

AVAILABILITY OF MANGANESE AND EFFECTS  
OF SOIL TEMPERATURE ON AVAILABILITY OF  
MANGANESE TO PLANTS GROWN ON ORGANIC SOILS

A Thesis  
Submitted To  
The Faculty of Graduate Studies  
University of Manitoba

In Partial Fulfillment  
of the Requirements for the Degree  
MASTER OF SCIENCE

by

J. Murray Reid  
June, 1982

AVAILABILITY OF MANGANESE AND EFFECTS  
OF SOIL TEMPERATURE ON AVAILABILITY OF  
MANGANESE TO PLANTS GROWN ON ORGANIC SOILS

BY

J. MURRAY REID

A thesis submitted to the Faculty of Graduate Studies of  
the University of Manitoba in partial fulfillment of the requirements  
of the degree of

MASTER OF SCIENCE

© 1982

Permission has been granted to the LIBRARY OF THE UNIVERSITY OF MANITOBA to lend or sell copies of this thesis, to the NATIONAL LIBRARY OF CANADA to microfilm this thesis and to lend or sell copies of the film, and UNIVERSITY MICROFILMS to publish an abstract of this thesis.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

## ACKNOWLEDGEMENTS

The author expresses his sincere appreciation to:

Professor G.J. Racz, Department of Soil Science, University of Manitoba, for supervision during the study and for aid in preparation of the manuscript.

Dr. L.A. Loewen-Rudgers, Department of Soil Science, University of Manitoba, and Dr. W. Woodbury, Department of Plant Science, University of Manitoba for their suggestions on experimental methods, helpful criticism of the manuscript and for their serving on the thesis examining committee.

Mrs. V. Huzel and Mr. G. Morden, Department of Soil Science, University of Manitoba, for their assistance in analytical procedures.

My parents for their understanding and support during my course of studies.

## ABSTRACT

Field experiments were conducted to determine the effects of Cu, Mn, and B fertilizers on the yield and chemical composition of rapeseed, wheat and barley grown on organic soils. Emphasis was placed on the effects of Mn fertilizers and effect of method of Mn fertilizer application on yield and chemical composition. The experiments were located at Piney, Marchand and Stead. A late spring frost destroyed the rapeseed at all three locations. Wheat grain yields were increased by copper fertilization at Piney and Stead. Applications of boron and manganese had little or no effect on wheat grain yields. Barley grain yields were increased by copper and boron fertilization at Stead whereas barley yields at Piney and Marchand were unaffected by application of micronutrients.

Banding manganese sulphate with the seed of barley and wheat was more effective in increasing the concentration of Mn in plant shoots than were broadcast applications. Foliar applications of manganese sulphate were very ineffective in increasing Mn concentrations in plant shoots.

A comparison of the results to those obtained in previous years showed that the Mn concentration in plant shoots varied greatly from year to year even though the experiments were conducted at the same locations. It was postulated that variations in weather,

particularly temperature, were responsible for the variations. Thus, the effects of soil temperature on Mn availability were investigated. Increasing soil temperatures from 10 to 20°C resulted in a two-fold increase in Mn concentrations in plant shoots of both wheat and barley.

Soil extraction studies were undertaken to investigate the effects of soil temperature on amounts of Mn extracted from soils. All methods of extraction resulted in greater amounts of Mn being extracted at the higher temperatures. There were very close relationships between the increases in extractable soil Mn levels and increases in Mn levels in barley and wheat shoots with increasing temperature. This indicated that a greater release of Mn from the soil-solid-phase into soil solution was operating as temperature was increased.

Varying the water content of an organic soil from 75 to 200% of field capacity had little or no effect on the availability of Mn as measured by Mn uptake by barley. However, barley plants grown at water contents greater than 100% of FC had greater shoot Cu concentrations and took up more total Cu than plants grown at lower water contents. The effect of water content on shoot Cu concentrations was probably a result of the influence of moisture on the availability of fertilizer applied  $\text{CuSO}_4$ .

## TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION.....	1
II. REVIEW OF LITERATURE.....	3
A. Soil Manganese.....	3
B. Functions of Manganese in Plants.....	6
C. Plant Requirements for Manganese.....	8
D. Manganese Deficiency Symptoms.....	10
E. Diagnostic Techniques for Prediction of Mn Supply From Soils.....	11
F. Manganese Fertilizers and Placement Methods.....	16
III. GENERAL MATERIALS AND METHODS.....	19
IV. RESULTS AND DISCUSSION.....	22
A. Study I - Effect of Cu, Mn and B fertilization on yield and chemical composition of wheat and barley....	22
B. Study II - The influence of soil temperature on the availability of Mn in organic soils.....	39
C. Study III - The influence of soil temperature on the availability of applied fertilizer Mn.....	45
D. Study IV - The effect of soil temperature on amounts of Mn extracted from soils by DTPA and $\text{NH}_4\text{OAc}$ .....	60
E. Study V - The influence of soil moisture content on the Mn uptake by barley.....	66
V. SUMMARY AND CONCLUSIONS.....	70
VI. APPENDIX.....	75
VII. BIBLIOGRAPHY.....	76

## LIST OF TABLES

TABLE	PAGE
1. Manganese critical levels for various agronomic crops.....	9
2. Soil properties of the soils investigated.....	20
3. Effect of Cu, Mn and B fertilizers on yield of wheat straw and grain (Kg/ha).....	24
4. Effect of Cu, Mn and B fertilizers on yield of wheat straw and grain at Stead (Kg/ha).....	26
5. Chemical composition of wheat at early flag leaf stage (Marchand).....	29
6. Chemical composition of wheat at early flag leaf stage (Piney)..	30
7. Chemical composition of wheat at early flag leaf stage (Stead)..	31
8. Yield of barley straw and grain (Kg/ha).....	33
9. Yield of barley straw and grain at Stead (Kg/ha).....	33
10. Chemical composition of barley at early boot stage (Marchand)..	35
11. Chemical composition of barley at early boot stage (Piney).....	36
12. Chemical composition of barley at early boot stage (Stead).....	37
13. Dry matter yields of wheat and barley at the 3 to 4 leaf stage and at the early boot stage as affected by soil temperature....	41
14. Chemical composition of wheat and barley at the 3 to 4 leaf stage.....	41
15. Chemical composition of wheat and barley at the early boot stage.....	42
16. Yields of barley at the three to four leaf stage as affected by soil temperature and Cu and Mn fertilization (g/pot).....	46

TABLE	PAGE
17. Yields of barley at the early boot stage as affected by soil temperature and Cu and Mn fertilization (g/pot).....	47
18. Manganese concentrations in barley at the three to four leaf stage as affected by the addition of Cu and/or Mn and soil temperature.....	48
19. Copper concentrations in barley at the three to four leaf stage as affected by the addition of Cu and/or Mn and soil temperature.....	49
20. Manganese concentrations in barley at the early boot stage as affected by the addition of Cu and Mn and soil temperature.....	50
21. Copper concentrations in barley at the early boot stage as affected by the addition of Cu and Mn and soil temperature.....	52
22. Zinc concentrations in barley at the early boot stage as affected by addition of Cu and Mn and soil temperature.....	53
23. Iron concentrations in barley at the early boot stage as affected by the addition of Cu and Mn and soil temperature.....	53
24. Total Mn uptake by barley at the early boot stage as affected by additions of Cu and Mn and soil temperature.....	54
25. Total Cu uptake by barley at the early boot stage as affected by addition of Cu and Mn and soil temperature.....	56
26. Extractable manganese (ug/g) after a two-week incubation at four different temperatures.....	62
27. Extractable manganese (ug/g) of two organic soils.....	63
28. Influence of extraction temperature on extractable Mn, Zn and Fe by DTPA and extractable Mn by NH <sub>4</sub> OAc.....	64



## TABLE

## PAGE

29. Influence of soil-moisture content on yield and Mn, Fe, Zn and Cu content of barley at the early boot stage.....	68
30. Influence of soil-moisture content on the total Mn, Fe, Zn and Cu uptake by barley at the early boot stage.....	69

## I INTRODUCTION

Soil fertility studies have shown organic soils in Manitoba to be nutrient deficient for production of most crops. In addition to deficiencies of nitrogen, phosphorus and potassium, micronutrient deficiencies have been encountered in crops grown on organic soils in Southeastern Manitoba. Although plants require only a few grams per hectare of these nutrients, these soils were often unable to provide the quantities necessary for good growth. Thus, crop grain yields were often very low and seed quality was usually poor. The very low yields of grain and poor seed quality were attributed mainly to deficiencies of copper and/or manganese.

Studies were therefore conducted to determine if the seed yields of rapeseed, wheat and barley obtained on these soils, could be improved by the use of chemical fertilizers. In this study major emphasis was placed on the effect of manganese fertilizers on yield and chemical composition of rapeseed, wheat and barley. Various methods of manganese fertilizer application were also studied.

A significant feature of the results obtained from the field studies conducted by the Department of Soil Science during 1977 to 1980 was the extreme year to year variability in yield and tissue concentrations of minor elements even though the experimental sites

were situated at the same locations. The variations in nutrient uptake and yield were thought to be due to variations in weather particularly soil temperature. Thus, the effects of soil temperature and moisture on minor element uptake by plants were extensively investigated in the growth chamber. Emphasis in these studies was placed on the effect of soil temperature and moisture on manganese uptake by plants. The effects of soil temperature on amounts of manganese extracted from the soils by two reagents commonly used to assess plant available soil manganese were also studied.

## II REVIEW OF LITERATURE

A. Soil Manganese

Manganese exists in soils in various oxidation states, the most important being the divalent form which is readily available for plant utilization, either as the  $Mn^{++}$  ion or as complexed or chelated  $Mn^{++}$ . Mann and Quastel (1946) proposed that a manganese cycle between  $Mn^{++}$ ,  $Mn_2O_3$ , and  $MnO_2$  was operative in soils. Both  $Mn^{++}$  and easily reducible Mn oxides are considered when estimating the Mn supplying power of a soil and are thought of as "active Mn" because of the rapid conversion between solution  $Mn^{++}$  and the easily reducible Mn oxides (Reid and Miller 1963). The reactions of the manganese cycle are controlled by the oxidation-reduction processes of the system, believed to be largely mediated by biological activity (Russell 1973). Under strongly reducing conditions, such as those in an anaerobic environment, the accumulation of the reduced form of Mn,  $Mn^{++}$ , is attributed to the lack of oxidation of this fraction by the soil microorganisms (Cheng et al. 1972). The oxidation of  $Mn^{++}$  by both biological and nonbiological auto-oxidation proceeds rapidly in neutral and alkaline aerobic soils. In contrast, the reduction of Mn in these soils has more specific requirements (Quastel 1963), although it does occur readily at the expense of available oxidizable sources such as thiol groups or ferrous ions (Quastel et al. 1948).

Soil pH is very important in governing divalent manganese levels. Lindsay (1972) found that the solubility of Mn compounds decreased 100 fold for each unit increase in soil pH. Snyder et al. (1979) attributed the inverse relationship between soil pH and Mn solubility in the range of pH 7 to 8 to increasing microbial oxidation of divalent Mn to less soluble forms with increasing pH. The oxidation of  $Mn^{++}$  by microbial activity was pH dependent having an optimum at approximately pH 7.0 (Jones 1957). In contrast, Page (1962) stated that the effect of increasing pH on Mn availability was that of greater complexation of  $Mn^{++}$  by organic matter and not one of biological activity. Mulder and Geeretsen (1952) found that at low pH,  $Mn^{++}$  levels increased with increasing organic matter, indicating that organic matter was responsible for the change in divalent Mn levels with pH.

Factors which affect redox potentials in a soil directly influence the amount of  $Mn^{++}$  in solution. Flooding of soils often resulted in the accumulation of  $Mn^{++}$  even to the extent that Mn toxicity resulted in some plant species (Harter and Mclean 1965; Cheng et al. 1972). Peech and Boynton (1937) reported that redox potentials in waterlogged soils decreased only when a readily oxidizable organic matter source was present, suggesting microbial activity was involved. In contrast, Pavanasasivan (1973) concluded from retention studies on soils with high organic matter levels that exchangeable processes were more important than redox processes in the retention of  $Mn^{++}$ , indicating that the increase in available  $Mn^{++}$  with lower redox values was the result of destruction of organic matter by microbial activity and not a microbial reduction.

Very obvious differences concerning the nature of the interaction of organic matter with soil pH were reported. Organic matter additions to a neutral or alkaline soil decreased active Mn (Takkar 1969), whereas the application of compost and/or peat to an acid soil increased the active Mn levels (Cheng and Ouellette 1970). Also, manganese deficiencies in neutral, alkaline or excessively limed acid soils did not occur unless a certain amount of organic matter was present in the soil (Mulder and Geeretsen 1952). It is evident from the literature cited that organic matter in soils does play a role in manganese availability or solubility. However, depending on other soil factors organic matter can increase manganese availability in some instances whereas under different conditions organic matter decreases plant availability of soil manganese.

Soil temperature also influences active soil Mn levels (Takkar 1969), as well as plant Mn concentrations and/or Mn uptake by plants (Nyborg 1970; Mederski and Hoff 1958; MacMillian and Hamilton 1971; Cheng et al. 1971). Cotter and Mishra (1968) reported that increasing soil temperature accelerated the reduction of Mn, and that variation in soil temperature could account for much of the seasonal variation in plant Mn concentrations. Ponnampuruma and Loy (1970) reported that rates of reduction and associated chemical changes in flooded soils were much higher at 25°C than at 15°C. Singh and Pathak (1970) reported an increase in active Mn levels in soils up to 25°C. The detrimental effect of very high temperatures on the populations of the oxidizing microbes could account for the continued increase in active Mn as temperatures rise into the lethal range. For example, Quastel (1963) suggested that the increase in active Mn levels upon sterilization of

soils was a result of the detrimental effects these conditions had on the oxidation of  $Mn^{++}$  by the microbial population.

It should be apparent from the preceding discussion that manganese deficiencies are most likely on neutral to alkaline soils containing high organic matter under low temperatures.

#### B. Functions of Manganese in Plants

Manganese was first shown to be an essential element for plant growth in 1922 by McHargue (1922). A deficiency of this micronutrient in plants was noted to result in decreased photosynthetic rates (Pirson 1937). The decreased rate of photosynthesis was later linked to a loss of  $O_2$  evolution capacity (Possingham 1964). Spencer and Possingham (1961) reported that the electron transport from water was impaired, but cyclic phosphorylation was unaffected in isolated Mn-deficient chloroplasts. In more recent studies Possingham and Spencer (1962) concluded that inadequate Mn levels in chloroplasts impaired the water-splitting reactions of PS II.

Cheniae and Martin (1970) isolated two Mn fractions from intact chloroplasts. One fraction consisted of three Mn atoms per  $O_2$  evolving center which they termed the loosely bound fraction. The other fraction consisted of one to two Mn atoms associated with the oxidant side of the PS II trapping system. This fraction was called the firmly bound fraction since it was fixed to the chloroplast membrane. It was established in more recent studies (Cheniae and Martin 1971) that four Mn atoms per PS II photosynthetic unit were required. Kessler (1970)

stated that the only essentiality of Mn in plants was for the oxygen evolving system in PS II.

It is thought that higher plants are capable of adapting to a limited supply of Mn by adjusting the number of chloroplasts per cell or by forming disorganized chloroplasts with low chlorophyll concentrations. These processes decrease the demand for Mn (Homann 1967), but result in chlorotic plants with greatly decreased photosynthetic capacities.

Some studies directly linked Mn with  $\text{NO}_2^-$  reduction (Nason and McElroy 1963). However, recent studies clearly demonstrated that Mn was only indirectly associated with the  $\text{NO}_2^-$  reduction step of  $\text{NO}_3^-$  assimilation (Hewitt 1970).

