 32.5	0.25 0.28 0.20	0.33 0.37 0.30	0.88 1.00 1.00
3	No Cu	2.5 2.5 2.5	52.5 62.5 62.5	21.9 22.8 21.9	50.0 47.5 43.8	0.50 0.47 0.50	0.45 0.47 0.45	0.84 0.72 0.63
J	10 Kg Cu/ha	7.5 7.5 7.5	37.5 33.8 35.0	22.8 21.0 22.8	43.8 32.5 37.5	0.48 0.44 0.48	0.48 0.47 0.48	0.64 0.58 0.77
Α	No Cu	1.3 1.3 1.3	48.8 56.3 50.0	16.9 20.0 16.3	37.5 46.3 38.8	0.38 0.41 0.38	0.37 0.44 0.36	0.78 0.91 1.00
T	10 Kg Cu/ha	6.9 5.8 6.3	22.6 18.5 20.3	17.5 15.6 17.5	32.5 25.0 31.3	0.30 0.25 0.28	0.28 0.21 0.23	0.78 0.81 0.78
5	No Cu	0.6 0.6 0.7	42.5 45.0 46.3	20.0 18.8 23.1	110 95.0 125	0.88 0.84 0.91	0.23 0.23 0.28	0.53 0.59 0.81
2	10 Kg Cu/ha	5.8 6.0 6.4	14.8 15.3 15.6	13.8 13.1 15.1	48.8 48.8 63.8	0.69 0.69 0.78	0.33 0.33 0.36	0.78 0.63 0.78

Effect of Copper Fertilizer on the Chemical Composition of Barley-Greenhouse Study

Soil No.	Treatment	Cu ppm	Mn ppm	Zn ppm	Fe ppm	Ca १	Mg %	К &
6	No Cu	2.5 2.5 2.5	20.0 15.0 21.3	11.9 10.0 10.0	219 219 210	0.77 0.78 0.77	0.44 0.36 0.44	0.88 0.88 0.72
	10 Kg Cu/ha	10.0 10.0 10.0	15.0 13.8 13.8	9.0 8.8 9.4	165 160 145	0.61 0.64 0.56	0.44 0.42 0.44	0.75 0.70 0.97
7	No Cu	1.3 1.3 1.3	65.0 68.8 71.3	25.4 25.4 21.9	56.3 57.5 55.0	0.67 0.75 0.77	0.27 0.30 0.25	0.89 0.61 0.83
,	10 Kg Cu/ha	9.4 5.6 5.6	28.8 23.8 22.5	20.0 16.5 16.5	43.8 32.5 32.5	0.63 0.56 0.55	0.45 0.38 0.38	0.81 0.73 0.80
9	No Cu	3.0 2.5 2.5	132 145 150	24.4 24.4 21.8	57.5 55.0 52.5	0.45 0.42 0.55	0.38 0.38 0.47	0.78 0.92 0.81
C	10 Kg Cu/ha	7.5 8.8 8.1	36.3 40.0 36.3	17.5 17.5 17.5	35.0 35.0 31.3	0.31 0.34 0.33	0.34 0.36 0.36	0.80 1.00 0.67
Q	No Cu	2.5 2.5 2.5	22.5 28.8 23.8	11.0 11.9 11.9	135 156 145	0.77 0.84 0.73	0.30 0.33 0.31	0.64 0.95 1.00
5	10 Kg Cu/ha	11.3 10.6 10.0	8.8 15.0 15.0	10.0 7.9 9.5	100 103 103	0.66 1.00 1.00	0.30 0.36 0.33	0.75 0.95 0.97
10	No Cu	1.1 1.1 1.1	22.3 24.0 22.6	16.9 16.3 17.5	62.5 62.5 60.0	0.44 0.50 0.47	0.36 0.38 0.38	0.69 0.59 0.75
10	10 Kg Cu/ha	8.1 8.4 8.6	14.8 16.5 17.3	20.0 21.3 21.3	43.8 52.5 57.5	0.53 0.47 0.53	0.41 0.41 0.41	0.75 0.78 0.69

Appendix Table 2A

Effect	œ	Opper	Fertilizer	an	the	Chanical	Composition of
			Wheat-Grea	nte	use	Study	

