

AN ABSTRACT OF THE THESIS OF

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of Barley and Oats

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A series of field experiments was established in 1978, 1979, and 1980 on Lower Klamath Lake where Mn deficiency of oats had been observed in previous years. The pH of the soils ranged from 7.6 to 8.3 and the organic matter content was between 17 and 19%. The objectives of the experiment were to (1) evaluate the effects of band application of different N sources with and without Mn on the Mn concentration and yield of barley and oats, (2) compare effects of band versus broadcast application of fertilizers on the Mn concentration and yield of barley and oats, and (3) determine the Mn critical level for barley and oats. Nitrogen was applied at 0, 22, or 45 kg N/ha as $(\text{NH}_4)_2\text{SO}_4$ (AmS), NH_4Cl (AmCl), Urea (Ur), granular urea-phosphate (UP 17-44), a urea-phosphoric acid solution (UP pH3), or a solution made from the granular urea-phosphate (UP). Phosphorus was applied at 0 or 19 kg P/ha as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (MCP) or 25 kg P/ha in the UP solutions. Manganese was applied at 0 or 5.6 kg Mn/ha as MnSO_4 and copper was applied as CuSO_4 at 0 or 2.2 kg Cu/ha in 1978 with all treatments receiving 5.6 kg Cu/ha in 1979 and 1980. The treatments were arranged in a randomized block design with four replications. 'Cayuse' oats (*Avena sativa* L.) and 'Steptoe' barley (*Hordeum vulgare* L.) were planted at 110 kg/ha.

In 1978, band application of 22 kg N/ha as AmS with P and Cu increased barley leaf Mn concentration and yield from 11 to 19 $\mu\text{g/g}$ and from 3240 to 5420 kg/ha, respectively; oat leaf Mn concentration and yield were increased from 15 to 19 $\mu\text{g/g}$ and from 1670 to 2560 kg/ha, respectively. Leaf Mn levels and yields were not increased by Ur

fertilization. When Mn was applied, leaf Mn levels and yields were similar regardless of N source. Band application of 45 kg N/ha as AmS with Mn, P, and Cu resulted in barley and oat yields of 6420 and 3060 kg/ha, respectively. Broadcast application of fertilizers did not increase leaf Mn concentration or yield. Similar results were obtained in 1979 and 1980. Responses to AmCl were similar to those from AmS while UP materials were intermediate in effectiveness between Ur and AmS. The Mn critical level in leaf samples collected at mid-tillering is 22 µg/g in barley and 29 µg/g in oats.

A series of laboratory experiments was designed to evaluate the effects of fertilizer application on the soil solution pH and Mn and P concentration. A centrifuge technique was developed which permitted the removal of an unaltered sample of the soil solution. Soil was collected adjacent to the field plots and placed in trays. Simulated fertilizer bands were added with fertilizer rates based on 25 cm row spacing. One week after fertilization the soil solution pH was decreased 0.82 and 0.54 units and increased 0.26 units by application of AmS, AmCl, and Ur, respectively, at 22 kg N/ha. When MCP was applied the pH was decreased from 8.12 to 7.01, 6.49, and 6.84 in the AmS, AmCl, and Ur bands, respectively. The soil solution Mn concentration increased from 0.04 to 0.18, 0.32, and 0.12 µg/ml one week after fertilization in the AmS, AmCl, and Ur bands, respectively, when MCP was applied. After four weeks the Mn levels were 0.25, 0.23, and 0.03 µg/ml in the AmS, AmCl, and Ur bands, respectively.

When Mn was included in fertilizer band with MCP the soil solution Mn concentration increased from 0.04 to 22.0, 16.6, and 26.5 µg/ml one week after fertilization in the AmS, AmCl, and Ur bands, respectively. The Mn levels in the AmS, AmCl, and Ur bands had fallen to 15.6, 12.1, and 4.9 µg/ml, respectively, after four weeks.

Soil solution P concentration was markedly increased by P fertilization but was consistently decreased by Mn application at two and four weeks after fertilization.