Other specific requirements for Mn appear to be limited to its involvement in IAA oxidation. Mumford et al. (1962) stated that Mn was an activator of IAA oxidases. This is in good agreement with findings of Taylor et al. (1968) who reported that Mn-deficient cotton leaves had extremely high IAA-oxidase activity levels and that the cofactor and inhibitor activities of the oxidase system were affected. Although it was reported that Mn catalyzed a number of enzymes involved with the TCA cycle and glycolysis, it is evident that these were largely non-specific biochemical functions, in that  $\text{Mn}^{++}$  could be replaced by other metal ions predominately  $\text{Mg}^{++}$ .



### C. Plant Requirements for Manganese

Plants require relatively small amounts of Mn with usual concentrations in oven dry plant material at 100 ppm or less. However, Mn can accumulate in plants up to concentrations of several thousand parts per million (ppm). Schachtschabel (1955) estimated that the average arable crop removed between 500 and 1000 grams of Mn/ha.

The minimal plant concentration of a nutrient below which a marked decrease (usually 5-15%) in plant growth occurs is termed the critical level. Munson and Nelson (1973) expanded this concept to include not only yield but also crop quality. They also stated that a critical level was not a fixed value but was dependent on the relative concentrations of interfering nutrients. Ulrich and Hills (1967) defined the critical value as one that resulted in a 5% reduction in yield which would indicate that it was in the middle of the hypothesized transition zone with lower values resulting in dramatically decreased yields.

Listed in Table 1 are the critical values cited in the literature for various agronomic crops. Discrepancies in the literature values are to be expected as the critical value is dependent on the variety of crop grown, stage of growth and plant part analyzed. Generally the critical values range between 15 and 25 ppm.

Table 1. Manganese critical levels for various agronomic crops.

Plant and growth stage	Plant part	Concentration in plant (ppm)	Reference
Potato	leaves	120	Cheng and Ouellette 1971
Corn, tassel	leaves opposite and below ear level	15	Melsted et al. 1969
Wheat, bootstage	whole plant	30	Melsted et al. 1969
Oats, bootstage	whole plant	15	Hammes and Berger 1960b
Oats, bootstage	whole plant	20-25	Martens et al. 1977
Grain Sorghum, bootstage	flag leaf	10	Ohki 1975
Alfalfa	upper stem	18	Jones 1967
Alfalfa, early flowering	upper stems	25	Melsted et al. 1969
Sugar beets	most recently matured leaf	30	Farley and Draycott 1973
Soybeans, R <sub>2</sub>	most recently matured blades	18	Parker et al. 1981
Soybeans, early bloom	most recently matured blades	10	Ohki 1981
Soybeans, blossom	most recently matured trifoliolate leaf	15-20	Randall et al. 1975
Soybeans, after first pod	youngest mature leaf and petioles	20	Melsted et al. 1969

#### D. Manganese Deficiency Symptoms

Visual Mn deficiency symptoms include a wide variety of chlorotic patterns and necrotic spotting. Such deficiency symptoms would be anticipated since Mn plays an integral role in plant photosynthesis. Since cereals vary in their susceptibility to Mn deficiency, the severity of Mn deficiency symptoms vary among cereals. Nyborg (1970) reported that oats were very sensitive to low Mn whereas barley was quite tolerant of low Mn with wheat being intermediate. Manganese deficiency is quite widespread in oats particularly on alkaline soils. Such Mn-deficient oats have a greatly decreased resistance to root infection by microorganisms (Gerresten 1937). Manganese deficiency symptoms in oats are often termed grey speck, because of grey spots on the leaves of Mn-deficient oat plants. Because Mn deficiency is relatively widespread in oats, it is sometimes referred to as "grey speck disease". The grey specks first appear between the veins on the basal-half of leaves. The interveinal streaks elongate and coalesce (Samuel and Piper 1929). The area becomes necrotic and dries out, with a resulting grey speckled pattern on the leaves. In advanced stages the leaves bend over sharply near the middle as a result of reduced turgor (Mengel and Kirkby 1979).

Brown lesions appear on the leaves of severely Mn deficient barley (Hewitt 1963). Manganese deficiency in wheat and rye is characterized by chlorotic streaks in the leaves which later turn pale green (Hewitt 1963).

Low Mn tissue concentrations are also associated with fewer tillers and heads and/or with glumes which are withered and devoid of grain (Hewitt 1963). Ohki (1975b) reported a decrease in overall plant height of cotton when Mn was limiting.

Nyborg (1970) reported that the severity of the leaf flecking, spotting and necrosis, characteristic of Mn deficiency in oats, was related to cultivar. Later Brown and Jones (1974) identified Mn-efficient and Mn-inefficient cultivars of oats grown in solution culture and Murray and Benson (1976) identified a Mn-efficient oat cultivar in the field based on their ability to tolerate low levels of Mn supply.

#### E. Diagnostic Techniques for Prediction of Mn Supply from Soils

##### (1) Extraction solutions

Numerous soil extracting solutions and various extracting techniques were employed in attempts to reliably predict soil Mn availability or Mn uptake by plants grown in various soils. Some extractants predicted Mn availability better than others under specific conditions for specific crops. However, no one particular extractant was universally better than others.

Total soil Mn was a poor indicator of plant available Mn and often gave very misleading predictions (Hoff and Mederski 1958; Reid and Webster 1969; Page et al. 1962). Therefore extractants that measured water soluble, exchangeable and/or easily reducible Mn were developed and evaluated by many workers.

Shuman and Anderson (1974) reported that Mn extracted by a solution containing 0.005 M DTPA, (diethylenetriamine pentatacetic acid), 0.1 M TEA (triethanolamine) and 0.01 M CaCl<sub>2</sub> buffered at pH 7.3 was an excellent predictor of soybean Mn tissue concentrations when soil pH was also considered. They evaluated six different extractants on soils varying in pH from 5.8 to 6.8 and found that DTPA extractable Mn gave the best correlation with plant Mn uptake by wheat and soybeans. However, they reported that (CH<sub>3</sub>COONH<sub>4</sub>) NH<sub>4</sub>OAc-extractable Mn was more highly correlated to Mn uptake by wheat than DTPA extractable Mn in soils varying in pH from 4.8 to 6.8. Similarly, Shuman et al. (1979) reported DTPA extractable Mn was useful in predicting soybean leaf Mn concentrations when soil pH was also considered. Rule and Graham (1976) found that Mn values obtained with soil-DTPA equilibration were consistent with those measured by clover uptake. In contrast to these findings, Hag and Miller (1972) stated that DTPA extractable Mn did not relate well to Mn uptake by maize. Salcedo and Warncke (1979) found that Mn extracted by either 0.1 N H<sub>3</sub>PO<sub>4</sub> or 0.1 N HCl reflected Mn uptake by plants more closely than that extracted by either 0.005 M DTPA or 1 N NH<sub>4</sub>OAc. Voth and Christenson (1980) also reported that 0.1 N H<sub>3</sub>PO<sub>4</sub> extractable Mn was more highly correlated with plant available Mn than was 0.005 M DTPA extractable Mn. Hoff and Mederski (1958) evaluated nine different extractants and reported correlation coefficients of 0.899, 0.860 and 0.856 for relationships between plant Mn concentration and 3.0 M NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, alcoholic hydroquinone, and 0.1 N H<sub>3</sub>PO<sub>4</sub> extractable Mn, respectively. These correlation coefficients were significantly higher than those for H<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>OAc, NH<sub>4</sub>OAc + hydroquinone,

total soil Mn,  $\text{HNO}_3$  and NaOAc. They attributed the good relationships between Mn extracted by the phosphate extractants and plant Mn uptake to the influence of P on Mn solubility and suggested that the phosphates extracted the easily-reducible Mn component of the soil Mn. Later work by Hammes and Berger (1960) and Brownman et al. (1969) indicated that Mn extracted by 0.1 N  $\text{H}_3\text{PO}_4$  was superior to either 1.5 M or 3.0 M  $\text{NH}_4\text{H}_2\text{PO}_4$  for prediction of Mn uptake by oats, peas and maize. This extractant was also better than others they evaluated, with the exception of 0.01 M EDTA (Brownman et al. 1969). Randall et al. (1976) extracted numerous soils which had been divided into two groups based on organic matter content. Eighteen extractants were evaluated on low organic matter soils or those containing less than 6% organic matter whereas 13 extractants were evaluated on soils containing more than 6% organic matter. Manganese extracted with 0.01 M EDTA and 0.05 M EDTA correlated best with plant Mn uptake on the low organic matter soils whereas 0.005 M DTPA, 0.01 M EDTA and 0.1 M  $(\text{NH}_4)_2\text{CO}_3$  extractable Mn correlated best with plant Mn uptake on the high organic matter soils.

Several workers were of the opinion that extractants which contained a reducing agent such as hydroquinone and an exchangeable cation and therefore would measure both exchangeable and easily-reducible Mn would be excellent predictors of plant available soil Mn over the growing season (Hoff and Mederski 1958; Adams 1965). However, Hoyt and Nyborg (1971) had little success using extractants containing  $\text{NH}_4\text{OAc}$  and hydroquinone. Shuman and Anderson (1974) reported that, in fact,  $\text{NH}_4\text{OAc}$  plus hydroquinone extractable Mn was inferior to  $\text{NH}_4\text{OAc}$  extractable Mn alone in predicting plant Mn concentrations. Brownman et al. (1969)

stated that the hydroquinone Mn test was unlikely to be superior to total Mn in determining available Mn and concluded from their work using eight soil Mn extractions that 0.01 M EDTA and 0.1 N  $\text{H}_3\text{PO}_4$  were the best diagnostic indicators of Mn levels in maize. However, when they included soil pH, a combination of  $\text{NH}_4\text{OAc}$  and soil pH gave the best prediction of Mn uptake by maize.

(2) Factors affecting extractable Mn values

The conditions under which the extractions for available Mn were conducted could have affected extractable Mn levels and therefore may have caused many of the discrepancies reported in the literature. A number of dependent variables are known to affect Mn extractability. These variables include concentration and pH of the extracting solution, temperature of extraction, solution to soil ratio, shaking time, sample preparation and moisture content of the sample prior to extraction.

Salcedo and Warncke (1979) reported that solution to soil ratios and shaking time were important considerations when extracting Mn with either 0.1 N HCl or 0.1 N  $\text{H}_3\text{PO}_4$  while Mn extractions with either 0.005 M DTPA or 1 N  $\text{NH}_4\text{OAc}$  were relatively independent of these factors. Lindsay and Norvell (1978) found that DTPA extractable Mn levels varied only slightly as long as shaking time remained between one to three hours and recommended a two hour shaking time for soil-DTPA equilibration.

Increasing the concentration of the extracting solution for DTPA, EDTA and  $\text{NH}_4\text{H}_2\text{PO}_4$  increased the amount of Mn extracted (Lindsay and Norvell 1979; Randall et al. 1976; Browman et al. 1969). Increasing the pH of DTPA and EDTA extracting solutions decreased the amount of Mn extracted (Lindsay and Norvell 1979; Randall et al. 1976).

Lindsay and Norvell (1979) investigated a number of factors which influenced DTPA extractable Mn values and concluded that extraction temperature was particularly important. Extractable Mn values increased an average of 54% for each 10°C rise in extraction temperature in the range of 15°C to 35°C.

Extractable soil Mn level was also influenced by method of sample preparation and handling. Air drying samples prior to extraction resulted in higher extractable Mn values than extracting fresh samples (Hammes and Berger 1960a; Sanchez and Kamprath 1959), the affect being most pronounced in high organic matter soils. Hammes and Berger (1960a) suggested that the increase in extractable Mn after air drying was due to the oxidation of organic matter and subsequent release of Mn<sup>++</sup>. Steam sterilization of soils resulted in very high exchangeable Mn concentrations in both organic (Cheng and Ouellette 1970) and mineral soils (Fujimoto and Sherman 1948).

Severson et al. (1979) working with DTPA, found significantly greater extractable Mn concentrations after grinding and seiving samples than after disaggregation. They recommended that standardized methods of sample preparation be established to allow for valid comparisons among extractants.

Soil properties also may have influenced extractable Mn levels and caused some of the anomalies reported in extractable Mn values. Some workers reported that including soil organic matter content and pH singly or as interaction terms in regression equations describing the relationship between extractable Mn and plant Mn uptake greatly



improved correlation coefficients (Randall et al. 1976; Dolar et al. 1971; Sanchez and Kamprath 1959).

#### F. Manganese Fertilizers and Placement Methods

There are a number of methods by which Mn can be applied to a crop. Soil and foliar applied Mn fertilizers were extensively studied. Generally, foliar applications of Mn, as  $\text{MnSO}_4$ , at 1.0 to 4.8 Kg Mn/ha were as good or better in improving leaf Mn levels and yields of most crops than soil applications at much higher amounts (Randall et al. 1970a; McCall and Davies 1953; Sheppard et al. 1979; Cox 1968; Murray and Benson 1976; Mishra and Tripathi 1973; Hammes and Berger 1960b; Sherman and Harmer 1941). In contrast, Shepherd et al. 1960 reported onion yields were greater with soil applied Mn than with foliar applied Mn; yields decreased in the order Mn banded into the soil > Mn broadcast and tilled into the soil > Mn applied as a foliar spray. The ineffectiveness of the foliar applied Mn in this experiment was attributed to the nature and limited leaf surface of onions available to intercept the Mn spray.

Ozaki (1955) found  $\text{MnSO}_4$  to be the most effective source of foliar applied Mn. Manganese EDTA was also a good source of foliar fed Mn, but the risk of leaf damage from (phytotoxicity) scorching was substantially greater with EDTA (Randall et al. 1970a). Thus, only very low application rates of EDTA could be used. Efficacy of foliar Mn applications was greatest when employed at the tillering stage for cereals (Murray and Benson 1976; Sheppard et al. 1979), early blossom or early pod set for soybeans (Randall et al. 1970a) and at the pre-blossom stage for peas and beans (Ozaki 1955).

Banding Mn with the seed in numerous studies resulted in higher leaf Mn concentrations and higher yields than broadcasting Mn (Harmer and Sherman 1943; Randall et al. 1975a; Shepherd et al. 1960). Broadcast applications often had to be twice the amount banded with the seed to obtain equal yield increases or Mn uptake. Wilson et al. (1981) found broadcast Mn applications to be very inefficient for Mn-deficient plants with less than 0.5% of the added Mn being accounted for in plant tops. Hammes and Berger (1960b) concluded that broadcast applications of  $\text{MnSO}_4$  were not satisfactory on neutral and alkaline soils. Soil applications of  $\text{MnSO}_4$  on calcareous organic soils was usually not recommended due to the rapid oxidation of  $\text{Mn}^{++}$  (Mengel and Kirkby 1979).

Fiskel and Mourkides (1955) reported that soil applied  $\text{MnSO}_4$  was more available than either  $\text{MnO}_2$  or Mn EDTA. Shepherd et al. (1960) reported that Mn EDTA had excellent residual benefits when either banded or mixed in a Houghton muck soil, whereas the other Mn sources had little residual benefit. However, soil application of Mn EDTA on organic soils usually increased severity of Mn deficiencies (Wilcox and Cantliffe 1969; Knezek and Greinert 1971). This phenomenon was due to a rapid substitution of soil Fe for Mn in the chelate molecule and inactivation of the replaced  $\text{Mn}^{++}$ . The increased Fe availability would have then widened the already critical Fe to Mn ratio within the plant. Manganese uptake was lowered which resulted in intensified chlorosis and yield reductions.