Soil		Q1 ((ppm)	Min (j	xxm)	Zn (p	дтп)	Fe (p	zem)	Ca (9	\$)	Mg (§	ŧ)	к (%)
NO.	Treatment.	Rl	R2	Rl	R2	Rl	R2	Rl	R2	Rl	R2	Rl	R2	Rl	R2
1	No Qu	1.3	1.1	28.8	26.3	42.5	42.5	45.0	46.3	0.39	0.32	0.38	0.33	0.94	0.61
	10 Kg Qu/ha	5.8	6.0	15.6	37.0	35.0	56.3	50.0	50.0	0.36	0.38	0.28	0.30	0.26	0.31
2	No Qu	1.3	1.3	200	208	27.5	33.8	52.8	46.3	0.36	0.38	0.51	0.53	0.80	0 .9 7
	10 Kg Qu/ha	4.7	4.8	130	152	30.3	29.8	25.0	31.3	0.23	0.27	0.28	0.33	0.26	0 .2 6
3	No Qu	1.5	1.6	35.0	36.3	57.5	83.8	32.5	40.0	0.20	0.22	0.30	0.33	0.59	0.44
	10 Kg Qu/ha	6.4	6.3	25.0	28.1	30.3	29.5	43.8	50.0	0.24	0.27	0.28	0.31	0.26	0.66
4	No Qu	1.1	1.1	42.5	38.8	40.0	31.3	46.3	50.0	0.34	0.36	0.42	0.42	1.00	1.03
	10 Kg Qu/ha	5.3	5.3	27.5	26.3	20.0	20.6	37.5	35.0	0.25	0.25	0.33	0.32	1.00	1.03
5	No Qu	1.3	1.3	13.8	15.0	25.0	23.8	60.0	60.0	0.55	0.56	0.22	0.22	୦.ଗ	0.62
	10 kg Qu/ha	5.8	5.3	7.8	6.3	18.8	18.8	50.0	43.8	0.38	0.42	0.18	0.18	୦.36	0.42
6	No Qu	1.2	1.9	16.7	-	16.7	16.7	103	-	0.43	0.37	0.42	-	-	0.85
	10 Kg Qu/ha	3.8	3.8	4.7	5.0	9.8	10.5	31.3	37.5	0.67	-	0.24	0.27	0.60	0.50
7	No Qu	1.4	1.7	-	-	-	-	-	-	-	-	-	-	-	-
	10 Kg Qu/ha	4.0	4.4	14.1	13.8	18.3	19.3	25.0	31.3	0.31	0.39	0.18	0.23	0.33	0.29
8	No Qu	1.0	1.0	56.3	51.9	36.3	28.3	60.0	78.4	0.30	0.35	0.38	0.38	1.06	0.90
	10 Kg Qu/ha	4.8	4.8	23.8	25.0	17.5	19.5	25.0	78.4	0.26	0.27	0.25	0.27	0.26	0.36
9	No Qu	2.0	2.0	-	-	-	-	-	-	-	-	-	-	-	-
	10 kg Qu/ha	7.3	7.8	4.7	4.7	11.3	11.3	119	119	0.ഒ	0.66	0.30	0.29	0.31	0.35
10	No Cu	1.3	1.5	13.8	14.5	18.8	20.3	52.5	43.6	0.41	0.51	0.36	0.27	1.49	1.15
	10 Kg Cu/ha	8.6	8.8	6.3	5.0	26.8	26.3	81.3	68.8	0.49	0.40	0.34	0.33	0.70	0.57