N Fertilizer Effects on Soil Solution
Mn and Mn Response of
Barley and Oats

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N FERTILIZER EFFECTS ON SOIL SOLUTION
Mn AND Mn RESPONSE OF BARLEY AND OATS

INTRODUCTION

Manganese (Mn) is an essential plant nutrient and substantial yield reductions can result from Mn deficiency. Mn deficiency is called 'grey speck' disease of oats (Gerretson, 1949) and is characterized by small chlorotic spots on the lower leaves which coalesce and become necrotic as the plant matures. In severe cases the entire lower foliage may senesce. Leaf Mn concentration is a more accurate criteria than visual symptoms for diagnosing Mn deficiency but critical levels for oats and barley have not been well established.

Soils of the Lower Klamath Lake are alkaline with organic matter contents ranging from 15 to 90%. These conditions are known to reduce the availability of Mn; unpublished data of Halvorsen (Klamath Experiment Station Annual Reports) confirmed that the potential existed for Mn deficiency on soils of Lower Klamath Lake. Increased rates of fertilizer application and better weed control along with higher yielding crop varieties have also combined to increase the possibility of Mn deficiency limiting yields.

Widespread Mn deficiency of oats was observed on Lower Klamath Lake during the 1977 growing season and oats yields were markedly reduced in many fields. Beginning in 1978, a series of field and laboratory experiments were conducted. Information generated by this research will be presented in three parts; each part will be submitted for publication in a refereed technical journal.

Chapter One is entitled "Effects of N fertilization on Mn concentration and yield of barley and oats" and reports the results of three years of field experiments. The objectives of this research were to

1. evaluate the effects of band application of different N sources with and without Mn on the Mn concentration and yield of barley and oats,
2. compare the effects of band versus broadcast application of fertilizers on the Mn concentration and yield of barley

and oats, and

3. determine the Mn critical level of barley and oats.

Chapter Two is entitled "Effects of fertilization on soil solution pH and Mn and P concentration". The objectives of the laboratory research were to evaluate the effects of band application of different N sources with and without Mn on the soil solution pH and Mn and P concentration in the fertilizer band and 2.5 cm from the fertilizer band.

Chapter Three fully describes and discusses the soil solution removal technique developed during the course of the laboratory experiment. This information will be submitted as a brief article entitled "Soil solution removal by centrifugation".

LITERATURE REVIEW

Mn in Plant Physiology

Manganese performs several specific and nonspecific biochemical functions in plants. It is a cofactor of many enzymes and may replace magnesium (Mg) in some enzymes including glucose kinase, hexokinase, phosphoglucokinase, phosphoglucomutase, and adenosine kinase without altering the activity of the enzyme (Nason and McElroy, 1963). Plants possessing the aspartate-type C_4 metabolism have an absolute requirement for Mn which cannot be satisfied by Mg while malate-type C_4 plants do not have this absolute requirement for Mn (Hatch and Kagawa, 1974). Manganese is also a cofactor for indole-acetic acid (IAA) oxidase (Mumford et al., 1962) and Mn deficient cotton plants have been observed to have unusually high IAA activity levels (Taylor et al., 1968).

Photosynthesis has an absolute requirement for Mn but the exact role of Mn is unclear (Bishop, 1971). Oats suffering from Mn deficiency had reduced rates of CO_2 assimilation which occurred regardless of the presence of visual symptoms (Gerretson, 1949; 1950). The activity of chloroplasts isolated from Mn deficient spinach plants was also reduced (Spencer and Possingham, 1960).

The role of Mn as the active agent in the photolysis of water was first proposed by Gerretson (1950). The photolysis of water releases electrons which enter the electron transport system and, ultimately, result in the production of ATP and reduced NADP (Gregory, 1977). This process, called photoreduction, was unaffected in Mn deficient algae (Kessler, 1957) and isolated chloroplasts (Spencer and Possingham, 1961) provided suitable electron donors other than water were provided. In both cases oxygen evolution was reduced. The photolysis of water occurs in photosystem II; each photosystem II complex has three Mn atoms associated with it (Cheniae and Martin, 1970). Two of the Mn atoms can be removed relatively easily abolishing oxygen evolution but photo-oxidation of other electron donors is unaffected. Complete removal of Mn results in the loss of all photoreduction. Bishop (1971) speculated that Mn undergoes valance changes during the photolysis of water but specific evidence is lacking (Gregory, 1977).