Phosphate fertilizers also influenced plant Mn uptake. Ammonium phosphate alone alleviated Mn-deficiency in soybeans and significantly increased plant Mn concentrations, plant weights and seed yields

(Randall et al. 1975b). A decrease in soil pH with the application of MAP or DAP in the fertilizer reaction zone was thought to have increased exchangeable Mn levels. Increased Mn uptake and extractability were also noted when MCP was banded (Voth and Christenson 1980). Application of MCP was as effective in supplying Mn to plants as was banding Mn alone.

Many workers reported a greater efficacy of Mn fertilizers when banded with a phosphate fertilizer (Bingham and Garber 1960; Mishra and Tripathi 1973; Hossner and Richards 1968; Voth and Christenson 1980; Randall et al. 1975b). Hossner and Richards (1968) found the effectiveness of various P sources on Mn uptake to be  $\text{MAP}=\text{APP} > \text{MCP} > \text{DAP}$ . This suggests that the effect was not entirely related to pH in the reaction zone as the lowest pH would have been associated with MCP. Larsen (1964) stated that a possible chemical mobilization of soil Mn induced by monocalcium reactions was operating when triple superphosphate was applied.

Soil acidification through the utilization of acid forming fertilizers also increased plant Mn uptake. For example,  $\text{CO}(\text{NH}_2)_2$  resulted in higher plant Mn uptake than  $\text{Ca}(\text{NO}_3)_2$  (Sims et al. 1975).

Reports in the literature suggested that on neutral or alkaline soils Mn should be applied as  $\text{MnSO}_4$ , either as a foliar spray or in a band with an acidic phosphate fertilizer such as monoammonium phosphate or ammonium polyphosphate.

## III GENERAL MATERIALS AND METHODS

The studies reported in this thesis included several individual studies where different procedures were used. Thus, for purposes of clarity, experimental procedures used for each individual study are discussed with the results obtained. The analytical procedures employed in all the pot studies and/or the field study are described in this section. A brief description of the soils used in the investigations is reported in this section.

Some characteristics of the soils used are given in Table 2. The pH of the soil samples was determined on a soil-water paste (3:1 (v/v)) using a glass-calomel electrode.

The crops grown, as described in each section, were barley (Horedum vulgare var Conquest), wheat (Triticum aestivum var Neepawa) and rapeseed (Brassica campestris var Torch).

Plant samples for chemical analysis were prepared in the same manner for all investigations. Total above ground plant material was harvested for analysis. The plant material was rinsed three times with deionized water, air-dried, finely ground and then stored in paper envelopes. A two-gram sample of the finely ground plant material was used for all quantitative determinations. The plant material was pre-digested at room temperature for twelve hours with 10.0 ml concentrated  $\text{HNO}_3$  in a micro-Kjeldahl flask. Five ml of 70%  $\text{HClO}_4$  were then added and the samples digested by heating on a micro-Kjeldahl unit until clear.

Table 2. Soil properties of the soils investigated.

Location	Legal Description	Great Group	Series	pH	Depth (cm)	Underlying Material
Piney	NW 24-1-11E	Terric Mesisol	Murray Hill	7.1	122	clay
Marchand	NW 10-5-8E	Terric Mesisol	Kirco	7.6	45	sand
Stead	SW 32-17-9E	Terric Mesisol	Cayer	6.2	90	clay

Digestions of plant material for studies reported in sections C and E were conducted using a Tecator Model 1006 block digestion unit.

The digested material was filtered through Whatman #42 filter paper into 25 ml volumetric flasks and diluted to volume with deionized water. Concentrations of Mn, Cu, Fe and Zn were determined by aspirating a portion of each solution into a Perkin-Elmer 560 Atomic Absorption Spectrophotometer. Concentrations of K, Ca and Mg were determined on a 1.0 ml aliquot of each sample diluted with 2.5 ml of a 2500 ppm  $\text{LiNO}_3$  solution and 25.0 ml of deionized water. A portion of this solution was then aspirated into the atomic absorption spectrophotometer and concentrations of K, Ca and Mg calculated.

Concentrations of sulphur were determined as described by Lazrus et al. (1966). A 0.2 ml aliquot of the original filtrate was diluted to 1 to 4l with deionized water and reacted with  $\text{BaCl}_2$  at pH 2.5-3.0. Exactly enough methylthymol blue to complex the amount of Ba originally present was added and adjusted to between pH 12.5 and 13. The amount of methylthymol blue not complexed was measured on an Auto Analyzer II at 460 nm, which reflected the amount of sulfate-sulphur in the sample.

Phosphorus concentrations were determined as described by Stainton et al. (1974). A 0.5 ml aliquot of the original plant digest was diluted to 10.5 ml using deionized water. A 0.5 ml aliquot of the dilute digest was then diluted 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.

## IV RESULTS AND DISCUSSION

A. Study I - Effect of Cu, Mn, and B fertilization on yield and chemical composition of wheat and barley.

## (1) Introduction

Studies conducted in 1978 and 1979 showed that deficiencies of major nutrients as well as copper severely limited yields of some crops grown on organic soils (Tokarchuk et al. 1979; Racz et al. 1978). However, even when major nutrients and copper fertilizers were applied in adequate amounts, yields of some crops such as wheat were very low. Yields of barley and rapeseed were also less than expected. An interesting feature of the results obtained was the extremely high straw yields in comparison to grain yields. Some of these low seed yields were associated with low concentrations of manganese or boron in the plant tissue.

Field experiments, using wheat, barley and rapeseed as test crops, were conducted in 1980 to study the effects of copper, manganese and boron fertilizers on yield and chemical composition. Another important objective of this study was to evaluate various methods of Mn fertilizer application.

## (2) Experimental Methods

Rapeseed, barley and wheat were seeded at 7, 100 and 110 Kg/ha, respectively, in 1980. Each treatment was replicated five times in a

randomized complete block design. Each treatment plot was 1.07 m x 6.10 m and consisted of six rows of crop 0.18 m apart.

The treatments used for each crop at Marchand and Piney are shown in Table 3. All plots were treated with a total of 120 KgN/ha, comprised of a mixture of commercial grade urea (46-0-0) and ammonium sulphate (21-0-0(24)). The nitrogen fertilizer was broadcast at time of seeding. In addition to the nitrogen fertilizer broadcast, nitrogen as monoammonium phosphate (11-48-0) was applied with the seed at 11.5 KgN/ha for the cereals and 5.8 KgN/ha for rapeseed. Phosphorus was applied to all plots as monoammonium phosphate and was drilled with the seed at 50 Kg  $P_2O_5$ /ha for the cereals and at 25 Kg  $P_2O_5$ /ha for the rapeseed. Potassium chloride (0-0-62) was applied to all plots at 200 Kg  $K_2O$ /ha. Copper and boron, when added, were applied at 20 Kg Cu/ha and 1.0 Kg B/ha as technical grade  $CuSO_4 \cdot 5 H_2O$  and  $Na_2B_4O_7 \cdot 10 H_2O$ . The  $CuSO_4 \cdot 5 H_2O$  was dissolved in deionized water, and sprayed onto the soil surface. The boron fertilizer was broadcast as a powder onto the soil surface. Method of adding manganese fertilizer ( $MnSO_4 \cdot H_2O$ ) was varied. Manganese fertilizer was applied broadcast, banded with the seed and as a foliar spray. Manganese fertilizers were banded with the seed at 10, 20 and 40 Kg Mn/ha. Broadcast applications consisted of one treatment applied at 80 Kg Mn/ha. Foliar fertilizer applications, as  $MnSO_4 \cdot H_2O$  dissolved in deionized water, were sprayed on the foliage twice during the vegetative stage for barley and three times for wheat. Foliar applications of 1.0 Kg Mn/ha were applied on each application date. The first spray was conducted when the crops were at the three to four leaf stage. The second spray for wheat and



Table 3. Effect of Cu, Mn and B fertilizers on yield of wheat straw and grain (Kg/ha).

Treatment	Piney		Marchand	
	Straw	Grain	Straw	Grain
Major nutrients (N, P, K and S) (1)	4027 a b*	334 a	2994 a b	2423 a b
(1) + Cu + B	3652 a	1471 b c	2901 a b	2356 a b
(1) + Cu + B + 10 Kg Mn/ha banded	3685 a	1449 b c	3123 b	2541 b
(1) + Cu + B + 20 Kg Mn/ha banded	3855 a b	1384 b	3289 b	2744 b
(1) + Cu + B + 40 Kg Mn/ha banded	4435 b	1539 b c	2772 a b	2245 a b
(1) + Cu + B + 80 Kg Mn/ha broadcast	4269 a b	1826 c	2541 a b	2171 a b
(1) + Cu + B + 3 Kg Mn/ha foliar	4267 a b	1485 b c	2929 a b	2476 a b
(1) + B + 20 Kg Mn/ha banded	4522 b	412 a	2356 a	1950 a
(1) + Cu + 20 Kg Mn/ha banded	4359 a b	1843 c	3114 b	2458 a b

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. Separate statistical analysis was conducted for each site.

barley and the third spray for wheat were conducted at four week intervals after the previous application.

All plots were rotovated to a depth of approximately 10 cm prior to seeding to ensure uniform incorporation of all fertilizers which had been broadcasted or sprayed.

The treatments used at the Stead experimental site are shown in Table 3. The amounts of each fertilizer used, method of application and experimental design was as described above, except for boron fertilization. Boron was applied at 1.0 or 2.0 Kg B/ha as  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$  dissolved in deionized water. These solutions were sprayed onto the soil surface and rotovated into the soil prior to seeding.

The Piney, Marchand and Stead sites were sown on May 8, 9 and 14, respectively. A late spring frost destroyed the rapeseed at all three sites.

Plant shoot samples were obtained from the second and fifth rows of each plot at the early flag leaf stage for wheat and at the early boot stage for barley. The chemical composition of the plant shoots was determined as previously described. Final harvests were taken 92, 97 and 111 days after seeding for barley at Stead, Marchand and Piney, respectively. Final harvests were taken 108, 120 and 121 days for wheat at Marchand, Stead and Piney, respectively. Each plot was harvested by cutting the plants at approximately 1.0 cm above the soil surface from the center 3.05 m of the third and fourth rows. The plant samples were then dried at 30°C to 40°C for two weeks, and then threshed. Straw and grain yields were then obtained.

Table 4. Effect of Cu, Mn and B fertilizers on yield of wheat straw and grain at Stead (Kg/ha).

Treatment	Straw	Grain
Major nutrients (N, P, K and S) (1)	4742 a b*	952 a
(1) + Cu	4373 a	1488 a
(1) + 1 Kg B/ha	5277 b	906 a
(1) + Cu + 1 Kg B/ha	4410 a	1506 a
(1) + Cu + 2 Kg B/ha	4935 a b	1580 a

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

### (3) Results and Discussion

#### Wheat

Grain yields were increased by copper fertilization at Piney and Stead, whereas grain yields at Marchand were usually unaffected by minor element fertilization (Tables 3 and 4). Applications of manganese and/or boron had very little effect on grain yields at any location except at Marchand where a decrease in yield of grain occurred when Mn and B were applied (Treatment 8). Copper was not applied to this plot and adding Mn and B probably accentuated the copper deficiency. Boron applications without copper had a detrimental effect on grain yields at Piney. Yields of grain with only Cu and Mn were also higher than when Cu, B and Mn were added (Treatment 9 vs Treatment 4). This suggests that application of boron resulted in boron toxicity.

Straw yields were variable (Tables 3 and 4). However, variations in straw yields, except for the Mn plus B treatment at Marchand were generally not related to applications of micronutrients.

Wheat grain yields at all locations in 1980 were greater than those obtained in previous years at the same locations. Grain yields with sufficient quantities of all fertilizers varied from about 200 to 500 Kg/ha in 1979 (Tokarchuk et al. 1979), whereas grain yields varied from about 1500 to 2000 Kg/ha in 1980. The greater yields in 1980 were most likely a result of high early spring temperatures and early seeding. Straw yields obtained in 1980 were similar to those obtained in previous years. Thus, it appears that weather conditions, particularly low soil and air temperatures, were partly responsible for the low grain yields obtained in previous years.

Copper concentrations of wheat grown without copper fertilization were very low to low at all three locations (Tables 5, 6 and 7). Copper concentrations in wheat shoots were increased significantly at all locations when 20 Kg Cu/ha were applied. However, as noted previously, wheat yields were increased at only two of the three experimental sites (Stead and Piney).

Manganese concentrations in plant shoots were relatively high in comparison to those obtained at these same locations in 1979. In 1979, manganese concentrations in wheat shoots varied from 14 to 17, 5 to 8 and 36 to 47 ppm at Piney, Marchand and Stead, respectively (Tokarchuk et al. 1979). Manganese concentrations in wheat shoots in 1980 varied from about 20 to 100 ppm when manganese fertilizers were not applied. Thus,

manganese concentrations in 1980 were about one and one-half, two and three times the Mn concentrations reported for wheat by Tokarchuk et al. (1979) for the Marchand, Stead and Piney sites, respectively. The large differences in Mn concentrations in wheat shoots between 1979 and 1980 were probably due to differences in environmental conditions encountered between the two years. In contrast to 1979, air temperatures in the spring of 1980 were high and soil moisture conditions were lower. This undoubtedly caused differences in soil temperatures between the two years which may have affected the availability and uptake of Mn by the plants.

Manganese concentrations in wheat shoots increased when Mn was applied to the soil. Foliar applications of Mn had little or no effect on the Mn concentrations in wheat. It should be noted, however, that foliar Mn was applied only once prior to sampling of the plants for analysis. At the Piney experimental site, broadcast and with-the-seed Mn fertilizer applications were about equal in increasing Mn concentration in wheat. However, at the Marchand site Mn applied with the seed at 40 Kg Mn/ha resulted in a significantly higher Mn concentration in wheat than Mn broadcast at 80 Kg Mn/ha. Broadcasting Mn at 80 Kg/ha at this site was equivalent to applying 20 Kg Mn/ha with the seed.

Amounts of Mg, Ca, S and P in wheat shoots were adequate for normal growth and were relatively unaffected by micronutrient fertilizer application. Potassium concentrations in wheat at Piney were not affected by micronutrient fertilization. Applications of Cu without B at Stead decreased K in plant shoots whereas applications of Cu and B

Table 5. Chemical composition of wheat at early flag leaf stage (Marchand).

Treatment	<u>Mn</u>	<u>Cu</u>	<u>Zn</u>	<u>Fe</u>	<u>Mg</u>	<u>K</u>	<u>Ca</u>	<u>S</u>	<u>P</u>
	-----ppm-----								
	-----%-----								
Major nutrients (1)	19 a b*	1.5 a	22 a	206 c	.28 a	1.9 a b	.32 a	.28 a	.24 a
(1) + Cu + B	14 a	4.3 c	18 a	110 a b	.29 a	2.4 c	.33 a	.23 a	.24 a
(1) + Cu + B + 10 Mn-Ba <sup>1</sup>	24 b c	3.9 b c	18 a	96 a	.26 a	2.0 b c	.31 a	.25 a	.32 a
(1) + Cu + B + 20 Mn-Ba	30 b c	3.0 b	17 a	78 a b	.29 a	2.0 b c	.32 a	.25 a	.27 a
(1) + Cu + B + 40 Mn-Ba	46 c d	3.7 b c	21 a	118 b	.28 a	1.8 a b	.31 a	.22 a	.26 a
(1) + Cu + B + 80 Mn-Br <sup>2</sup>	31 c	4.7 c	21 a	69 a	.30 a	1.7 a b	.32 a	.21 a	.26 a
(1) + Cu + B + 3 Mn-Fo <sup>3</sup>	20 a b	4.2 b c	23 a	95 a b	.28 a	1.8 a b	.32 a	.22 a	.25 a
(1) + B + 20 Mn-Ba	51 d	1.8 a	25 a	217 c	.29 a	1.6 a b	.34 a	.22 a	.25 a
(1) + Cu + 20 Mn-Ba	33 c	4.5 c	21 a	87 a b	.27 a	1.5 a	.33 a	.23 a	.24 a

\*Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. Separate statistical analysis was conducted for each nutrient.