Appendix 3A

<u> </u>								
Soil No.	Treatment	Cu ppm	Mn ppm	Zn ppm	Fe ppm	Ca %	Mg %	К 8
1	No Cu	2.5 2.5 2.5	23.8 23.8 20.0	22.8 23.5 21.0	47.5 43.8 33.8	0.45 0.39 0.39	0.45 0.44 0.41	0.72 0.84 0.95
- -	10 Kg Cu/ha	6.0 5.6 5.6	13.8 23.8 21.3	24.4 21.3 21.0	47.5 43.8 37.5	0.33 0.38 0.36	0.33 0.42 0.38	0.77 0.77 0.73
2	No Cu	1.3 1.0 1.1	250 250 269	50.0 37.5 34.4	71.3 56.3 57.5	0.35 0.34 0.34	0.50 0.53 0.53	0.81 0.81 0.74
-	10 Kg Cu/ha	5.8 6.0 5.6	21.8 254 0 238 3	28.8 32.5 32.5	46.3 53.8 55.0	0.30 0.25 0.30	0.44 0.47 0.47	0.75 0.75 0.66
2	No Cu	3.0 3.0 3.0	30.0 33.8 31.3	22.8 25.4 24.4	37.5 40.0 40.0	0.64 0.73 0.58	0.64 0.70 0.63	0.73 0.67 0.63
J	10 Kg Cu/ha	6.5 6.5 6.5	27.5 33.8 40.0	23.4 24.4 21.9	32.5 47.5 40.0	0.53 0.53 0.88	0.58 0.55 0.63	0.67 0.64 0.61
4	No Cu	2.5 1.9 1.0	37.5 38.8 42.5	20.0 20.6 20.0	32.5 51.3 50.0	0.34 0.31 0.31	0.47 0.42 0.48	0.81 0.75 0.94
-	10 Kg Cu/ha	4.4 4.0 5.3	27.5 28.8 36.3	16.3 18.1 18.1	48.8 46.3 45.0	0.28 0.30 0.30	0.37 0.40 0.42	0.81 0.81 0.81
5	No Cu	1.1 0.9 1.0	21.9 19.8 22.6	21.9 18.2 20.0	157 140 156	0.81 0.69 0.91	0.39 0.37 0.45	0.91 0.63 0.88
5	10 Kg Cu/ha	3.0 3.3 3.3	10.1 12.3 11.5	20.6 14.4 15.6	52.5 55.0 50.0	0.53 0.93 0.56	0.22 0.36 0.24	0.91 0.75 0.59

Effect of Copper Fertilizer on the Chemical Composition of Oats-Greenhouse Study

Appendix 3A (cont'd)

Soil No.	Treatment	Cu ppm	Mn ppm	Zn ppm	Fe ppm	Ca १	Mg %	& &
6	No Cu	2.5 2.5 2.5	17.5 13.8 16.3	11.0 9.5 11.0	193 150 145	1.00 0.75 0.82	0.58 0.44 0.53	0.80 0.81 0.77
Ū	10 Kg Cu/ha	3.3 3.3 3.3	9.0 9.0 9.0	10.0 10.0 11.3	43.8 47.5 75.0	1.41 0.78 0.64	0.44 0.42 0.39	0.75 0.92 0.75
7	No Cu	2.5 2.5 2.5	33.8 32.5 43.8	23.5 21.9 23.5	80.0 80.0 93.8	0.84 0.95 1.06	0.63 0.59 0.73	0.83 0.77 0.77
	10 Kg Cu/ha	3.3 3.3 3.3	23.8 23.8 23.8	15.6 15.6 15.0	77.5 40.0 37.5	0.68 0.80 0.77	0.61 0.36 0.48	0.75 0.55 0.64
0	No Cu	0.9 1.1 1.0	60.0 85.0 77.5	15.6 20.0 20.0	71.3 97.5 86.3	0.34 0.41 0.38	0.47 0.53 0.52	0.97 0.87 0.75
Ū	10 Kg Cu/ha	3.3 3.4 3.4	43.8 48.8 46.3	11.9 13.1 13.1	51.3 55.0 66.3	0.28 0.28 0.31	0.41 0.41 0.47	0.66 0.78 0.88
٩	No Cu	1.0 1.0 1.1	11.5 11.5 12.8	8.1 7.5 8.1	211 179 239	0.53 0.69 0.78	0.41 0.44 0.45	0.81 1.03 0.91
,	10 Kg Cu/ha	5.4 5.6 4.6	8.5 8.0 8.0	6.9 6.3 6.3	71.3 140 92.5	0.44 0.47 0.44	0.34 0.36 0.33	0.81 1.03 0.91
10	No Cu	3.3 3.0 2.5	10.0 12.5 12.5	16.9 15.0 13.5	52.5 50.0 50.0	0.26 0.36 0.72	0.30 0.31 0.39	0.67 0.55 0.61
1 0	10 Kg Cu/ha	5.6 5.6 5.6	7.5 8.8 8.8	12.5 12.5 15.0	50.0 50.0 47.5	0.33 0.28 0.33	0.31 0.30 0.33	0.70 0.67 0.80