Reduced rates of chlorophyll synthesis also result from Mn deficiency (Bishop, 1928). Chloroplasts of Mn deficient spinach plants are abnormally structured while other organelles are unaffected (Possingham et al., 1964). The stroma proliferates and the number of intergrana connections is reduced. As the Mn deficiency worsens, the entire lamella system becomes disorganized.

The critical level for a nutrient is the minimum concentration required for optimum plant growth with all other nutrients present in sufficient concentrations. It is important to specify plant part when determining critical levels; for example, 50-60% of the Mn taken up by grain sorghum was found in the leaf blades and sheaths while only 5% was found in the heads (Jacques et al., 1975). The Mn concentration in corn leaf blades is greater along the margin than in the midrib or petiole (Jones, 1970). Stage of maturity also affects the critical level. The Mn concentration in grain sorghum leaves increased throughout the growing season (Jacques et al., 1975) while the Mn concentration in corn leaf blades tended to decrease during the growing season (Gorlsine et al., 1965).

Species differences are also important. Nyborg (1970), ranking small grains in sensitivity to Mn deficiency, reported oats > wheat > barley. He attributed the greater sensitivity of oats to lack of uptake and not a higher plant requirement.

The Mn critical level for a number of crops is around 20 ug/g measured in leaf tissue although some workers have used whole plant samples. Gheesling and Perkins (1970) suggest a critical level of 15 ug/g for cotton leaf blades while Ohki (1974; 1975) suggests a critical level of only 10 ug/g for cotton leaves. Hammes and Berger (1960) place the Mn critical level for oat flag leaves collected at the boot stage at 25-30 ug/g. Reporting on the results of 15 years of research in Illinois, Melsted et al. (1969) suggest Mn critical levels for corn leaves, whole wheat plants, soybean leaves, and alfalfa stem cuttings as 15, 30, 20, and 25 ug/g, respectively.

Forms of Mn in the Soil System

The chemistry of Mn in soil systems is complex; Mn exists in both primary and secondary minerals as well as in complexes with organic matter. Manganese has six oxidation states: +1, +2, +3, +4, +6, +7; however, Mn exhibits only +2, +3, and +4 states in naturally occurring minerals (Krauskopf, 1972). Commonly occurring minerals containing Mn are pyrolusite (MnO_2), hausmannite (Mn_3O_4), manganite (MnOOH), baumanite ($(\text{Mn}, \text{Si})_2\text{O}_3$), rhodochrosite (MnCO_3) and rhodonite (MnSiO_3).

At redox potentials commonly found in soils, Mn forms many complex secondary minerals and may exhibit two or three oxidation states in one mineral. Pure oxides or hydroxides of Mn are rare in soil systems. In a study of 26 clay-sized Mn nodules from different Australian soils Taylor et al. (1964) found 10 nodules were lithiophorite, 10 were berne-site, 3 were hollandite and one each were todokorite, pyrolusite, and lithiophorite/hollandite; only pyrolusite is a pure Mn oxide. Lithiophorite ($\text{Li}_2\text{Al}_8(\text{Mn}^{2+}, \text{Co}, \text{Ni})_2\text{Mn}^{4+}_{10}\text{O}_{35} \cdot 14\text{H}_2\text{O}$) was found in acid soil horizons while berne-site ($(\text{Ca}, \text{Mg}, \text{Na}_2, \text{K}_2)_x \text{Mn}^{4+}\text{Mn}^{2+}(\text{O}, \text{OH})_2$) was found in alkaline soil horizons.

In secondary minerals Mn is commonly found associated with iron (Fe). The behavior of both Mn and Fe in mono-elemental systems closely follows that predicted by Eh-pH relationships (Collins and Buol, 1970; Hem, 1963a, 1963b) while mixed precipitates of Mn and Fe occur at Eh-pH conditions under which Mn alone would not precipitate. Manganese removal from solution occurs at pH values as low as 6.5 if Fe is present (Hem, 1963a, 1963b; Mehlich, 1957) but precipitation from a pure Mn system does not begin until the pH is above 8.5 (Mehlich, 1957). The Fe precipitate which forms initially is thought to remove Mn from solution by occlusion within the precipitate as well as adsorption on the precipitate (Collins and Buol, 1970; Hem, 1963a, 1963b; Mehlich, 1957).