<sup>1</sup>Banded

<sup>2</sup>Broadcast

<sup>3</sup>Foliar

Table 6. Chemical composition of wheat at early flag leaf stage (Piney).

Treatment	Mn	Cu	Zn	Fe	Mg	K	Ca	S	P
	-----ppm-----%								
Major nutrients (1)	54 a*	1.9 a	40 a	70 a	.25 a	2.1 a	.38 a	.26 a	.47 a
(1) + Cu + B	62 a b	5.1 b c	41 a	65 a	.26 a	1.9 a	.36 a	.28 a	.54 a
(1) + Cu + B + 10 Mn-Ba <sup>1</sup>	70 a b	4.9 b c	42 a	66 a	.28 a	2.1 a	.39 a	.28 a	.51 a
(1) + Cu + B + 20 Mn-Ba	76 a b	6.2 c	40 a	63 a	.26 a	1.5 a	.38 a	.32 a	.52 a
(1) + Cu + B + 40 Mn-Ba	76 a b	5.8 c	42 a	62 a	.27 a	1.5 a	.39 a	.35 a	.50 a
(1) + Cu + B + 80 Mn-Br <sup>2</sup>	81 a b	5.5 b c	40 a	69 a	.28 a	1.5 a	.39 a	.35 a	.53 a
(1) + Cu + B + 3 Mn-Fo <sup>3</sup>	58 a b	4.4 b	39 a	63 a	.26 a	1.4 a	.38 a	.27 a	.51 a
(1) + B + 20 Mn-Ba	84 b	3.1 a b	39 a	72 a	.26 a	1.6 a	.39 a	.26 a	.49 a
(1) + Cu + 20 Mn-Ba	81 a b	6.1 c	35 a	69 a	.27 a	1.8 a	.38 a	.28 a	.49 a

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. Separate statistical analysis was conducted for each nutrient.

<sup>1</sup>Banded  
<sup>2</sup>Broadcast  
<sup>3</sup>Foliar

Table 7. Chemical composition of wheat at early flag leaf stage (Stead).

Treatment	ppm						%			
	Mn	Cu	Zn	Fe	Mg	K	Ca	S	P	
Major nutrients (1)	99 c*	2.6 a	51 b	61 c	.31 a	1.9 b	.21 a	.30 a	.53 a	
(1) + Cu	88 b	8.6 b	45 a	50 a	.29 a	1.2 a	.18 a	.30 a	.50 a	
(1) + 1 Kg B/ha	103 c	2.2 a	48 a b	55 b	.31 a	2.0 b	.22 a	.31 a	.55 a	
(1) + Cu + 1 Kg B/ha	79 a	8.1 b	44 a	49 a	.29 a	1.7 b	.19 a	.38 a	.51 a	
(1) + Cu + 2 Kg B/ha	84 a b	9.1 b	45 a	52 a b	.28 a	1.8 b	.19 a	.33 a	.49 a	

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. Separate statistical analysis was conducted for each nutrient.



(Treatment 2) increased K in plant shoots at Marchand. Zinc concentrations in wheat shoots were high at Piney and Stead. Zinc concentrations in wheat at Marchand, although adequate, were much lower than at Piney or Stead. There was a decrease in Zn concentrations in wheat at Stead with the addition of Cu. Iron concentrations in wheat were in the adequate range at all locations. Iron concentrations in wheat at Stead decreased when Cu was applied. The effects of Cu fertilizers on Fe concentrations were much more pronounced at the Marchand site, where Fe tissue concentrations were about two-fold greater without than with copper fertilization. No effect of Cu fertilizers on the Fe concentrations in wheat grown at Piney were noted.

#### Barley

Yields of barley grown at Marchand and Piney were not affected significantly by application of micronutrients (Table 8). Grain yields at Piney were variable. The barley crop lodged after heading at Piney. This undoubtedly accounted for some of the variability in grain yields. Grain yields of barley at Stead were increased by both copper and boron fertilization (Table 9). Yield of barley with Cu plus B at 2.0 Kg/ha was significantly higher than yield with only NPK and S. The response to B at the Stead site was not expected, based on soil pH. The Stead site had a pH of 6.1 whereas pH values for the Marchand and Piney sites were 7.6 and 7.2, respectively.

Barley grain yields were moderate and varied from about 2700 to 3300 Kg/ha for the three experimental sites.

Table 8. Yield of barley straw and grain (Kg/ha).

Treatment	Piney		Marchand	
	Straw	Grain	Straw	Grain
Major nutrients (N, P, K and S) (1)	4614 a b*	2726 a	3447 a	3576 a
(1) + Cu + B	4616 a b	2864 a	2864 a	2790 a
(1) + Cu + B + 10 Kg Mn/ha banded	4086 a b	2920 a	2853 a	3021 a
(1) + Cu + B + 20 Kg Mn/ha banded	4402 a b	2818 a	3073 a	3326 a
(1) + Cu + B + 40 Kg Mn/ha banded	4419 a b	3160 a	3079 a	3271 a
(1) + Cu + B + 80 Kg Mn/ha broadcast	4079 a b	2495 a	3166 a	3631 a
(1) + Cu + B + 2 Kg Mn/ha foliar	4561 a b	3262a	2757 a	3169 a
(1) + B + 20 Kg Mn/ha banded	3574 a	2643 a	2717 a	3095 a
(1) + Cu + 20 Kg Mn/ha banded	5318 b	3400 a	2957 a	3215 a

\*Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. Separate statistical analysis was conducted for each site.

Table 9. Yield of barley straw and grain at Stead (Kg/ha).

Treatment	Straw	Grain
Major nutrients (N, P, K and S) (1)	4382 a*	2273 a
(1) + Cu	4446 a	2689 a b
(1) + 1 Kg B/ha	4976 a	3086 a b
(1) + Cu + 1 Kg B/ha	4362 a	2846 a b
(1) + Cu + 2 Kg B/ha	4568 a	3297 b

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

Straw yields were very high at Piney and Stead and moderate to high at Marchand. Variations in straw yields were not related to applications of any nutrient.

Copper concentrations in barley were at sufficiency levels ( $>2.3$  ppm) for all treatments and experimental sites except for the boron plus manganese treatment at Marchand and the boron only treatment at Stead (Tables 10, 11 and 12). Copper concentrations in barley shoots, when only major nutrients were applied, varied from 4.2 to 6.8 ppm. In contrast, Cu concentrations in wheat shoots at the same sites varied from 1.5 to 2.6 ppm. These results demonstrate that barley was able to acquire a greater amount of Cu from the soil than wheat under conditions of low available Cu.

Manganese concentrations were in the sufficiency range for barley grown at Piney and Stead. Manganese concentrations were at about the critical level in barley grown at Marchand without manganese fertilizer. Both broadcast and with-seed applications of manganese increased manganese concentrations in the plants at Piney. Broadcast application of manganese were ineffective in increasing manganese concentrations in plants grown at Marchand, whereas with-seed applications were effective. Foliar applications were ineffective in increasing Mn concentrations. Copper and/or boron additions at the Stead site significantly decreased Mn concentrations in barley shoots. However, the highest yields were usually associated with this treatment at this site and therefore a dilution effect was most likely responsible for the reduction in Mn concentration.

Table 10. Chemical composition of barley at early boot stage (Marchand).

Treatment	Mn	Cu	Zn	Fe	Mg	K	Ca	S	P
	-----ppm----- -----%-----								
Major nutrients (1)	17 a*	4.2 b	37 b	162 a	.28 a	1.6 a	.62 a	.22 a	.34 a
(1) + Cu + B	16 a	4.6 b	23 a	146 a	.28 a	1.8 a	.61 a	.21 a	.30 a
(1) + Cu + B + 10 Mn-Ba <sup>1</sup>	25 b e d	5.2 b	25 a	164 a	.29 a	1.6 a	.64 a	.24 a	.33 a
(1) + Cu + B + 20 Mn-Ba	21 a b	4.7 b	31 a b	127 a	.28 a	1.7 a	.67 a	.26 a	.31 a
(1) + Cu + B + 40 Mn-Ba	26 c d	4.9 b	25 a	120 a	.26 a	1.6 a	.57 a	.22 a	.29 a
(1) + Cu + B + 80 Mn-Br <sup>2</sup>	17 a	4.2 b	24 a	148 a	.27 a	1.8 a	.60 a	.25 a	.31 a
(1) + Cu + B + 2 Mn-Fo <sup>3</sup>	19 a	3.6 a b	24 a	125 a	.24 a	1.6 a	.55 a	.24 a	.30 a
(1) + B + 20 Mn-Ba	29 d	2.1 a	21 a	145 a	.26 a	2.0 a	.61 a	.22 a	.32 a
(1) + Cu + 20 Mn-Ba	23 b c	4.1 b	25 a	118 a	.27 a	1.7 a	.60 a	.24 a	.31 a

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

<sup>1</sup> Banded

<sup>2</sup> Broadcast

<sup>3</sup> Foliar

Table 11. Chemical composition of barley at early boot stage (Piney).

Treatment	-----ppm-----									
	<u>Mn</u>	<u>Cu</u>	<u>Zn</u>	<u>Fe</u>	<u>Mg</u>	<u>K</u>	<u>Ca</u>	<u>S</u>	<u>P</u>	<u>-----</u>
										-----%
Major nutrients (1)	43 a*	6.8 b	41 a	60 a	.29 a	1.8 a	.41 a	.26 a	.43 a	
(1) + Cu + B	30 a	9.0 c	36 a	52 a	.26 a	1.7 a	.38 a	.24 a	.42 a	
(1) + Cu + B + 10 Mn-Ba <sup>1</sup>	34 a	7.8 b	37 a	58 a	.26 a	1.4 a	.39 a	.27 a	.40 a	
(1) + Cu + B + 20 Mn-Ba	46 a b	8.6 b c	41 a	57 a	.28 a	1.6 a	.44 a	.26 a	.45 a	
(1) + Cu + B + 40 Mn-Ba	55 b c	9.2 c	39 a	56 a	.30 a	1.9 a	.46 a	.27 a	.43 a	
(1) + Cu + B + 80 Mn-Br <sup>2</sup>	76 c	8.4 b c	38 a	57 a	.29 a	1.5 a	.44 a	.28 a	.45 a	
(1) + Cu + B + 3 Mn-Fo <sup>3</sup>	39 a	8.6 c	39 a	55 a	.30 a	1.5 a	.44a	.30 a	.46 a	
(1) + B + 20 Mn-Ba	48 a b	3.4 a	38 a	69 b	.26 a	1.7 a	.42 a	.28 a	.48 a	
(1) + Cu + 20 Mn-Ba	47 a b	8.1 b	37 a	56 a	.28 a	1.8 a	.44 a	.28 a	.42 a	

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

<sup>1</sup>Banded

<sup>2</sup>Broadcast

<sup>3</sup>Foliar

Table 12. Chemical composition of barley at early boot stage (Stead).

Treatment	<u>Mn</u>	<u>Cu</u>	<u>Zn</u>	<u>Fe</u>	<u>Mg</u>	<u>K</u>	<u>Ca</u>	<u>S</u>	<u>P</u>
	ppm			%					
Major nutrients (1)	56 b*	3.2 b	34 b	49 b	.30 a	2.3 a	.24 a	.35 a	.47 a
(1) + Cu	42 b	4.6 c	25 a	39 a	.30 a	1.9 a	.27 a	.36 a	.46 a
(1) + 1 Kg B/ha	40 b	1.7 a	38 b	59 c	.29 a	1.8 a	.26 a	.33 a	.45 a
(1) + Cu + 1 Kg B/ha	29 a	5.0 c	35 b	49 b	.29 a	1.8 a	.25 a	.31 a	.43 a
(1) + Cu + 2 Kg B/ha	42 b	7.6 d	42 b	59 c	.33 a	1.6 a	.37 b	.29 a	.40 a

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

Zinc, Fe, Cu, Mg, K, S and P concentrations in barley shoots were generally at sufficiency levels. Although there was some variability in tissue chemical composition, no trends could be attributed to the nutrients applied. Concentrations of iron in plant tissues at Stead and Piney were close to levels at which yield decreases may be expected to occur.

#### (4) Summary

Wheat grain yields were increased by copper fertilization at Piney and Stead. Applications of boron and manganese had little or no effect on wheat grain yields. Yields of wheat were generally higher in 1980 than in previous years at the same locations. This was attributed to the higher early spring temperatures in 1980.

Barley grain yields were increased by copper and boron fertilization at Stead. Manganese, copper and boron fertilizers had little or no effect on yields at Piney and Marchand.

Banding manganese fertilizers with the seed of barley and wheat were very effective in increasing manganese concentrations in plant shoots. Broadcast applications of manganese were generally not as effective as with-seed applications. Foliar applications of manganese were ineffective in increasing concentrations of manganese in plant shoots.

A significant feature of the results obtained in 1980 when compared to those obtained in previous years was the extreme year to year variability in concentrations of manganese and other elements in plant shoots even though the experimental locations were the same.

Yields of crops also varied greatly from year to year. The variations in nutrient uptake and yield were most likely due to yearly variations in weather conditions, particularly air and soil temperatures.



B. Study II - The influence of soil temperature on the availability of Mn in organic soils.

(1) Introduction

It was noted in the previous study, that yield and manganese concentrations in plant shoots varied greatly from year to year when grown on organic soils at the same locations. It was postulated that weather conditions, particularly soil temperature variations, were largely responsible for the variations in Mn concentrations. An experiment was initiated to investigate the effects of soil temperature in a controlled environment growth room on the manganese uptake by wheat and barley.

(2) Experimental Methods

Wheat and barley were grown in four temperature controlled water baths set at  $10 \pm 1^{\circ}\text{C}$ ,  $15 \pm 1^{\circ}\text{C}$ ,  $20 \pm 1^{\circ}\text{C}$  and  $25 \pm 2^{\circ}\text{C}$ . The baths were situated in a Conviron Model P6W36 environmental growth chamber.

All pots were treated with 120 Kg N/ha as  $\text{NH}_4\text{NO}_3$ , 200 Kg  $\text{K}_2\text{O}$ /ha as  $\text{K}_2\text{SO}_4$ , 110 Kg  $\text{P}_2\text{O}_5$ /ha as  $\text{NH}_4\text{H}_2\text{PO}_4$  and 40 Kg S/ha as  $(\text{NH}_4)_2\text{SO}_4$ . Amounts of fertilizer applied were calculated on an area basis. The  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  added supplied an additional 65 Kg N/ha. All nutrients (technical grade chemicals) were sprayed onto 400 grams of air-dried soil in solution form and well mixed with the soil. The soil used was a Terric Mesisol from the Stead location. The treated samples were placed into clean plastic bags and placed into cylindrical pots (11 cm dia. x 35 cm).

Six barley or wheat seeds were placed in each pot at a soil depth of 1.5 cm. The pots were watered to field capacity moisture content.

Plants were thinned to five seedlings per pot shortly after emergence. Plants were checked daily to maintain water content between 75% and 100% of field capacity. A daylength of 16 hours was employed with day/night air temperatures of 20/13°C.

The above ground portion of three plants from each pot were harvested three weeks after emergence and dried. The plants varied in stage between the three to four leaf stage depending on soil temperature and date of emergence. The plants were harvested 18, 19, 21 and 21 days after emergence for the 10, 15, 20 and 25°C temperature treatments, respectively. A final harvest of the remaining two plants was conducted when the plants reached the early boot stage. The plants achieved boot stage at various times after emergence depending on soil temperature. Days to harvest were 32, 32, 36 and 37 days for plants at 25, 20, 15 and 10°C, respectively. The plant material was air-dried, weighed, ground and analyzed for nutrient composition.