Appendix 4A

Soil No.	Treatment	Cu ppm	Mn ppm	Zn ppm	Fe ppm	Ca %	Mg %	К %
1	No Cu	2.8 2.5 2.5	46.4 31.7 34.2	32.6 34.3 31.2	31.0 28.0 25.0	2.73 2.33 2.23	0.54 0.49 0.49	1.50 1.50 1.40
Ŧ	10 Kg Cu/ha	3.4 3.3 3.4	28.8 23.2 24.7	28.2 23.2 28.2	19.0 25.0 21.0	2.49 1.94 2.26	0.47 0.43 0.53	1.40 1.20 1.50
2	No Cu	2.4 2.2 7.6	380 460 420	112 112 150	212 280 200	1.43 1.36 1.25	0.98 1.27 1.03	1.22 1.65 1.32
۷	10 Kg Cu/ha	8.8 9.6 12.0	270 220 234	80.2 78.4 89.0	84.0 63.2 91.8	1.32 1.27 1.21	0.84 0.88 0.86	1.10 1.35 1.03
	No Cu	4.6 4.8 5.2	90.6 90.8 86.2	27.8 25.4 27.6	38.2 42.4 44.2	2.14 2.03 1.72	1.16 1.02 1.19	1.04 1.16 1.21
5	10 Kg Cu/ha	7.6 7.0 5.6	71.8 63.0 62.8	20.6 20.6 19.4	37.4 39.0 33.6	1.56 1.64 1.76	1.01 1.02 1.06	1.69 1.26 1.34
Δ	No Cu	4.4 5.2 6.0	34.6 43.8 43.2	23.8 35.4 30.6	33.8 34.8 35.6	1.81 1.87 1.61	0.60 0.73 0.61	1.50 1.26 1.20
-	10 Kg Cu/ha	7.0 6.2 6.2	25.8 33.0 21.4	18.6 22.8 17.2	22.8 33.8 24.2	1.73 1.70 1.45	0.58 0.60 0.50	1.01 1.26 0.99
5	No Cu	1.8 1.6 1.6	26.2 23.6 25.6	23.6 22.0 20.4	57.2 53.4 60.8	3.06 2.85 3.26	0.30 0.35 0.36	1.16 1.74 1.76
	10 Kg Cu/ha	5.2 5.2 13.6	18.8 20.6 20.6	19.2 19.0 16.4	49.2 51.4 50.4	2.58 2.78 2.76	0.34 0.38 0.37	1.43 1.21 1.15

Effect of Copper Fertilizer on the Chemical Composition of Canola-Greenhouse Study

Appendix 4A (cont'd)

Soil No.	Treatment	Cu ppm	Mn ppm	Zn ppm	Fe ppm	Ca १	Mg %	К &
6	No Cu	3.6 5.6 4.0	16.0 14.4 13.4	13.4 10.6 9.8	56.6 59.2 57.0	3.28 3.33 2.96	0.80 0.81 0.78	1.44 1.71 1.53
U	10 Kg Cu/ha	5.2 3.4 3.7	9.0 8.9 9.4	10.2 8.6 9.5	48.0 38.0 44.0	2.70 2.75 3.04	0.65 0.55 0.61	1.19 2.10 2.10
7	No Cu	2.3 2.4 2.7	56.9 57.9 60.4	29.4 30.1 34.7	46.0 53.0 50.0	2.69 _ 4.63	0.45 - 0.94	2.00 - 2.30
	10 Kg Cu/ha	5.3 5.3 2.6	53.8 46.7 57.9	26.5 26.3 32.9	47.0 47.0 55.0	2.31 2.16 2.14	0.43 0.46 0.43	1.40 1.90 1.90
Ω	No Cu	4.8 4.0 2.2	106 107 97.8	29.4 31.6 35.8	55.6 49.6 46.0	2.08 2.24 2.13	0.88 0.91 0.91	1.51 1.04 1.59
	10 Kg Cu/ha	5.2 4.6 4.0	85.6 74.8 64.4	24.0 24.0 22.0	43.6 45.6 41.6	2.36 2.21 2.23	0.95 0.89 0.93	1.30 1.24 1.29
Q	No Cu	2.6 2.0 2.1	13.7 15.7 12.9	8.7 14.6 13.3	46.0 51.0 44.0	2.70 2.62 2.26	0.39 0.41 0.41	1.80 2.10 1.60
-	10 Kg Cu/ha	3.9 4.1 4.7	8.6 9.1 9.0	9.0 8.7 8.7	42.0 44.0 46.0	2.81 2.30 2.13	0.44 0.47 0.44	1.70 2.00 1.90
10	No Cu	2.6 1.7 1.9	14.2 13.9 13.8	20.0 21.3 23.3	29.4 25.0 28.0	1.87 2.50 2.44	0.48 0.51 0.48	1.28 1.70 1.60
10	10 Kg Cu/ha	3.6 4.0 3.5	10.9 13.8 11.3	19.0 17.8 19.5	18.0 23.0 29.0	1.80 2.75 2.04	0.44 0.58 0.42	1.90 1.70 2.00