Geering et al. (1969) studied the soil solution collected from soils in New York, North Carolina, Colorado, and Washington states. The soil solution Mn concentration was generally less than 1 $\mu\text{g}/\text{ml}$ but one soil solution had 13 $\mu\text{g Mn}/\text{ml}$. The complexed Mn ranged from 39 to 99% of the total Mn in solution but most soils had more than 80% of the

Mn complexed. No attempt was made to identify the specific complexing agent.

Mn Availability

The average Mn concentration in granite, basalt, and sedimentary rocks is 400, 1500, and 850-1100 ppm, respectively (Taylor, 1964; Turekian and Wadepohl, 1961); the average Mn concentration in the earth's crust is 950 ppm. The total Mn concentration in soils in the United States generally ranges from 0.001 to 1.27% although some tropical soils may have as much as 15% Mn (Robinson, 1929). The total uptake by crops is low and usually ranges from 500 to 1000 gm Mn/ha (Schachtschabel, 1955, as cited by Mengel and Kirkby, 1979). Thus, in most soils, the availability of Mn is of far greater importance than the total amount of Mn present.

Three major factors influencing the availability of Mn are redox potential, pH, and microbiological activity. The redox potential, or Eh, is a quantitative measure of the oxidizing/reducing capability of the soil. A positive redox potential is indicative of oxidizing conditions while a negative redox potential is indicative of reducing conditions in the soil. An element will be reduced when the redox potential of the soil is less than the redox potential of that element (Bohn et al., 1979).

A convenient method of illustrating the effects of Eh and pH on the soluble species and controlling solid phases is the stability field diagram. A stability field diagram for Mn in an aqueous solution in contact with the atmosphere was developed by Hem (1963a) and is shown in Fig. 1. The solid lines represent the boundaries when the Mn activity is 0.01 $\mu\text{g/ml}$ or 1.8×10^{-7} molar. The dashed line represents the boundaries where the Mn activity is 100 $\mu\text{g/ml}$ or 1.8×10^{-3} molar. The boundaries represent the maximum Mn activity which can occur at given Eh-pH conditions. For example, at pH 7 and an Eh value of +0.60 volts the maximum Mn activity which can occur is 0.01 $\mu\text{g/ml}$.