### (3) Results and Discussion

Dry matter yields at the three to four leaf stage increased with soil temperature for both wheat and barley (Table 13). Maximum yields at the three to four leaf stage were obtained at 20 and 25°C for wheat and barley, respectively. The lower yields at the lower temperatures were due mainly to delayed emergence at the low temperatures. Dry matter yields at the boot stage, indicate that the optimum soil temperature for growth of wheat and barley was approximately 15°C.

Manganese concentrations in wheat and barley at the three to four leaf stage increased with increasing temperature over the range of 10°C to

Table 13. Dry matter yields of wheat and barley at the 3 to 4 leaf stage and at the early boot stage as affected by soil temperature.

Treatment	3 to 4 Leaf Stage (g/pot)	Early Boot stage (g/pot)	Total Dry Matter (g/pot)
Wheat 10°C	.69 a*	5.16 a	5.85
Wheat 15°C	1.00 a b	7.10 b	8.10
Wheat 20°C	1.95 c	5.02 a	6.16
Wheat 25°C	1.60 b c	4.48 a	6.08
Barley 10°C	1.42 a	12.23 b	13.65
Barley 15°C	2.37 b	13.90 c	16.29
Barley 20°C	4.00 c	10.21 a	14.21
Barley 25°C	4.52 d	11.26 a b	15.78

\*Duncan's Multiple Range Test: Numbers followed by the same letter are not significantly different at the 5% level. Separate analyses done on both crops.

Table 14. Chemical composition of wheat and barley at the 3 to 4 leaf stage.

Treatment	Mn	Cu	Fe	Zn	P	K	S
	-----ppm-----				-----%-----		
Wheat 10°C	55 a*	3.7 a	105 a	44 a	.51 a	4.2 b	.24 a
Wheat 15°C	70 a b	2.9 a	91 a	55 a	.63 a	3.2 b	.23 a
Wheat 20°C	101 b	3.0 a	94 a	42 a	.71 a	1.5 a	.28 a
Wheat 25°C	95 b	2.6 a	90 a	42 a	.67 a	2.0 a	.28 a
Barley 10°C	17 a	4.1 a	76 a	21 a	.42 a	1.9 b	.17 a
Barley 15°C	25 a b	3.2 a	100 a	27 a	.45 a b	1.6 a b	.26 b
Barley 20°C	40 a b	3.6 a	85 a	25 a	.49 b c	0.8 a	.26 b
Barley 25°C	46 b	4.0 a	97 a	31 a	.52 c	1.1 a b	.27 b

\*Duncan's Multiple Range Test: Numbers followed by the same letter are not significantly different at the 5% level. Separate analyses done on both crops.

20°C (Table 14). Increasing the soil temperature from 10°C to 20°C resulted in a two-fold increase in Mn tissue concentrations of both crops. Changes in the concentrations of other nutrients in the plant with increasing temperature were variable. Concentrations of Cu, Fe and Zn were generally not affected by soil temperature and S concentrations tended to increase with soil temperatures whereas K concentrations decreased with soil temperature. Decreases in concentration of some elements with increasing soil temperature would be expected due to the greater yields (biological dilution) at the higher temperatures.

The final harvest of wheat and barley, taken at the early boot stage, also showed that soil temperature was an important factor in controlling manganese concentrations in plant shoots (Table 15). The trends obtained

Table 15. Chemical composition of wheat and barley at the early boot stage.

Treatment	Mn	Cu	Fe	Zn	P	K	S
	-----ppm-----				-----%-----		
Wheat 10°C	40 a*	1.4 a	45 a	24 a	.37 a	.80 a	.18 a
Wheat 15°C	59 a	1.8 a	45 a	26 a b	.40 a	.80 a	.20 a b
Wheat 20°C	83 b	1.5 a	51 a	36 c	.51 b	.80 a	.24 a b
Wheat 25°C	86 b	1.5 a	57 a	34 b	.56 b	.80 a	.26 b
Barley 10°C	15 a	1.7 a b	47 a b	13 a	.22 a	.82 a	.08 a
Barley 15°C	25 b	2.3 b	55 b	17 a	.22 a	.80 a	.08 a
Barley 20°C	35 c	1.5 a b	46 a b	13 a	.25 a	.90 a	.08 a
Barley 25°C	26 b	1.4 a	39 a	14 a	.24 a	.85 a	.09 a

\*Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. Separate statistical analysis was conducted for each crop.

were similar to those obtained for the earlier sampling date. There was a two-fold increase in the Mn concentrations in plants as soil temperature was increased from 10°C to 20°C. Above a soil temperature of 20°C there was little or no effect on Mn concentrations in wheat, whereas a decrease in Mn concentration occurred in barley. Soil temperature had little or no effect on the concentrations of the other nutrients in barley, except for higher concentrations of Cu and Fe reported for the 15°C treatment, which also resulted in the highest dry matter yields. Increasing soil temperatures had a slight positive influence on the S, Zn, Fe and P concentrations in wheat. Wheat grown at 15°C had slightly higher Cu concentrations than at the other temperatures and resulted in the highest wheat yields obtained. The increased yields of wheat and barley at 15°C were possibly due to higher Cu concentrations in these plants, particularly for wheat which exhibited Cu deficiency symptoms at the higher soil temperatures. This would indicate that wheat and barley plants grown at the higher temperatures had a higher functional requirement for Cu.

Since the sampling time was varied so that all plants were at the same stage of development the results from the final harvest probably reflect more accurately the influence of soil temperature on the chemical composition of these crops than the sampling taken at the three to four leaf stage.

Manganese concentrations in the barley plants grown at 10°C were relatively low and were probably inadequate for maximal plant growth. In contrast, Mn concentrations in barley plants grown at 15, 20 and 25°C were

relatively high and considered to be adequate for growth. All Mn concentrations in wheat shoots were well above the reported critical levels at all soil temperatures.

(4) Summary

Manganese availability in the organic soil studied was a function of soil temperature. A good relationship between Mn concentration in wheat and barley shoots and soil temperature in the range of 10°C to 20°C was obtained.

C. Study III - The influence of soil temperature on the availability of applied fertilizer Mn.

(1) Introduction

An interesting result from the previous study was the low Mn concentrations in barley plants grown at a soil temperature of 10°C. This study was initiated to determine the influence of soil temperature on the availability of applied Mn fertilizer as measured by barley uptake.

The low Cu levels in both the wheat and barley in the previous study indicated that fertilizer Cu was required for optimum yields, especially at the higher soil temperatures. Therefore, another objective of this study was to evaluate the efficacy of applied Cu at the various soil temperatures.

(2) Experimental Methods

Experimental design, equipment, amounts of nutrients applied and all other procedures were as described in the previous study except that Mn and Cu fertilizers were applied to some of the pots and only barley was grown. Manganese application per pot was equivalent to 50 Kg Mn/ha, while copper applications were equivalent to 10 Kg Cu/ha. Amounts of Cu and Mn applied were calculated on an area basis. These nutrients were applied as technical grade  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ . The fertilizers were dissolved in deionized water, sprayed onto the soil and then thoroughly mixed. Three barley plants were harvested from each pot for tissue analysis at the three to four leaf stage, 17, 20, 22 and 22 days after emergence for the 10, 15, 20 and 25°C temperature baths,

respectively. A final harvest of the remaining two plants was conducted at the bootstage which occurred at 35, 34, 35 and 35 days after emergence for the 10, 15, 20 and 25°C temperature baths, respectively.

### (3) Results and Discussion

Micronutrient fertilizers had no effect on barley yields at the three to four leaf stage (Table 16). Yields increased with increases in soil temperature. Yields obtained at the 25°C temperature were not recorded as an incidence of root rot reduced the number and size of plants at this sampling date.

Table 16. Yields of barley at the three to four leaf stage as affected by soil temperature and Cu and Mn fertilization (g/pot).

Treatment	Soil Temperature			
	10°C (g/pot)	15°C (g/pot)	20°C (g/pot)	25°C (g/pot)
NPKS (1)	1.16 a* A	3.53 a B	4.40 a C	---
(1) + Cu	1.30 a A	3.62 a B	4.66 a B	---
(1) + Mn	1.40 a A	3.30 a B	4.32 a C	---
(1) + Cu + Mn	1.23 a A	3.50 a B	4.53 a C	---

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.



Yields of barley obtained at the early boot stage were increased by Mn fertilization when grown at a soil temperature of 15°C (Table 17).

Table 17. Yields of barley at the early boot stage as affected by soil temperature and Cu and Mn fertilization (g/pot).

Treatment	Soil Temperature			
	10°C (g/pot)	15°C (g/pot)	20°C (g/pot)	25°C (g/pot)
NPKS (1)	12.2 a* A	11.7 a A	10.5 a A	10.9 a A
(1) + Cu	12.5 a A	14.6 a b A	13.3 a A	11.2 a A
(1) + Mn	11.2 a A	15.0 b B	12.5 a A	11.3 a A
(1) + Cu + Mn	12.7 a A	14.5 a b A	12.2 a A	12.3 a A

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

Neither Cu and/or Mn increased yields significantly at any other soil temperature, although yields generally tended to be greater with the addition of micronutrients. Optimum yields were obtained at a soil temperature of 15°C, except when only major nutrients were applied. The highest yield with major nutrients only was obtained at 10°C. In contrast to the previous study, the days to final harvest were very nearly the same at the various temperatures in this study. This was a result of increased days to maturity for plants at 25°C and 20°C and a decrease in days to maturity for the plants grown at the lower soil temperatures. Manganese concentrations in barley at the three to four leaf stage were

increased significantly with the addition of  $\text{MnSO}_4$  compared to plants grown at soil temperatures of 15 and 20°C (Table 18). There was also an increase in Mn concentrations in shoots at the lower soil temperature with Mn fertilization but differences were not significant.

Table 18. Manganese concentrations in barley at the three to four leaf stage as affected by the addition of Cu and/or Mn and soil temperature.

Treatment	Soil Temperature			
	10°C (ug/g)	15°C (ug/g)	20°C (ug/g)	25°C (ug/g)
NPKS (1)	16.5 a* A	27.0 a A B	35.3 a B	---
(1) + Cu	14.2 a A	28.5 a A B	35.3 a B	---
(1) + Mn	28.0 a A	45.3 b A B	76.0 b B	---
(1) + Cu + Mn	15.5 a A	29.1 a B	43.3 a b C	---

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

Copper concentrations in barley at the three to four leaf stage were increased when  $\text{CuSO}_4$  was added (Table 19). This response was anticipated as it was shown in previous studies (Tokarchuck et al. 1979, Reid and Racz 1980), that additions of Cu to organic soils usually increased Cu tissue concentrations.

Manganese concentrations in barley at the early boot stage increased with increases in soil temperature (Table 20). The findings were similar to those

Table 19. Copper concentrations in barley at the three to four leaf stage as affected by the addition of Cu and/or Mn and soil temperature.

Treatment	Soil Temperature			
	10°C (ug/g)	15°C (ug/g)	20°C (ug/g)	25°C (ug/g)
NPKS (1)	2.6 a* A	2.8 a A	2.4 a A	---
(1) + Cu	7.8 b A	6.4 b A	6.1 b c A	---
(1) + Mn	3.7 a A	3.0 a A	3.9 a b A	---
(1) + Cu + Mn	6.6 b A	6.6 b A	8.1 c A	---

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

noted in the previous study, except that in the previous study manganese concentrations did not increase between 20 and 25°C. In this study there was a significant increase in manganese concentrations in barley between the two highest soil temperatures (20 and 25°C) investigated. It is interesting to note that, in this study, an increase in soil temperature from 20 to 25°C resulted in a very large increase in Mn concentrations in plant shoots. It is difficult to suggest reasons why differences in Mn concentrations in plants grown at 20 and 25°C were obtained in this experiment and not in the first experiment. However, since soil temperatures above 20°C would not be expected to be encountered in organic soils particularly below the surface few cm of soil (Appendix, Table 1), the differences encountered between the two studies in the Mn concentrations of the plants grown at 20 and 25°C have little or no practical importance.

Applications of Mn at 50 Kg Mn/ha had no effect on Mn concentrations in barley at the early boot stage regardless of soil temperature (Table 20).

Table 20. Manganese concentrations in barley shoots at the early boot stage as affected by the addition of Cu and Mn and soil temperature.

Treatment	Soil Temperature			
	10°C (ug/g)	15°C (ug/g)	20°C (ug/g)	25°C (ug/g)
NPKS (1)	17.2 a* A	25.0 a A B	33.5 a B	55.8 b c C
(1) + Cu	13.3 a A	19.8 a B	25.7 a B	37.5 a C
(1) + Mn	21.7 a A	25.5 a A B	37.5 a B	61.2 c C
(1) + Cu + Mn	16.7 a A	22.2 a A	28.3 a B	45.6 b C

\*Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

A response in plant Mn concentration to applied Mn was obtained when plants were sampled at the three to four leaf stage. The transitory effect of the applied  $\text{MnSO}_4$  could have been due to slow oxidation of the applied  $\text{Mn}^{++}$  and fixation of the applied Mn into forms not available to the plant. An interesting observation noted at this sampling date was the antagonistic effect of  $\text{CuSO}_4$  on Mn assimilation by barley. Manganese concentrations in plant shoots decreased when  $\text{CuSO}_4$  was added with or without  $\text{MnSO}_4$ . These decreases, however, were significant only at 25°C. Similar trends were noted in the field studies conducted on this soil where  $\text{CuSO}_4$  additions decreased Mn concentrations in plant shoots. These findings are contrary to those in the literature which indicated that additions of  $\text{CuSO}_4$  increased Mn availability

through an exchange of Cu for organically bound Mn (Hemstock and Low 1953). Nyaki (1981) found that increasing  $\text{CuSO}_4$  additions to corn resulted in not only greater assimilation of Cu but also of Mn in plant shoots. However, McLaren and Crawford (1973) demonstrated a relatively high specific adsorption of  $\text{Cu}^{++}$  on Mn oxides, which could decrease the rate of reduction of these oxides to more soluble Mn forms.

The application of  $\text{MnSO}_4$  in combination with  $\text{CuSO}_4$  usually increased Cu concentrations in plant shoots above that obtained with  $\text{CuSO}_4$  alone or  $\text{MnSO}_4$  alone (Table 21). Copper concentrations in plant shoots were increased with the addition of this nutrient at all soil temperatures. Copper applications at 10 Kg Cu/ha were effective in increasing Cu concentrations in plant shoots from levels that were inadequate to levels that were in the sufficiency range (McAndrew 1980), thus alleviating the Cu deficiencies.

Barley shoots grown at a soil temperature of  $25^\circ\text{C}$  contained significantly less copper than barley shoots grown at a soil temperature of  $10^\circ\text{C}$ , when similar nutrient applications were made. The copper concentrations of the plants grown at  $15^\circ\text{C}$  and  $20^\circ\text{C}$  were intermediate between those reported for the high and low temperature regimes. A similar observation was reported for the barley grown in the previous study, where decreases in Cu concentrations in plant shoots were associated with increases in soil temperature. Decreases in Cu concentrations in barley shoots with increasing soil temperature were not related to increases in yield obtained for plants harvested at the boot stage.

Table 21. Copper concentrations in barley shoots at the early boot stage as affected by the addition of Cu and Mn and soil temperature.