Appendix 5A

Amounts of Co	oper Extracted	Using Various	Extractants
Marchan	ð Barley - Fie	ld Experiments	(ppm)

Treatment	Replicate	INHCL	DTPA	1% Na ₂ EDPA	1% Na ₂ EDTA	Na2DP
CONTROL	1 2 3 4 5 6	3.5 4.0 2.5 2.0 2.5 3.5	5.3 3.1 2.8 1.8 1.7 2.0	4.3 5.3 2.9 2.0 1.3 1.5	9.2 6.9 4.8 3.8 3.0 5.1	7.7 6.9 8.3 5.7 6.4 7.5
5 Kg Cu/ha	1 2 3 4 5 6	20.5 5.0 13.5 9.5 8.3 18.0	16.9 4.1 12.7 9.3 7.5 17.3	2.6 20.8 3.8 11.3 8.8 7.1	36.4 10.9 8.3 17.5 12.7 31.1	27.6 10.5 21.3 11.9 12.2 24.7
10 Kg Cu/ha	1 2 3 4 5 6	35.5 22.5 24.8 22.0 32.0 8.3	30.4 22.7 21.4 20.9 26.7 5.7	35.1 26.7 26.3 25.5 29.4 7.1	35.5 45.0 37.5 40.0 58.6 14.5	36.2 26.1 24.5 32.4 36.8 9.0
20 Kg Cu/ha	1 2 3 4 5 6	105 45.0 63.0 70.0 35.0 12.8	106 52.1 52.6 35.7 28.0 49.3	110 53.9 62.0 62.0 44.0 10.0	170 78.0 106 105 56.8 22.5	115 47.2 71.7 65.5 34.9 14.3
4 0 Kg Cu/ha	1 2 3 4 5 6	88.0 55.0 165 108 110 83.0	79.4 50.8 127 96.7 118 65.8	56.0 56.0 162 102 128 75.0	150 94.1 244 180 175 132	106 58.5 171 112 107 81.0

Appendix 6A

Amounts of Copper Extracted Using Various Extractants Marchand Wheat - Field Experiments (ppm)

Treatment	Replicate	INHCL	DTPA	1% Na ₂ EDPA	1% Na ₂ EDTA	Na2DP
CONTROL	1 2 3 4 5 6	1.5 2.0 3.3 2.0 3.1 2.5	2.3 2.4 2.6 2.3 3.1 3.0	4.0 4.0 3.0 9.0 5.0	6.7 6.2 8.5 7.4 7.4 6.6	6.3 5.4 4.0 1.5 0.7 3.1
5 Kg Cu/ha	1 2 3 4 5 6	10.6 20.8 27.0 6.7 16.0 8.0	8.8 19.2 9.4 6.8 14.2 6.4	16.6 24.0 11.3 8.1 16.4 10.8	15.8 33.8 11.2 8.0 18.4 11.8	23.9 3.9 14.5 10.7 10.9 19.6
10 Kg Cu/ha	1 2 3 4 5 6	22.4 19.2 41.8 74.0 10.6 17.6	23.3 17.1 42.0 85.6 8.3 14.9	28.1 20.3 49.1 100 13.1 20.1	30.2 22.1 57.2 104 13.4 24.5	36.0 27.2 25.2 134 39.1 7.7
20 Kg Cu/ha	1 2 3 4 5 6	74.0 43.0 68.0 15.2 16.0 17.6	71.8 49.8 70.3 13.5 16.7 13.5	82.9 61.2 85.0 20.3 22.6 18.5	101 67.7 85.3 23.7 26.0 19.2	108 50.9 74.9 69.0 38.5 15.1
4 0 Kg Cu/ha	1 2 3 4 5 6	43.0 50.0 29.3 74.0 136 55.0	44.4 49.9 27.1 85.6 135 54.5	52.1 65.6 31.0 100 66.6 187	197 73.2 62.5 104 194 79. 5	105 65.1 174 134 110 86.0

Appendix 7A

Amounts of Copper Extracted Using Various Extractants Marchand Canola - Field Experiments (ppm)