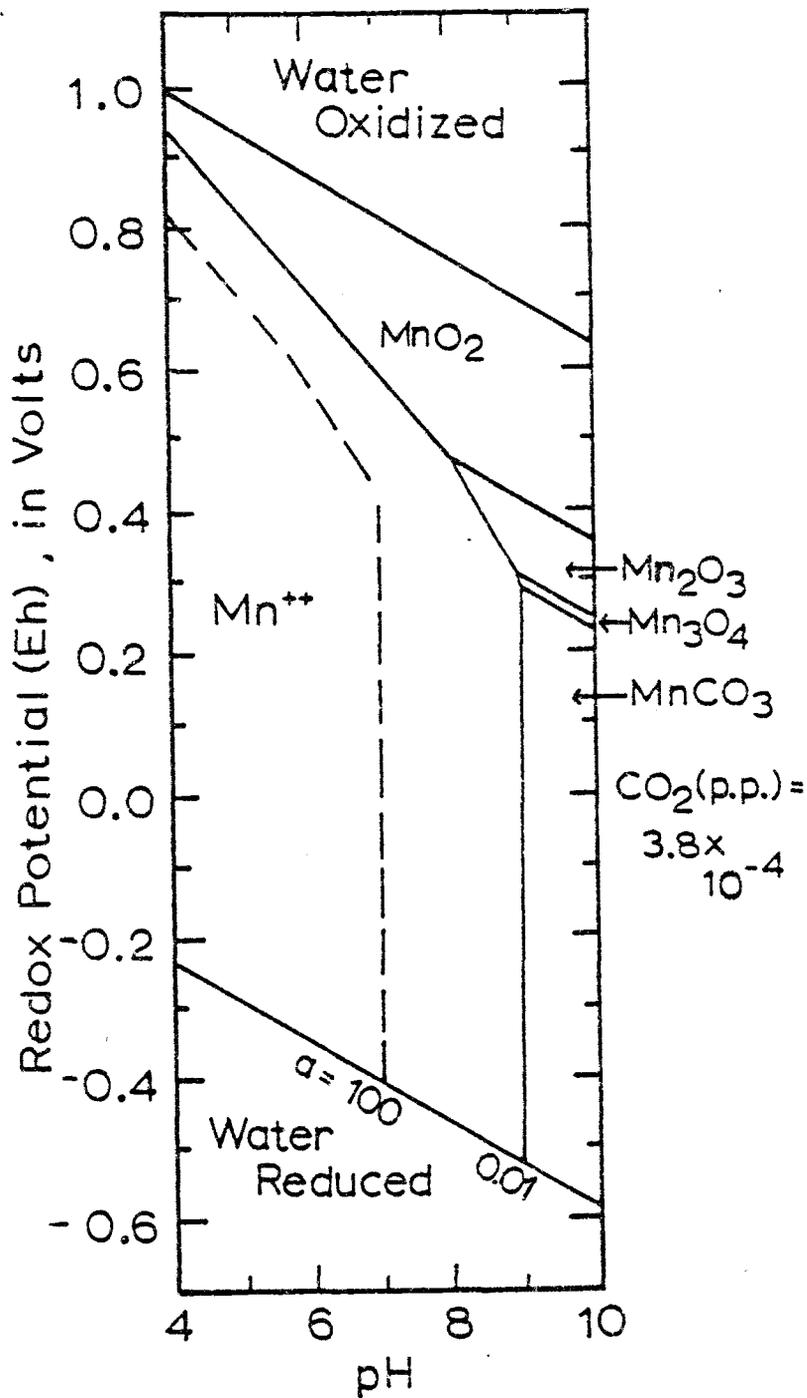


Fig. 1. Stability fields of Mn species in an aqueous environment for the pH range 4.0 to 10.0 and at a constant partial pressure of CO₂ = 3.8 × 10⁻⁴ atmosphere, free of any other interfering ions. (Hem, 1963a). Dissolved Mn at 0.01 and 100 ug/ml.

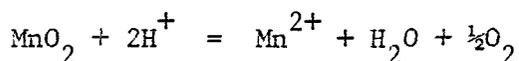
Certain assumptions are made in constructing stability field diagrams and these must be taken into consideration when utilizing them. The system is assumed to be in equilibrium and the controlling solid phases in their standard states. Data on the kinetics of various reactions involving Mn in the soil system are limited; they are slower than similar reactions involving Fe but are generally assumed to reach equilibrium in natural systems (Hem, 1963a). Solids in the standard state are assumed to be pure, perfectly crystalline compounds but Mn is known to exist in compounds of mixed composition and mineralogy (Taylor et al., 1964). The stability product of these compounds may differ markedly from the pure compounds.

The "activity" of the dissolved species is used rather than the concentration. These are nearly identical at low concentration and ionic strength but differ markedly as the concentration and ionic strength increase (Daniels and Alberty, 1975). The activity coefficient is used to convert the concentration to activity and may be estimated using the Debye-Huckel theory or the Davies equation (Stumm and Morgan, 1970).

Stability-field diagrams are usually calculated assuming 25°C and 1 atm pressure but may be used between 10 and 40°C and up to a several atm pressure without significant errors. For ease of calculation the presence of competing ions and biological activity are usually ignored.

The deviations from ideality that occur in natural soil systems generally cannot be satisfactorily evaluated. Thus, stability field diagrams have been of limited value of predicting soluble Mn levels in the soil solution (Bohn, 1970; Geering et al., 1969). They have proven useful in predicting changes that occur in flooded soils (Ponnamperuma et al., 1967).

Pyrolusite (MnO_2) is a very stable Mn mineral and is commonly considered the solid phase controlling Mn solubility (Lindsey, 1972). The solubility of Mn^{2+} is given by the equation:



The equilibrium constant for this reaction was calculated (Robie and Waldbaum, 1968) and at 0.20 atm O_2 $\log K_{\rightarrow 0} = 0.92$. The activity of Mn^{2+} and other soluble Mn species as developed by Lindsey (1972) is