Treatment	Soil Temperature			
	10 <sup>o</sup> C (ug/g)	15 <sup>o</sup> C (ug/g)	20 <sup>o</sup> C (ug/g)	25 <sup>o</sup> C (ug/g)
NPKS (1)	2.2 a* B	1.7 a A B	1.5 a A	1.3 a A
(1) + Cu	3.9 b B	3.3 b A B	2.6 b A	2.8 b A
(1) + Mn	2.1 a B	1.3 a A B	1.8 a A B	1.1 a A
(1) + Cu + Mn	4.8 c B	3.3 b A	3.4 c A	3.5 c A

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

Zinc concentrations in the barley plants were at adequate levels at all temperatures and for all treatments (Jones 1972). Zinc concentrations in barley shoots were lower with NPKS plus Cu than with NPKS; the differences being significant at 15 and 25<sup>o</sup>C (Table 22). Manganese fertilizer applications had no obvious effects on zinc concentrations in the barley plants. Iron concentrations in barley were significantly lower with the addition of CuSO<sub>4</sub> at the three higher soil temperatures (Table 23). A similar effect was noted in the field studies for wheat grown at both Stead and Marchand. The effect of manganese applications on Fe concentrations in barley shoots were variable. The addition of both Cu and Mn significantly decreased Fe concentrations in plants grown at 15<sup>o</sup>C. Decreases in iron concentrations in barley with added Cu plus Mn were also noted for plants grown at 20<sup>o</sup> and 25<sup>o</sup>C although the differences were not significant. Zinc concentrations in plants were highest when grown at 25<sup>o</sup>C.

Table 22. Zinc concentrations in barley at the early boot stage as affected by addition of Cu and Mn and soil temperature.

Treatment	Soil Temperature			
	10°C (ug/g)	15°C (ug/g)	20°C (ug/g)	25°C (ug/g)
NPKS (1)	21 a* A	24 c A	25 a A	34 b B
(1) + Cu	19 a A	18 a A	19 a A	24 a B
(1) + Mn	27 b B C	21 b A	25 a A B	33 b C
(1) + Cu + Mn	20 a A	21 b A	18 a A	31 a b B

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

Table 23. Iron concentrations in barley at the early boot stage as affected by the addition of Cu and Mn and soil temperature.

Treatment	Soil Temperature			
	10°C (ug/g)	15°C (ug/g)	20°C (ug/g)	25°C (ug/g)
NPKS (1)	42 a* A B	50 b B	47 b A B	40 b A
(1) + Cu	36 a A	40 a A	36 a A	33 a A
(1) + Mn	41 b A	40 a A	42 a b A	39 a b A
(1) + Cu + Mn	42 a B	38 a A B	42 a b B	36 a b A

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

Total Mn uptake by barley at the early boot stage was largely unaffected by Cu and/or Mn additions, except for plants treated with Mn and grown at a soil temperature of 15°C (Table 24). Total Mn uptake by barley was significantly increased by Mn application when grown at a soil temperature of 15°C. The total Mn uptake by barley increased with increases in soil temperature for all treatments.

Table 24. Total Mn uptake by barley at the early boot stage as affected by additions of Cu and Mn and soil temperature.

Treatment	Soil Temperature			
	10°C (ug/pot)	15°C (ug/pot)	20°C (ug/pot)	25°C (ug/pot)
NPKS (1)	210 a* A	292 a A B	356 a B	610 a C
(1) + Cu	165 a A	288 a B	340 a C	420 a D
(1) + Mn	238 a A	382 b A B	465 a B	687 a C
(1) + Cu + Mn	212 a A	333 a b B	365 a B	531 a C

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

Total Cu uptake by barley at the early boot stage increased with the addition of  $\text{CuSO}_4$ . Copper uptake from  $\text{CuSO}_4$  was enhanced when  $\text{CuSO}_4$  was also applied (Table 25). In contrast to results obtained for Mn, the amount of Cu assimilated by the plants decreased with increasing soil temperature. The influence of temperature was most pronounced when  $\text{CuSO}_4$  was not applied. The effect of temperature on Mn uptake was also the most pronounced for this treatment. These results suggest that an interaction



Table 25. Total Cu uptake by barley at the early boot stage as affected by addition of Cu and Mn and soil temperature.

Treatment	Soil Temperature			
	10°C (ug/pot)	15°C (ug/pot)	20°C (ug/pot)	25°C (ug/pot)
NPKS (1)	27 a* B	20 a B	16 a A B	14 a A
(1) + Cu	49 b B	48 b B	35 b A B	32 b A
(1) + Mn	24 a A	20 a A	25 a B	12 a A
(1) + Cu + Mn	61 c B	48 b A	41 b A	43 c A

\*Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. The small letters were used for comparisons among fertilizer treatments at a particular temperature whereas the capital letters were used for comparisons among temperature for a particular fertilizer treatment.

between these two micronutrients was operating which ultimately influenced their assimilation in plants. It is not clear if these interactions occurred in the soil, affecting their relative availabilities, or occurred in the plant, affecting their uptake and/or translocation to plant tops. The net effect was an antagonistic effect of Cu on Mn accumulation in aerial plant parts and a synergistic effect of Mn on copper uptake.

Soil temperature had a very pronounced and interesting effect on Mn uptake by wheat and barley. It is possible that the increases in Mn uptake were a result of increased plant respiration (root respiration) at the higher temperatures. Maas et al. (1968) showed that manganese uptake was metabolically mediated in six-day old barley seedlings. Thus, it could be concluded that the influx of Mn into the plant was temperature dependent and was responsible for the results obtained. Page and Dainty (1964), however, reported a lack of metabolic regulation in the uptake of Mn by four-week old oat seedlings.

It is also possible that increased root growth at the higher temperatures may have been responsible for the higher Mn uptake at the higher temperatures. Fulton (1968) reported that maximum root growth and grain and straw yields of oats occurred at soil and air temperatures of 13°C. In this study barley and wheat yields at the boot stage were greatest when these plants were grown at about 15°C. Woodbury (1982) stated that the optimum temperature for root growth of cereals was near 12°C. Also, in the study reported in this manuscript, the differences in root soil contact at the various temperatures was expected to be small

as a limited volume of soil was used. Since differences in root growth in this study were most likely small and root growth rates are at a maximum at about 15°C, differences in root growth were most likely not responsible for differences in Mn uptake over the temperature range studied.

The greater Mn values reported at the higher soil temperatures may have been due to an increase in the supply of soluble Mn in the soil solution. Halstead and Barber (1968) indicated that the diffusion of Mn from the soil to the root was the dominant feature governing plant uptake. Cox and Ghazalea (1981) studied relative growth rates and manganese accumulation rates in soybeans and obtained results which supported the observations noted by Halstead and Barber (1968). Cox and Ghazalea (1981) varied both soil and air temperatures and reported a slight decrease in Mn concentrations in leaves with increasing temperatures. However, increasing the Mn concentration of the solution resulted in greater leaf Mn tissue contents. This suggested that Mn uptake by plants was dependent on the supply of Mn in the soil solution. However, in the study reported in this manuscript, increasing the concentration of soluble Mn by the addition of  $MnSO_4$  had little effect on Mn concentrations in plant shoots. However, it is possible the applied Mn was fixed by the soil into plant unavailable forms.

The increases in Mn uptake with increases in soil temperature could have been due to one or all of the factors noted above. The studies reported in this manuscript and those in the literature did not provide sufficient

information to determine which of the factors discussed above, if any, were responsible for the increases in Mn uptake with increases in soil temperature.

(4) Summary

Increasing soil temperature from 10 to 25°C increased Mn concentrations in barley shoots. The application of fertilizer  $\text{MnSO}_4$  did not increase Mn concentrations in plant shoots. The application of  $\text{CuSO}_4$  decreased the assimilation of Mn from  $\text{MnSO}_4$  by barley at the 25°C soil temperature.

The addition of  $\text{CuSO}_4$  increased Cu tissue concentrations at all temperatures. The addition of  $\text{MnSO}_4$  enhanced the uptake of Cu by barley significantly at all temperatures except at 15°C.

Optimum yields, as in the previous study, were obtained at a soil temperature of 15°C with the exception of the major nutrient only treatment.

D. Study IV - The effect of soil temperature on amounts of Mn extracted from soils by DTPA and  $\text{NH}_4\text{OAc}$ .

(1) Introduction

The reported increases in Mn tissue concentrations with increasing soil temperature in the previous studies led to the initiation of this study. This study was designed to determine if soil temperature directly influenced the supply of Mn from the soil. Chemical extractions of soil samples were conducted at the temperatures previously employed. Two extractants, DTPA and  $\text{NH}_4\text{OAc}$ , were used to study the chemical availability of manganese in organic soils. The effects of method of sample handling prior to extraction was also investigated.

(2) Experimental Methods

Experiment I. Effect of incubation temperature and extraction temperature on amounts of Mn extracted from soils.

Two soils, one from the Marchand experimental site and one from the Stead experimental site, were studied. The equivalent to five grams of air-dried soil was placed in a 40.0ml tube. The glass tubes were sealed tightly and placed into temperature controlled water baths set at  $10 \pm 1^\circ\text{C}$ ,  $15 \pm 1^\circ\text{C}$ ,  $20 \pm 1^\circ\text{C}$  and  $25 \pm 2^\circ\text{C}$ . Two sets of soil from the Stead site were incubated. One set of soils was air-dried whereas a second set was not air-dried prior to incubation. The soil from Marchand was air-dried prior to incubation. The soils were maintained at field capacity moisture content during incubation. All treatments were replicated three times. After a 14 day incubation period the samples were extracted with 20.0 ml of 0.005 M DTPA (extracting solution

was 0.005 M with respect to diethylenetriaminepentaacetic acid, 0.1 M with respect to  $\text{Ca Cl}_2$  adjusted to pH 7.3) and/or 1.0 M  $\text{NH}_4\text{OAc}$  at the respective incubation temperatures. Samples were extracted for two hours using a rotary shaker submerged in the water baths. The suspensions were then filtered through Whatman #42 filter paper and the Mn concentration of the filtrate was determined by aspirating a portion of the liquid into a Perkin-Elymer Model 560 Atomic Absorption Spectrophotometer.

A second set of extractions was conducted which included the sample pre-treatments as previously outlined above. However in this experiment the samples were not incubated prior to extraction. The samples were taken after storage at room temperature and extracted at 10, 15, 20 and 25°C.

Experiment II. Effect of extraction temperature on amounts of Mn, Fe and Zn extracted from soils.

Five grams of air-dried soil (from the Stead location) were wetted to 75% of field capacity, placed into 125 erlenmeyer flasks, and extracted immediately with the extracting solutions as described for Study I. However, in this study 30.0 ml of the extracting solution were added. The samples were extracted at 10<sup>+0.5</sup> C, 15<sup>+0.5</sup> C, 20<sup>+0.5</sup> C and 25<sup>+0.5</sup> C. All treatments were duplicated. Extraction procedures used were as previously described. The DTPA filtrates were analyzed for concentrations of Mn, Fe and Zn whereas the  $\text{NH}_4\text{OAc}$  filtrates were analyzed for only concentration of Mn.

## (3) Results and Discussion

Experiment I. Effect of incubation temperature and extraction temperature on amounts of Mn extracted from soils.

Amounts of manganese extracted increased with soil temperature for both soils and both methods of extraction (Table 26). Amounts of Mn extracted increased very markedly with extraction temperature at temperatures of 10°C to 20°C. Except for the DTPA extractions on the Stead soil, which was air-dried prior to incubation, increasing the temperature from 20°C to 25°C did not increase amounts of Mn extracted. Sample handling prior to incubation also affected amounts of Mn extracted. DTPA extracted greater amounts of Mn from samples maintained at field moisture level than for samples air-dried prior to incubation, particularly when the extractions were conducted at low soil temperatures. Ammonium acetate extracted more Mn than DTPA at 10, 15 and 20°C but not at 25°C.

Table 26. Extractable manganese (ug/g) after a two-week incubation period at four different temperatures.

Temperature	Stead Air Dried	Stead Moist DTPA	Marchand Air Dried	Stead Air Dried —NH <sub>4</sub> OAc—
10°C	6.5 a*	19 a	44 a	11 a
15°C	9.5 a	28 b	60 b	18 a b
20°C	16 b	29 b	70 b	20 b
25°C	25 c	30 b	65 b	20 b

\*Duncans's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. Separate analysis was conducted on each extraction treatment.

Amounts of Mn extracted from soils at the various temperatures but without pre-incubation at the various temperatures also increased as temperature of extraction was increased (Table 27). Amounts of Mn extracted increased with extraction temperature for both methods of extraction, for both soils and for all methods of pre-treatment. Amounts of Mn extracted without pre-incubation prior to analysis was much less than for samples that were incubated prior to extraction. It is possible that microbial activity during incubation may have caused reducing conditions which may have increased the solubility of soil Mn. In contrast to the results obtained for soils which were incubated prior to extraction,  $\text{NH}_4\text{OAc}$  extracted less Mn than DTPA.

Table 27. Extractable manganese (ug/g) of two organic soils.

Temperature of Extraction	Stead Air Dried	Stead Moist	Marchand Air Dried	Stead Air Dried
	-----DTPA-----		-----	----- $\text{NH}_4\text{OAc}$ -----
10°C	4.9 a b *	2.9 a	2.9 a b	1.0 a
15°C	6.4 b	4.5 a	3.5 a b	.9 a
20°C	6.3 b	7.8 b	4.2 b	1.2 a
25°C	13.9 c	9.1 b	10.5 c	1.5 b

\* Duncan's Multiple Range Test: Values followed by the same letter are not significantly different at the 5% level. Separate analysis was conducted on each extraction treatment.



Experiment II. Effect of extraction temperature on amounts of Mn, Fe and Zn extracted from soils.

The amounts of Fe and Zn extracted increased with increasing temperature of extraction (Table 28). However, Fe and Zn availability as measured by barley or wheat uptake in the growth chamber, indicated there was little or no relationship between soil temperature and Fe or Zn concentrations in plant shoots. The data presented shows that amounts of micronutrients extracted from organic soils by DTPA or other extractants were affected by extraction temperature. Generally amounts extracted increased with soil temperature which suggests that soil temperature modifies the capacity factor of a particular nutrient in the soil. The capacity factor, the ability of the soil to replenish ions, being a rate reaction would be expected to increase with increasing temperature .

Table 28. Influence of extraction temperature on extractable Mn, Zn and Fe by DTPA and extractable Mn by  $\text{NH}_4\text{OAc}$

Temperature of Extraction	Zn (ug/g)	DTPA Fe (ug/g)	Mn (ug/g)	$\text{NH}_4\text{OAc}$ Mn (ug/g)
10°C	4.8 a*	83	28 a	10 a
15°C	6.3 a b	107	42 b	11 a
20°C	8.1 c	168	60 c	15 b
25°C	7.1 b	187	68 c	17 b

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

In general both extraction studies and the incubation study indicated that the extractable Mn in organic soils increased with increasing soil temperature. The increases in DTPA and  $\text{NH}_4\text{OAc}$  extractable Mn closely reflected the increases in Mn content of plants with increasing temperature. Thus, the greater assimilation of manganese by plants at the higher soil temperatures was most likely due to increases in the availability of Mn from these soils.

#### (4) Summary

For all methods of extraction, for both soils and for both extracting solutions, greater amounts of Mn were extracted at the higher temperatures. The close relationship between the increases in extractable Mn levels with those found in barley and wheat shoots with increasing temperature indicate that a greater release of Mn from the soil-solid-phase into soil solution was operating as temperature was increased.

E. Study V - The influence of soil moisture content on the Mn uptake by barley.

(1) Introduction

Manganese status of plants is usually enhanced under soil conditions of limited aeration. Aeration of soils is dependent upon factors such as water content and microbial activity. Thus, it was postulated that variations in the water content of organic soils may also affect Mn uptake by plants. Increasing water content would increase concentration of the reduced form of manganese,  $Mn^{++}$ , which is readily available for plant utilization. To test this hypothesis, four soil moisture regimes, 75, 100, 150 and 200% of field moisture content were imposed on barley grown in the growth chamber. Soil aeration status was measured for each water regime by use of electrodes sensitive to oxygen concentrations in the soil. The influence of aeration on Mn availability was measured by growing barley and measuring Mn uptake.