Treatment	Replicate	INHCL	DIPA	1% Na ₂ EDPA	1% Na2EDTA	Na ₂ DP
CONTROL	1 2 3 4 5 6	2.0 2.0 2.5 2.0 2.0 -	2.8 2.9 3.0 2.1 2.0 -	8.0 4.0 3.0 2.0 2.0 -	6.6 6.5 7.7 5.4 5.6 -	5.9 5.4 5.11 8.6 3.6 -
5 Kg Cu/ha	1 2 3 4 5 6	3.5 12.8 6.5 10.0 20.5 -	2.8 13.6 7.0 11.6 24.8 -	3.0 12.0 7.0 12.0 26.0 -	7.3 24.0 14.9 24.3 47.2 -	5.5 17.0 7.3 11.9 28.7 -
10 Kg Cu/ha	1 2 3 4 5 6	- 58.0 5.0 17.5 4.0 -	- 52.9 6.0 22.4 4.0 -	- 58.0 7.0 18.0 27.0 -	- 97.5 12.7 41.6 11.3 -	- 6.1 25.5 5.2 3.4 -
20 Kg Cu/ha	1 2 3 4 5 6	16.8 20.5 9.5 50.0 21.0 -	16.6 24.4 12.0 50.5 20.8	19.0 24.0 14.0 60.0 25.0 -	34.7 45.1 16.2 97.1 43.8 -	23.5 32.4 8.9 58.9 19.9 -
40 Kg Cu/ha	1 2 3 4 5 6	17.5 93.0 55.0 45.0 75.0 -	21.6 102 47.1 46.7 73.3	21.0 103 58.0 48.0 89.0 -	37.1 158 96.3 86.3 144 -	21.3 97.1 58.4 62.9 52.4 -

Appendix 8A

Treatment	Replicate	INHCL	DTPA	1% Na ₂ EDPA	1% Na ₂ EDTA	Na2DP
CONTROL	1 2 3 4 5 6	2.4 2.2 2.0 3.0 2.4 2.8	0.9 0.7 0.7 2.4 1.8 1.4	6.6 5.8 6.2 7.4 6.0 6.4	5.0 4.7 4.7 7.1 5.7 6.6	4.0 3.0 3.8 5.8 4.8 5.3
5 Kg Cu/ha	1 2 3 4 5 6	9.8 10.2 13.9 11.0 14.3 6.9	8.0 11.9 9.0 9.6 13.0 4.1	17.1 16.7 25.4 23.7 22.4 10.3	17.8 18.9 38.6 21.7 24.5 1.7	15.9 16.3 24.8 17.9 19.7 7.4
10 Kg Cu/ha	1 2 3 4 5 6	31.6 24.9 24.1 8.6 30.7 56.0	34.0 24.0 26.6 7.5 3.5 55.0	47.9 37.4 29.3 14.3 49.0 88.0	49.8 40.1 50.3 17.6 43.3 97.7	39.8 35.6 41.6 14.2 43.8 73.7
20 Kg Cu/ha	1 2 3 4 5 6	52.0 34.0 113 34.0 44.0 34.0	4.9 3.8 33.7 114 4.7 3.5	81.1 53.8 181 68.3 66.8 57.5	87.8 60.5 176 54.3 64.3 55.9	76.0 48.0 127 48.9 62.1 46.4
40 Kg Cu/ha	1 2 3 4 5 6	148 48.0 85.0 56.0 41.0 148	182 51.6 106 59.1 46.4 157	233 74.8 163 131 70.3 228	223 74.4 137 100 72.3 250	188 56.7 103 67.5 55.0 164

Amounts of Copper Extracted Using Various Extractants Piney Barley - Field Experiments (ppm)