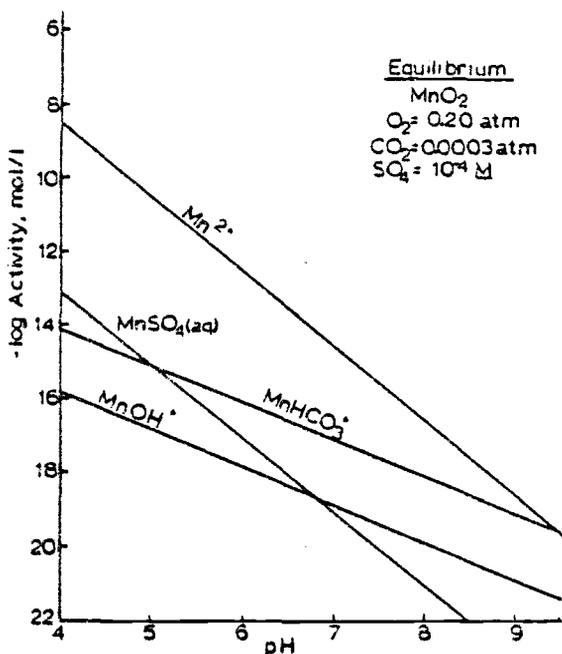


Fig. 2. Soluble Mn species in solution in equilibrium with MnO_2 . (Lindsey, 1972).

shown in Fig. 2. The activity of Mn^{2+} is considerably greater than that of other Mn species present particularly at low pH. Manganese concentration is seen to decrease 100-fold for each one unit pH increase.

The solubility of several Mn minerals is shown in Fig. 3 (Lindsey, 1972); MnO_2 is clearly more stable than the other minerals. Information on the actual Mn concentration in the soil solution is limited. Data from Bohn (1970) and Geering et al. (1969) show that Mn concentration in the soil solution is pH-dependent and intermediate between MnO_2 and other Mn minerals. The discrepancy is attributed to uncertainty about the controlling solid phase as well as microbial activity.

Although it is a major factor controlling Mn availability, altering the redox potential of soils per se, is beyond the scope of present soil management capabilities. The redox potential of soils in situ is most often altered by changing the aeration through waterlogging or flooding. The primary management purpose of flooding soils is generally to control weeds or reduce wind erosion and subsidence on organic soils. Well aerated soils tend to have oxidizing conditions while poorly

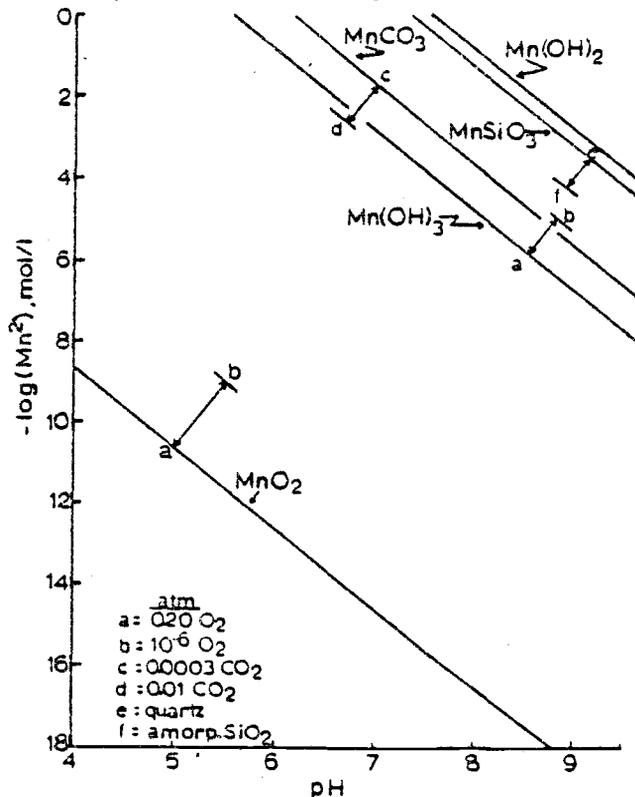


Fig. 3. The solubility of various Mn(II) and Mn(III) minerals compared to that of MnO₂. (Lindsey, 1972).

aerated soils tend to have reducing conditions (Pearsall, 1950). Many reports in the literature have shown that flooding usually results in increased Mn availability (Graven et al., 1965; Leeper, 1947; Olumu and Racz, 1974; Pearsall, 1950). The literature also contains many reports that increasing pH results in lowered availability of Mn and vice versa (Christensen et al., 1950; Graven et al., 1965; Page, 1962; Randall et al., 1976).