(2) Experimental Methods

Three hundred and fifty grams of air-dried soil from the Stead experimental site treated with the equivalent of 185 Kg N/ha as  $NH_4NO_3$ , 130 Kg  $P_2O_5$ /ha as  $NH_4H_2PO_4$ , 200 Kg  $K_2O$ /ha as  $K_2SO_4$  and 40 Kg Cu/ha as  $CuSO_4$  were placed into each pot. Amounts of all fertilizers were calculated on an area basis. The  $NH_4H_2PO_4$  supplied an additional 30 Kg N/ha. The  $K_2SO_4$  and  $CuSO_4$  supplied the equivalent to 100 Kg S/ha. All fertilizers (technical grade chemicals dissolved in deionized water) were sprayed onto the soil and well mixed. The treated soils were placed in clean plastic bags and placed into the (11 cm dia x 35 cm)

cylindrical pots. The pots were placed on growth benches with day/night temperatures of 13/21<sup>o</sup>C and a day length of 17 hours. Three barley plants were grown per pot. All pots were replicated three times.

During the first two weeks after emergence of the barley the pots were maintained between 75% and 100% of field capacity moisture content. During the remainder of the growth period plants were grown at either 75, 100, 150 or 200% of field moisture capacity. Oxygen diffusion rates were measured every second day after the water regimes were imposed. Measurements were made by measuring the electrical potential generated between a platinum microelectrode. Five readings were taken at 10 cm and at 20 cm depths for each pot.

The total above ground plant was harvested 42 days after emergence when plants were in the early heading stage. The Mn concentrations in the plant shoots were then determined.

### (3) Results and Discussion

The data obtained for the oxygen diffusion rates (O.D.R.) was not included in this manuscript. The variability among readings obtained at the same depth for a particular water regime was extremely large and differences among treatments, if they existed, could not be clearly defined. Similar difficulties were encountered by Black (1968) who considered ODR values of no meaning when measurements were made on waterlogged soils. Since the moisture regimes employed in this study were within the saturated to waterlogged range, it is not surprising that meaningful measurements were not obtained.

Barley yields were affected by soil water content (Table 29). The dry matter yields were significantly higher at water contents of 100% and 150% of F.C. than at water contents of 75% or 200% of F.C. Yield of barley obtained at the 75% moisture level was greater than yields of barley obtained at the 200% of moisture level. Optimum yields would be expected at moisture levels of 100% to 150% of field capacity, as these levels would represent nearly ideal soil-moisture levels for plant growth.

Table 29. Influence of soil-moisture content on yield and Mn, Fe, Zn and Cu content of barley at the early boot stage.

Water Treatment % of F.C.	Dry Matter Yield (g/pot)	Mn (ug/g)	Fe (ug/g)	Zn (ug/g)	Cu (ug/g)
75	6.19 b <sup>*</sup>	100 a	56 b	27 b	6.8 a
100	8.59 c	96 a	57 b	24 a b	7.3 a
150	9.03 c	88 a	48 a	26 b	11 b
200	4.82 a	140 b	44 a	20 a	10 b

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

Manganese concentrations in barley shoots were unaffected by soil water content, except at the highest water regime (Table 29). Total Mn uptake per pot was significantly higher for plants grown at 100% of F.C. than for plants grown at 75% of field capacity (Table 30). Manganese uptake by plants grown at 100, 150 and 200% of F.C. were similar.

Iron concentrations in barley shoots were decreased by increasing the water content to 150 and 200% of F.C. Zinc concentrations in barley shoots decreased when soil water content was increased to 200% of F.C.

Table 30. Influence of soil-moisture content on the total Mn, Fe, Zn and Cu uptake by barley at the early boot stage.

Treatment % of F.C.	Mn (mg/pot)	Fe (mg/pot)	Zn (mg/pot)	Cu (mg/pot)
75	614 a*	344 a b	168 b	42 a
100	836 b	393 b	207 c	63 b
150	791 a b	430 b	216 c	96 c
200	676 a b	217 a	97 a	50 a

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

In contrast, Cu concentrations in barley shoots increased when soil water contents were increased to 150 and 200% of F.C. Copper uptake decreased in the order, 150 > 100 > 200 = 75% of F.C. water treatments.

Total Fe uptake by barley was lower at the 200% of F.C. water treatment. Similarly, the total Zn uptake was also lower at this water content. These findings would be a consequence of the lower dry matter production of barley at the 200% F.C. water treatment.

#### (4) Summary

It was postulated that soil water content, particularly water contents above field capacity, would influence Mn uptake. However, soil water content had very little direct effect on Mn concentrations and uptake in barley shoots. Increasing water contents of soils from 75 to 100% of field capacity had a slight positive affect on Mn uptake. Manganese uptake by barley shoots at very high water levels were similar to that at 75% of field capacity. The reducing conditions imposed by waterlogging an organic soil, did not appear to influence Mn availability.

## V. SUMMARY AND CONCLUSIONS

Field studies were conducted to determine if the seed yields of rapeseed, wheat and barley, obtained on organic soils in Manitoba, could be improved by the use of Cu, Mn and B fertilizers. Major emphasis was placed on the effects of manganese fertilizer on yield and chemical composition. Various methods of manganese fertilizer application were also studied. The field experiments were located near Piney, Marchand and Stead.

The rapeseed at all locations was destroyed by a late spring frost. Wheat grain yields were increased by copper fertilization at Piney and Stead. Applications of boron and/or manganese had little or no effect on wheat grain yields. Yields of wheat were generally higher in 1980 than in previous years at the same locations. This was attributed to the higher early spring temperatures in 1980.

Barley grain yields were increased by copper and boron fertilization at Stead. Manganese, copper and boron fertilizers had little or no effect on barley grain yields at Piney and Marchand.

Straw yields for both wheat and barley were variable and were not related to micronutrient fertilization.

Banding manganese sulphate with the seed of barley and wheat was generally very effective in increasing manganese shoot concentrations.

Broadcast manganese applications were about one-half as effective as with-seed applications in increasing Mn shoot concentrations, except for barley grown at Marchand where broadcast Mn was very ineffective. Foliar applications appeared to be very ineffective in increasing Mn concentrations in plant shoots.

A significant feature of the results obtained in 1980 and in previous years was the extreme year to year variability in shoot concentrations of manganese and other minor elements even though the experimental sites were situated at the same locations. Yields of crops also varied greatly from year to year. The variations in nutrient uptake and yield were most likely a result of year to year variations in weather, particularly weather affecting air and soil temperatures.

The results obtained in the field study led to the initiation of an environmental growth chamber study to determine if the assimilation of Mn and other nutrients by wheat and barley were related to soil temperature. Four soil temperatures 10, 15, 20 and 25°C were investigated. The aerial portions of wheat and barley were harvested at two stages of development and yield and chemical composition of the shoots determined.

Optimum yields at the three to four leaf stage for wheat and barley were obtained at 25°C soil temperature. This was attributed to the delayed emergence and slower growth rate of the plants grown at the lower soil temperatures. Yields of both wheat and barley, at the boot stage (when plants reached the same morphological and physiological development) were greatest at a soil temperature of 15°C.



The Mn shoot concentrations of both wheat and barley increased two-fold when the soil temperature was increased from 10 to 20°C for both harvest dates. Increasing soil temperatures above 20°C had a slight positive effect on wheat shoot Mn concentrations, while increasing the soil temperature in this range resulted in a decrease in barley shoot Mn concentrations. Interesting features of the results obtained in this study were the low Mn shoot concentrations in barley grown at the 10°C soil temperature and the low Cu shoot concentrations for both crops at all soil temperatures.

A similar study was conducted to determine the influence of soil temperature on the assimilation of fertilizer Cu and Mn by barley. Barley was grown with and without Cu and/or Mn at the same four soil temperatures. Barley yields, obtained at the boot stage, were highest at a soil temperature of 15°C. The addition of  $\text{MnSO}_4$  increased vegetative yields of barley at this stage compared to barley grown without micronutrient fertilization. Copper and/or manganese additions had little effect on the dry matter yields of barley at all other soil temperatures.

The addition of  $\text{MnSO}_4$  increased shoot Mn concentrations of barley at the three to four leaf stage when grown at soil temperatures of 15 and 20°C. Increased shoot Mn concentrations at the boot stage of barley was only evident at the 25°C soil temperature. In contrast to the previous study, shoot Mn concentrations were increased when soil temperatures were increased from 20 to 25°C in this study.

The addition of  $\text{CuSO}_4$  increased shoot Cu concentrations of barley at all soil temperatures. The additions of Mn and Cu indicated that an interaction existed between these nutrients. The addition of Cu along with Mn generally suppressed Mn assimilation by barley, while the addition of Mn enhanced the uptake of Cu.

Soil extraction studies were undertaken to investigate the possibility that an increase in the supply of manganese from the soil was responsible for the noted increase in plant shoot Mn concentrations with increases in soil temperature. Incubated and non-incubated organic soils were extracted with either 0.005 M DTPA or 1 N  $\text{NH}_4\text{OAc}$ . In all extraction studies greater amounts of Mn were extracted when extraction temperatures were increased from 10 to 20°C.

The increases in extractable Mn values with increasing incubation temperature closely paralleled the effect of soil temperatures in Mn concentrations in wheat and barley shoots. The increases in shoot Mn concentrations was therefore probably due to an increase in the release of Mn from the soil-solid-phase into the soil solution. The results obtained suggest that the yearly variations in shoot Mn concentrations of crops grown on organic soils was most likely due to variations in soil temperature .

Since the Mn status of plants has been shown to vary with variations in soil aeration, studies were also conducted to determine the effects of soil water content on Mn content and uptake by barley shoots.

Four soil moisture regimes were imposed on an organic soil to investigate the influence of water content on the micronutrient status of barley at the boot stage. Measurements of the oxygen diffusion rates were also obtained. However readings obtained for oxygen diffusion rates were extremely variable and were of no or little value in assessing the aeration status of wet or waterlogged organic soils.

Barley dry matter yields at the boot stage were greatest for plants grown at 100 and 150% of FC. The Mn shoot concentrations were greatest at 200% of FC. However total Mn uptake was not different at water contents greater than 75% of field capacity.

Copper shoot concentrations and total uptakes were greater at the higher moisture regimes. It is possible these observations were the result of the influence of water content on the availability of the applied  $\text{CuSO}_4$ .

The studies reported in this manuscript, as well as those reported by other workers, showed that organic soils in Manitoba may not supply sufficient quantities of Cu, Mn and perhaps B for optimal growth of agricultural crops. The studies reported here also showed that soil temperatures played a dominant role in governing the Mn supply to plants. Mn concentrations in wheat and barley shoots increased with increases in soil temperature. It is therefore possible that increasing soil temperature, through improved soil drainage, may greatly enhance Mn uptake and yield.

## VI. APPENDIX

Table 1. Mean summer and maximum temperatures of two organic soils to a depth of 150 cm near Whitemouth, Manitoba.

Location	Depth	Mean Summer	Maximum
Meadow	2.5	20.1*	21.6
	5.0	17.9	19.3
	10.0	13.3	14.5
	20.0	9.3	10.8
	50.0	5.8	7.8
	100.0	3.8	6.2
	150.0	2.7	4.9
Forest	2.5	19.5	20.0
	5.0	18.0	19.3
	10.0	16.3	17.6
	20.0	13.9	15.5
	50.0	11.9	13.8
	100.0	8.7	11.3
	150.0	6.6	9.4

\*Krupan 1982.

## VII. BIBLIOGRAPHY

1. Adams, F. 1965. Manganese. In *Methods of Soil Analysis: Chemical and Microbiological Properties*. C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger, and F.E. Clark (Eds.). *Agronomy* 9: 1011-1018. American Soc. of Agron., Madison, Wisconsin.
2. Bingham, F.T. and Garber, M.J. 1960. Solubility and availability of micronutrients in relation to phosphorus fertilization. *Soil Sci. Soc. Amer. Proc.* 24: 209-213.
3. Black, C.A. 1968. In *Soil-Plant Relationships*. John Wiley and Sons, New York. pp 153-197.
4. Brown, J.C. and Jones, W.E. 1974. Differential response of oats to manganese stress. *Agron. J.* 61: 624-626.
5. Browman, M.G., Chesters, G. and Pionke, H.B. 1969. Evaluation of tests for predicting the availability of soil manganese to plants. *J. Agric. Sci.* 72: 335-340.
6. Cheng, B.T., Bourget, S.J. and Ouellette, G.J. 1971. Effect of some soil physical properties on growth and manganese, iron, aluminum, and molybdenum content of oats. *Can. J. Soil Sci.* 51: 123-126.
7. Cheng, B.T. and Ouellette, G.J. 1970. Effects of steam sterilization and organic amendments on the manganese status and associated characteristics of acid soils. *Soil Sci.* 110: 383-388.
8. Cheng, B.T. and Ouellette, G.J. 1971. Manganese availability in soil. *Soils and Fertilizers* 34: 589-594.
9. Cheniae, G.M. and Martin, I.F. 1970. Sites of function of manganese within photosystem II. Roles in  $O_2$  evolution and system II. *Biochem. Biophys. Acta* 197: 219-239.
10. Cheniae, G.M. and Martin, I.F. 1971. Effects of hydroxylamine on photosystem II. I-Factors affecting the decay of  $O_2$  evolution. *Plant Physiol.* 47: 568-575.
11. Cheng, B.T., Ouellette, G.J. and Bourget, S.J. 1972. Interaction of temperature and moisture on iron and manganese availability in soils. *Le Naturaliste Canadien* 99: 515-521.
12. Cotter, D.J. and Mishra, U.N. 1968. The role of organic matter in soil manganese equilibrium. *Plant and Soil* 29: 439-448.

13. Cox, F.R. 1968. Development of a yield response prediction and manganese soil test interpretation for soybeans. *Agron. J.* 60: 521-524.
14. Dolar, S.G., Keeney, D.R. and Walsh, L.M. 1971. Availability of Cu, Zn, and Mn in soils. III.- Predictability of plant uptake. *J. Sci. Fd. Agric.* 22: 282-286.
15. Farley, R.F. and Draycott, A.P. 1973. Manganese deficiency of sugar beet in organic soil. *Plant and Soil* 38: 235-244.
16. Fiskel, J.G. and Mourkides, G.A. 1955. A comparison of Mn sources using tomato plants grown on marl, peat, and sand soils. *Plant and Soil* 6: 313-331.
17. Fujimoto, C.K. and Sherman, G.D. 1948. Manganese availability as influenced by steam sterilization of soils. *J. Amer. Soc. Agron.* 40: 527-534.
18. Fulton, J.M. 1968. Growth and yield of oats as influenced by soil temperature, ambient temperature and soil moisture supply. *Can. J. Soil Sci.* 48: 1-5.
19. Ghazali, N.J. and Cox, F.R. 1981. Effect of temperature on soybean growth and manganese accumulation. *Agron. J.* 73: 363-367.
20. Halstead, E.H. and Barber, S.A. 1968. Manganese uptake attributed to diffusion from soil. *Soil Sci. Soc. Amer. Proc.* 32: 540-542.
21. Hammes, J.K. and Berger, K.C. 1960a. Chemical extraction and crop removal of manganese from air-dried and moist soils. *Soil Sci. Soc. Amer. Proc.* 24: 361-364.
22. Hammes, J.K. and Berger, K.C. 1960b. Manganese deficiency in oats and correction of plant manganese with various soil tests. *Soil Sci.* 90: 239-244.
23. Haq, A.U. and Miller, M.H. 1972. Prediction of available soil Zn, Cu, and Mn using chemical extractants. *Agron. J.* 64: 779-782.
24. Harmer, P.M. and Sherman, G.D. 1943. The effect of manganese sulfate on several crops growing on organic soil when applied in solution as a stream or spray on the crop. *Soil Sci. Soc. Am. Proc.* 8: 334-340.
25. Harter, R.D. and McLean, E.O. 1965. The effect of moisture level and incubation time on the chemical equilibria of a Toledo clay loam soil. *Agron. J.* 57: 583-588.
26. Hemstock, G.A. and Low, P.F. 1953. Mechanisms responsible for the retention of manganese in the colloidal fraction of soil. *Soil Sci.* 76: 331-343.