Appendix 9A

Treatment	Replicate	INHCL	DIPA	1% Na ₂ EDPA	1% Na ₂ EDTA	Na ₂ DP
CONTROL	1 2 3 4 5 6	1.3 3.7 1.9 3.4 2.0 4.0	0.9 3.7 1.0 3.2 1.8 3.4	1.5 5.0 2.2 4.3 2.4 5.6	0.6 7.5 4.0 5.7 3.9 7.1	10.1 14.5 12.6 12.2 11.4 13.4
5 Kg Cu/ha	1 2 3 4 5 6	16.2 18.0 9.0 17.0 20.5 16.4	16.1 19.6 12.2 15.3 19.5 15.1	15.0 28.0 19.0 24.0 31.0 25.0	29.1 32.2 24.0 23.7 32.8 27.3	27.3 30.5 23.6 22.8 28.4 26.1
10 Kg Cu/ha	1 2 3 4 5 6	21.0 18.0 27.0 52.0 21.0 41.0	31.4 18.8 31.0 55.3 22.5 44.6	46.0 30.0 45.0 75.0 36.0 62.0	55.4 30.5 54.7 71.6 38.6 98.3	38.4 19.7 36.8 45.1 25.3 57.0
20 Kg Cu/ha	1 2 3 4 5 6	52.0 56.0 48.0 38.0 27.0 38.0	46.9 54.9 37.4 33.3 28.3 34.5	78.2 82.8 58.0 51.0 39.0 60.0	104 87.3 84.4 75.6 49.2 85.7	64.1 54.1 51.2 44.9 33.4 51.3
40 Kg Cu/ha	1 2 3 4 5 6	70.0 52.0 80.0 170 70.0 65.0	60.5 29.8 76.5 237 69.0 61.7	95.0 72.0 121 254 103 83.0	131 59.2 140 297 133 79.7	75.4 35.7 86.2 160 79.0 64.0

Amounts of Copper Extracted Using Various Extractants Piney Wheat - Field Experiments (ppm)

Appendix 10A

Amounts	of	Copper	Exti	racted	Using	Various	s Extractants
]	Pine	y Canol	la –	Field	Experi	iments	(ppm)

Treatment	Replicate	INHCL	DTPA	1% Na ₂ EDPA	1% Na ₂ EDTA	Na2DP
CONTROL	1 2 3 4 5 6	1.9 3.3 3.0 2.4 2.6 1.9	1.1 2.3 1.6 2.2 1.8 1.4	6.1 6.9 6.7 7.1 6.3 5.7	17.2 7.5 6.8 36.7 6.8 6.3	4.9 4.4 5.1 5.4 5.1 5.0
5 Kg Cu/ha	1 2 3 4 5 6	7.7 10.5 16.2 15.4 10.0 18.8	8.5 13.1 21.1 13.0 5.2 15.4	17.6 22.7 29.8 25.4 11.0 25.0	15.7 23.1 27.8 25.6 13.6 27.0	12.4 17.9 23.6 21.2 13.6 22.6
10 Kg Cu/ha	1 2 3 4 5 6	34.0 95.0 27.0 18.0 12.0 12.0	37.2 199 31.4 20.1 16.3 15.9	58.0 151 46.0 29.0 24.0 25.0	58.4 149 50.4 34.3 30.3 29.5	48.9 117 39.9 29.2 24.3 25.5
20 Kg Cu/ha	1 2 3 4 5 6	34.0 48.0 120 48.0 60.0 48.0	36.0 58.1 185 54.8 63.4 43.7	54.0 77.0 175 75.0 74.0 56.0	51.2 90.9 266 82.5 125 72.3	37.3 62.8 129 63.6 83.4 54.3
40 Kg Cu/ha	1 2 3 4 5 6	128 75.0 56.0 27.0 128 48.0	172 149 67.9 45.0 210 55.9	193 138 101 55.2 193 78.2	291 139 159 58.1 286 96.4	152 84.4 94.7 53.7 131 58.4

Appendix 11A

Amounts of Copper Extracted Using Various Extractants Piney Barley - Field Experiments (ppm)

Treatment	Replicate	INHCL	DTPA	1% Na ₂ EDPA	1% Na ₂ EDTA	Na2DP
CONTROL	1 2 3 4 5 6	4.6 1.7 7.4 12.3 4.9 4.8	5.6 2.3 8.2 14.0 4.8 4.3	6.0 1.0 9.0 20.0 5.0 4.0	7.2 2.2 12.1 22.2 6.4 6.0	7.7 3.6 9.8 17.4 6.6 5.9
5 Kg Cu/ha	1 2 3 4 5 6	34.8 19.8 20.3 18.5 21.2 33.7	35.0 20.7 23.0 22.5 17.5 34.8	48.0 27.0 27.0 29.0 47.0 27.0	43.4 26.5 36.2 24.8 28.2 42.3	74.5 5.5 55.1 49.7 143 21.4
10 Kg Cu/ha	1 2 3 4 5 6	31.8 27.6 11.9 24.0 85.0 60.0	30.7 29.1 14.3 19.2 91.2 59.4	44.0 35.0 17.0 27.0 97.0 80.0	48.2 33.0 21.3 19.9 87.3 68.6	39.6 97.7 122 50.4 35.8 22.0
20 Kg Cu/ha	1 2 3 4 5 6	52.0 41.0 137 15.0 60.0 120	56.0 42.9 195 20.7 66.7 165	71.0 55.0 235 28.0 85.0 152	65.7 61.2 238 211 67.4 122	27.1 50.6 239 33.2 35.7 25.1
40 Kg Cu/ha	1 2 3 4 5 6	128 48.0 41.0 75.0 105 220	147 47.3 39.2 84.0 127 251	184 64.0 63.0 119 153 316	172 58.6 61.0 150 121 132	14.1 18.9 47.6 94.1 98.7 195