Gotoh and Patrick (1972) studied Mn in the soil under controlled Eh and pH conditions and divided total Mn into three fractions: (1) water soluble plus exchangeable, (2) reducible, and (3) residual. Decreasing the Eh converted reducible to water soluble plus exchangeable Mn at all pH levels. A low pH also increased the conversion from reducible to water soluble plus exchangeable Mn. A redox potential of

+0.2 to +0.3 volts was necessary for conversion of reducible to water soluble plus exchangeable Mn at pH 6, 7, and 8. These values are in good agreement with those of Takai (1961) who found Mn reduction to occur at pH 6.1 and redox potential of +0.14 to +0.32 volts and Patrick and Turner (1968) who found the conversion of easily reducible to exchangeable Mn occurred at Eh of +0.40 volts corrected to pH 7.

Incorporation of easily decomposed organic material into soil commonly results in increased Mn availability (Christensen et al., 1950; Sanchez and Kamprath, 1959; Fujimoto and Sherman, 1948). Organic matter was found to lower the redox potential from +0.5 volts to as low as 0 volts leading to increased concentration of soluble Mn (Meek et al., 1968).

Microbial activity also plays an important role in Mn availability. An associative action between two organisms, one a Cornybacterium and the other a Chromobacterium or Flavobacterium, has been shown to oxidize Mn thus reducing its availability (Bromfield and Skerman, 1950). On the other hand some organisms can utilize higher oxides of Mn, such as MnO_2 , as terminal electron acceptors when gaseous oxygen is unavailable (Hochster and Quastel, 1952). This mechanism is thought to be responsible for most reduction of Mn that occurs under anaerobic conditions. Sulfur oxidation by Thiobacillus thiooxidans reduced the pH and increased Mn availability (Vavra and Frederick, 1952). The effect was pH-independent since acidification of the growth media with H_2SO_4 resulted in less availability of Mn at the same pH. It was thought that MnO_2 was utilized as an electron acceptor resulting in increased levels of Mn^{2+} .

Timonin (1946) found that an oat variety susceptible to Mn deficiency harbored a greater number of Mn-oxidizing bacteria in its rhizosphere than a resistant variety. No attempt was made to identify the bacteria.

Fertilizers

Most soils contain sufficient total Mn for optimum plant growth but the pH, redox potential, or organic matter content of the soils are such that only a fraction of the Mn is in a form available for plant uptake.

Fertilizers are applied to increase the quantity of available Mn by (1) supplying additional Mn^{2+} in forms such as $MnSO_4$ or MnO or (2) altering the pH or redox conditions in the soil to enhance the availability of native Mn.

The most common inorganic Mn fertilizer is $MnSO_4$ (Murphy and Walsh, 1972) although MnO is also used as a Mn source. Both $MnSO_4$ and MnO were equally effective at increasing Mn concentration and yield of onions and corn when banded with the N-P-K fertilizer (Shepherd et al., 1960) but $MnSO_4$ was more effective at increasing Mn concentration in soybeans than MnO when banded 3.75 cm below and 3.75 cm to the side of the seed (Mederski et al., 1960). Band application of Mn fertilizers has been superior to broadcast application (Mortvedt and Giordano, 1975; Randall et al., 1975; Voth and Christenson, 1980) because soil-fertilizer contact is minimized and oxidation of Mn^{2+} to less available forms is slowed.

In contrast with other micronutrients which can be successfully applied in chelated form (Murphy and Walsh, 1972), Mn-EDTA is generally an ineffective Mn fertilizer. The Mn in the chelate is replaced in less than 24 hours by other cations in the soil solution which have a higher stability constant than Mn (Norvell and Lindsey, 1969). Application of Mn-EDTA has accentuated Mn deficiencies in soybeans (Randall and Schulte, 1971) and navy beans (Knezek and Greinert, 1971). Iron replaced Mn in the chelate which increased Fe uptake and further reduced Mn uptake.