27. Hewitt, E.J. 1963. Essential nutrient elements for plants. In *Plant Physiology III*. F.C. Steward (Ed.). Academic Press, New York pp 137-329.
28. Hewitt, E.J. (1970). Physiological and biochemical factors which control the assimilation of inorganic nitrogen supplies by plants. In *Nitrogen Nutrition of the Plant*. E.A. Kirkby (Ed.). The Univ. of Leeds, pp 78-103.
29. Hoff, D.J. and Mederski, H.J. 1958. The chemical estimation of plant available soil manganese. *Soil Sci. Soc. Amer. Proc.* 22: 129-132.
30. Homann, P.H. 1967. Studies on the manganese of the chloroplast. *Plant Physiol.* 42: 997-1007.
31. Hossner, L.R. and Richards, G.E. 1968. The effect of phosphorus source on the movement and uptake of band applied manganese. *Soil Sci. Soc. Amer. Proc.* 32: 83-85.
32. Hoyt, P.B. and Nyborg, M. 1971. Toxic metals in acid soil. II. - Estimation of plant available Mn. *Soil Sci. Soc. Amer. Proc.* 35: 241-244.
33. Jones, J.B., Jr. 1972. Plant tissue analysis for micronutrients. In *Micronutrients in Agriculture*. J.J. Mortvedt, P.M. Giordano and W.L. Lindsay (Eds.). Soil Sci. Soc. Am., Inc., Madison, Wis.
34. Jones, L.H.P. 1957. Effect of liming a neutral soil on the cycle of manganese. *Plant and Soil* 8: 315-327.
35. Kessler, E. 1970. Photosynthesis, photooxidation of chlorophyll, and fluorescence of normal and manganese-deficient *Chlorella* with and without hydrogenase. *Planta* 92: 222-234.
36. Knezek, B.D. and Greinert, H. 1971. Influence of soil Fe and Mn EDTA interactions upon the Fe and Mn nutrition of bean plants. *Agron. J.* 63: 617-619.
37. Krpan, J.D.B. 1982. The characteristics and estimation of soil temperatures in Manitoba. M.Sc. Thesis, University of Manitoba, Winnipeg, Manitoba.
38. Larsen, S. 1964. The effect of phosphate application on manganese content of plants grown on neutral and alkaline soils. *Plant and Soil* 21: 37-41.
39. Lazrus, A.J., Hill, K.C. and Lodge, J.P. 1966. A new colometric micro-determination of sulphate ion. *Automation in Analytical Chemistry, Technicon Symposium 1965*. Mediad: 291-293.

40. Lindsay, W.L. 1972. Inorganic phase equilibria of micronutrients in soils. In *Micronutrients in Agriculture*, J.J. Mortvedt, P.M. Giordano and W.L. Lindsay (Eds.). Soil Sci. Soc. Am., Madison Wisconsin pp 41-57.
41. Lindsay, W.L. and Norvell, W.A. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* 42: 421-428.
42. MacMillian, K.A. and Hamilton, H.A. 1971. Carrot response to soil temperature and copper, manganese, zinc and magnesium. *Can. J. Soil Sci.* 51: 293-297.
43. Mann, P.J.G. and Quastel, J.H. 1946. Manganese metabolism in soils. *Nature* 158: 154-156.
44. Martens, J.W., McKenzie, R.I.H. and Bendelow, V.M. 1977. Manganese levels of oats in Western Canada. *Can. J. Plant Sci.* 57: 383-387.
45. Maas, E.V., Moore, D.P. and Mason, B.J. 1968. Manganese absorption by excised barley roots. *Plant Physiol.* 44: 796-800.
46. McAdrew, D.W. 1979. Copper and Zinc Nutrition of Cereal Crops in Manitoba. M. Sc. Thesis, University of Manitoba, Winnipeg, Manitoba.
47. McCall, W.W. and Davies, J.F. 1953. Foliar applications of plant nutrients to crops grown on organic soils. *Mich. Agric. Exp. Stn. Quart. Bull.* 35: 373-383.
48. McHarque, T.S. 1922. The role of manganese in plants. *J. Am. Chem. Soc.* 44: 1592-1598.
49. McLaren, R.G., and Crawford, 1973. Studies on Soil Copper III.- Isotopically exchangeable copper in soils. *J. Soil Sci.* 25: 111-119.
50. Mederski, H.G. and Hoff, D.J. 1958. Manganese deficiency in soybeans. In *Trace Elements*, C.A. Lamb (Ed.). Academic Press, Inc., New York pp 99-108.
51. Melsted, S.W., Motto, H.L., and Peck, T.R. 1969. Critical plant nutrient composition values useful in interpreting plant analysis data. *Agron. J.* 61: 17-21.
52. Mengel, K. and Kirkby, E.A. 1979. *Principles of Plant Nutrition*. International Potash Inst., Switzerland pp 441-450.
53. Mishra, B. and Tripathi, B.R. 1973. Effect of N, P and K fertilizers on the availability of native and applied manganese to wheat. *J. Agric. Sci., Camb.* 81: 369-373.



54. Mulder, E.G. and Gerretsen, F.C. 1952. Soil manganese in relation to plant growth. *Advance Agron.* 4: 221-227.
55. Mumford, F.E., Stark, H.M. and Smith, D.H. 1962. A naturally-occurring cofactor for indoleacetic acid oxidase. *Plant Physiol.* 37: Proc. of the Plant Physiology Meetings 693.
56. Munson, R.D. and Nelson, W.L. 1973. Principles and practices in plant analysis. In *Soil Testing and Plant Analysis*. L.M. Walsh and J.O. Beaton (Eds.). Soil Sci. Soc. Amer., Madison, Wis. pp 223-248.
57. Murray, G.A. and Benson, J.A. 1976. Oat response to manganese and zinc. *Agron. J.* 68: 615-616.
58. Nason, A. and McElroy W.D. 1963. Modes of action of the essential mineral elements. In *Plant Physiology III*, F.C. Steward (Ed.). Academic Press, Inc., New York pp 451-522.
59. Nyaki, A.S.K. 1981. Zinc and Copper Nutrition of Corn on Manitoba Soils. M. Sc. Thesis, University of Manitoba, Winnipeg, Manitoba.
60. Nyborg, M. 1970. Sensitivity to manganese deficiency of different cultivars of wheat, oats and barley. *Can. J. Plant Sci.* 50: 198-200.
61. Ohki, K. 1975a. Manganese supply, growth, and micronutrient concentration in grain sorghum. *Agron. J.* 67: 30-32.
62. Ohki, K. 1975b. Mn and B effects on micronutrients and P in cotton. *Agron. J.* 67: 204-207.
63. Ohki, K. 1981. Manganese critical levels for soybean growth and physiological processes. *Journ. of Plant Nut.* 3: 271-284.
64. Ozaki, L.G. 1955. Effectiveness of foliar manganese sprays on peas and beans. *Amer. Soc. Hort. Proc.* 66: 313-316.
65. Page, E.R. 1962. Studies in soil Mn II.-The relationship of soil pH to Mn availability. *Plant and Soil* 16: 247-256.
66. Page, D.W. and Dainty, J. 1964. Manganese uptake by excised oat roots. *J. Exp. Bot.* 15: 428-433.
67. Page, E.R., Schofield-Palmer, E.K. and McGregor, A.J. 1962. Studies in soil Mn I.- Mn in soil and its uptake by oats. *Plant and Soil* 16: 238-246.
68. Parker, M.B., Boswell, F.C., Ohki, K., Shuman, L.M. and Wilson, D.O. 1981. Manganese effects on yield and nutrient concentration in leaves and seed of soybean cultivars. *Agron. J.* 73: 643-646.

69. Pavanasasivan, V. 1973. Manganese studies in some soils with a high organic matter content. *Plant and Soil* 38: 245-255.
70. Peech, M. and Boynton, D. 1937. Soils in relation to fruit growing in New York, Part 10. Susceptibility of various New York orchard soils to reduction upon water-logging. *Corn. Univ. Agr. Expt. Sta. Bull.* 667.
71. Pirson, A. 1958. Manganese and its role in photosynthesis. In *Trace Elements*. C.A. Lamb (Ed.). Academic Press, New York pp 81-98.
72. Ponnampetuma, F.N. and Loy, T.A. 1970. Influence of temperature on the chemical kinetics of flooded soils and the growth of rice. *Agron. Abstr.* pp 99.
73. Possingham, J.V. and Spencer, D. 1962. Manganese as a functional component of chloroplasts. *Aust. J. Biol. Sci.* 15: 58-68.
74. Quastel, J.H. 1963. Microbial activities of soil as they affect plant nutrition. In *Plant Physiology III*, F.C. Steward (Ed.). Academic Press, Inc., New York pp 671-743.
75. Quastel, J.H., Hewitt, E.J. and Nicholas, D.J.D. 1948. The control of manganese deficiency in soils. I.- The effects of sulphur and thiolsulphates on crops growing on manganese deficient soils. *J. Agric. Sci.* 38: 315-322.
76. Racz, G.J., McAndrew, D.W. and Tokarchuk, J.M. 1978. Major and minor element requirements of crops grown on organic soils. *Proceedings of the 22nd Annual Manitoba Soil Science Meetings*. University of Manitoba, Winnipeg, Manitoba. pp 64-68.
77. Randall, G.W., Schulte, E.E. and Corey, R.B. 1975a. Effect of soil and foliar-applied manganese on the micronutrient content and yield of soybeans. *Agron. J.* 67: 502-507.
78. Randall, G.W., Schulte, E.E. and Corey, R.B. 1975b. Soil Mn availability to soybeans as affected by mono and diammonium phosphate. *Agron. J.* 67: 705-709.
79. Randall, G.W., Schulte, E.E. and Corey, R.B. 1976. Correlation of plant manganese with extractable soil manganese and soil factors. *Soil Sci. Soc. Am. J.* 40: 282-287.
80. Reid, A.S.J. and Miller, M.H. 1963. The manganese cycle in soils II.- Forms of soil manganese in equilibrium with solution manganese. *Can. J. Soil Sci.* 43: 250-259.

81. Reid, A.S.J. and Webster, G.R. 1969. The manganese status of some Alberta soils. *Can. J. Soil Sci.* 49: 143-150.
82. Reid, J.M. and Racz, G.J. 1980. Effect of Cu, Mn and B fertilizer on yield and chemical composition of wheat and barley. *Proceedings of the 24th Annual Manitoba Soil Science Meetings. University of Manitoba, Winnipeg, Manitoba.* pp 107-114.
83. Rule, J.H. and Graham, E.R. 1976. Soil labile pools of manganese, iron, and zinc as measured by plant uptake and DTPA equilibrium. *Soil Sci. Soc. Amer. J.* 40: 853-857.
84. Russell, E.W. 1973. *Soil Conditions and Plant Growth* 10th ed. Longman Group Ltd., London. pp
85. Salcedo, I.H. and Warncke, D.D. 1979. Studies in soil manganese I.- Factors affecting manganese extractability. *Soil Sci. Soc. Am. J.* 43: 135-138.
86. Samuel, G. and Piper, C.S. 1929. Manganese. *Ann. Applied Biol.* 16: 493-524.
87. Sanchez, C. and Kamprath, E.J. 1959. Effect of liming and organic matter content on the availability of native and applied manganese. *Soil Sci. Soc. Amer. Proc.* 23: 302-304.
88. Schachtschabel, P. 1955. Manganese in soil. *Die Phosphorsäure* 15: 133-139.
89. Severson, R.C., McNeal, J.M. and Dickson, J.J. 1979. Effects of soil preparation on DTPA-extractable elements in soils of the Northern Great Plains. *Soil Sci.* 128: 70-78.
90. Sherman, G.D. and Harmer, P.M. 1941. Manganese deficiency of oats on alkaline organic soils. *J. Am. Soc. Agron.* 33: 1080-1092.
91. Shepherd, L., Lawton, K. and Davies J.F. 1960. The effectiveness of various Mn materials in supplying Mn to crops. *Soil Sci. Soc. Am. Proc.* 24: 218-221.
92. Sheppard, S., Lucas, J. and Bates, T.E. 1979. Manganese on winter wheat. 1979. *Progress Report of the Ontario Department of Land Res. Sci.* pp 38-39.
93. Shuman, L.M. and Anderson, O.E. 1974. Evaluation of six extractants for their ability to predict manganese concentrations in wheat and soybeans. *Soil Sci. Soc. Amer. Proc.* 38: 788-790.
94. Shuman, L.M., Boswell, F.C., Ohki, K., Parker, M.B. and Wilson, D.O. 1979. Soybean yield, leaf manganese, and soil manganese as affected by sources and rates of manganese and soil pH. *Agron. J.* 71: 989-991.

95. Sims, J.L., Atkinson, W.O. and Smitobol, C. 1975. Mo and N effects on growth, yield and Mo composition of burley tobacco. *Agron. J.* 67: 824-828.
96. Singh, M. and Pathak, A.N. 1970. Effect of steam sterilization on soil manganese. *Plant and Soil* 33: 244-248.
97. Snyder, G.H., Burt, E.O. and Gasho, G.J. 1979. Correcting pH-induced manganese deficiency in bermundagrass turf. *Agron. J.* 71: 603-608.
98. Spencer, D. and Possingham, J.V. 1961. The effect of manganese deficiency on photophosphorylation and the oxygen evolving sequence in spinach chloroplasts. *Biochim. Biophys. Acta* 52: 379-381.
99. Stainton, M.P., Capel, M.J. and Armstrong, J.A.J. 1974. The chemical analysis of fresh water. *Environ. Can., Fisheries and Marine Services, Miscellaneous Special Publication* 25:59-61.
100. Takkar, P.N. 1969. Effect of organic matter on soil iron and manganese. *Soil Sci.* 108: 108-112.
101. Taylor, R.M., Morgan, P.W., Joham, H.E. and Amin, J.V. 1968. Influence of substrate and tissue manganese on the IAA-oxidase system in cotton. *Plant Physiol.* 43: 243-247.
102. Tokarchuk, J.M., Racz, G.J. and Reid, J.M. 1979. Effect of copper additions on the yield and chemical composition of rape, barley and wheat grown on organic soils. *Proceedings of the 23rd Annual Manitoba Soil Science Meetings. University of Manitoba, Winnipeg, Manitoba,* pp 130-139.
103. Voth, R.D. and Christenson, D.R. 1980. Effect of fertilizer reaction and placement on availability of manganese. *Agron. J.* 72: 769-773.
104. Wilcox, G.E. and Cantliffe, D.J. 1969. Plant response to manganese source, rate and method of application. *J. Am. Soc. Hort. Sci.* 99: 354-356.
105. Wilson, D.O., Boswell, F.C., Ohki, K., Parker, M.B. and Shuman, L.M. 1981. Soil distribution and soybean plant accumulation of manganese in manganese-deficient and manganese-fertilized field plots. *Soil Sci. Soc. J.* 45: 549-552.
106. Ulrich, A. and Hills, F.J. 1967. Principles and practices of plant analysis. In *Soil Testing and Plant Analysis. Part II. SSSA Special Publ. Series No. 2. Soil Sci. Soc. of Amer., Madison, Wis.,* pp 11-24.
107. Woodbury, W. 1982. Personal communication. Professor of Plant Physiology, Department of Plant Sci., University of Manitoba. Winnipeg, Manitoba.