Appendix 12A

Treatment	Replicate	INHCL	DTPA	1% Na ₂ EDPA	1% Na ₂ EDTA	Na ₂ DP
CONTROL	1 2 3 4 5 6	2.0 7.0 12.8 4.5 2.5 5.5	9.9 18.2 7.3 4.4 6.8 7.4	3.4 - 11.5 12.6 8.6 5.9 9.6	7.9 17.6 29.5 11.5 7.5 11.7	4.7 8.3 14.4 6.6 4.8 5.8
5 Kg Cu/ha	1 2 3 4 5 6	14.0 11.5 28.0 9.5 48.0 22.0	17.0 14.0 27.8 10.3 42.2 23.1	25.6 22.8 45.3 18.1 60.7 29.1	39.6 29.3 50.4 23.3 71.8 42.0	22.9 16.9 28.7 14.6 47.4 25.2
10 Kg Cu/ha	1 2 3 4 5 6	22.5 50.0 14.0 105 24.0 18.0	25.0 45.9 17.5 119 29.5 18.8	32.2 63.0 22.3 168 42.2 26.6	54.1 83.1 39.1 212 62.1 41.4	30.1 46.9 23.0 101 35.5 24.6
20 Kg Cu/ha	1 2 3 4 5 6	100 75.0 108 53.0 55.0 16.8	108 64.5 95.7 48.5 55.0 24.7	154 107 164 72.6 72.2 82.2	155 147 209 104 85.3 51.1	73.3 68.8 109 46.9 50.5 23.1
4 0 Kg Cu/ha	1 2 3 4 5 6	100 73.0 37.5 70.0 63.0 103	106 77.3 42.8 72.3 68.4 105	35.0 136 99.8 58.0 98.7 94.8	176 140 114 140 125 192	88.0 72.3 57.3 66.8 63.2 9.8

Amounts of Copper Extracted Using Various Extractants Stead Wheat - Field Experiments (ppm)

Appendix 13A

Amounts of Copper Extracted Using Various Extractants Stead Canola - Field Experiments (ppm)

Treatment	Replicate	INHCL	DIPA	1% Na2EDPA	1% Na ₂ EDTA	Na ₂ DP
CONTROL	1 2 3 4 5 6	2.0 2.0 2.5 2.0 4.5 3.3	7.5 5.4 3.3 4.1 6.5 6.7	4.8 3.4 4.1 2.9 5.4 2.6	4.1 3.0 3.5 2.7 5.0 4.6	4.3 5.7 6.0 5.4 7.1 6.1
5 Kg Cu/ha	1 2 3 4 5 6	15.5 26.3 13.5 14.8 23.3 24.0	18.6 29.4 17.3 19.5 21.2 28.8	24.7 41.4 21.6 25.3 3.0 3.9	21.9 35.0 19.2 22.3 36.1 28.9	20.2 24.8 17.5 22.3 24.0 26.8
10 Kg Cu/ha	1 2 3 4 5 6	60.0 53.0 34.0 45.0 25.5 27.5	54.9 54.7 40.1 47.4 26.0 33.2	54.0 74.0 66.0 65.0 46.0 61.0	52.8 74.5 49.4 56.5 40.2 28.2	48.0 56.0 41.7 46.8 35.1 28.9
20 Kg Cu/ha	1 2 3 4 5 6	45.0 63.0 55.0 80.0 45.0 39.5	46.3 85.9 94.8 57.6 54.0 243	60.0 110 86.0 125 69.0 74.0	53.1 105 78.9 115 66.2 86.6	43.6 72.4 62.0 85.5 53.7 56.7
4 0 Kg Cu/ha	1 2 3 4 5 6	205 110 80.0 120 200 73.0	138 87.3 75.7 86.3 235 4.4	29.4 160 101 176 291 109	344 198 145 200 320 146	195 99.8 74.8 111 175 71.9