Application of acid forming P or N fertilizers has been shown to increase Mn availability and uptake. The pH surrounding a granule of $Ca(H_2PO_4)_2$ (MCP) was reduced from 5.5 to 2.1 resulting in a marked increase in soluble Mn (Lindsey and Stephenson, 1959a, 1959b; Lehr et al., 1959). As the wetting front moved outward into the soil, the pH rose and Mn slowly precipitated as a poorly crystalline, somewhat soluble Mn-phosphate. Manganese concentration and uptake by sugarbeet seedlings was markedly increased by band application of MCP (Voth and Christenson, 1980). Application of superphosphate was observed to increase Mn concentration in a 5 x 5 factorial lime x P experiment (Page et al., 1963); liming reduced Mn uptake at each P level. Unfortunately, the method of fertilizer application was not described. Band application of superphosphate with $MnSO_4$ resulted in greater Mn concentration in oats and

barley than when MnSO_4 was applied alone.

Numerous authors have reported that band application of acid forming N fertilizers increased Mn uptake and yield (Hammes and Berger, 1960; Jackson and Carter, 1976; Mederski et al., 1960; Sims and Atkinson, 1974). The increased acidity concentrated in a relatively small volume of soil increases Mn availability and slows the oxidation of Mn to less available forms. Decreasing the pH of soils has also been shown to enhance the conversion of reducible Mn to water soluble plus exchangeable Mn (Gotoh and Patrick, 1972).

In studying the potential for acid disposal on calcareous soils, Ryan et al. (1974) found that application of H_2SO_4 at 25 and 50% of the acid titratable basicity initially depressed pH values and elevated water soluble and DTPA-extractable Mn. The pH rapidly returned to pre-treatment levels but the Mn concentrations remained elevated at least four weeks. Application of sulfur (S) flour has corrected Mn deficiency on alkaline muck soils if the pH was reduced below 7.0 (Sherman and Harmer, 1941). Sulfur oxidation has also been shown to increase Mn availability in growth media (Vavra and Frederick, 1952). The effect was independent of pH and assumed to be due to the utilization of MnO_2 as an electron acceptor.

The effects of Cl on the availability and uptake of Mn have been reported by numerous authors. Application of 9 metric tons of CaCl_2 /ha increased exchangeable Mn but application of 9 metric tons of KCl/ha had little effect on exchangeable Mn (Fujimoto and Sherman, 1948). The soil used in this experiment had been steam sterilized and this is known to markedly increase exchangeable Mn; thus the treatment differences may have been masked by initially large amounts of exchangeable Mn. Stewart and Leonard (1963) found that 613 gm of Mn as MnSO_4 applied to the soil around citrus trees increased leaf Mn concentration from 20 to 129 $\mu\text{g/g}$ on an acid soil and from 14 to 25 $\mu\text{g/g}$ on an alkaline soil. When 1360 gm of CaCl_2 was applied with the Mn, leaf Mn concentration was increased to 1613 $\mu\text{g/g}$ on the acid soil and 129 $\mu\text{g/g}$ on the alkaline soil; Mn toxicity was suspected in the plants growing on the acid soil.

Application of KCl or CaCl_2 was found to increase leaf Mn levels in both bush beans and sweet corn grown on an acid soil (Jackson et al.,

1966). Application of lime raised the soil pH from 5.0 to 6.5 and reduced the leaf Mn concentration in all cases. In a companion study, Westermann et al. (1971) found that KCl application increased $\text{Mg}(\text{NO}_3)_2$ - extractable Mn more than KNO_3 or K_2SO_4 on both sterile and non-sterile soils. They suggested that Cl increased extractable Mn through a redox couple; the following reaction:



was chosen as the most thermodynamically feasible under the conditions of the study.

Chloride may also increase Mn availability by altering the diffusion rate through the soil solution. Application of MCP is known to increase the concentration of Mn in the soil solution (Lindsey and Stephenson, 1959a, 1959b); application NH_4Cl or KCl with MCP was found to increase both the level of Mn found in the soil solution and the rate of diffusion of Mn away from the fertilizer (Hamilton and Lathwell, 1965). The effect was independent of pH since application of NH_4Cl or KCl increased the pH surrounding the MCP granula.

Fertilizer application may also increase Mn availability through alteration of the microbial population. Application of inorganic N fertilizers such as $\text{Ca}(\text{NO}_3)_2$ or $(\text{NH}_4)_2\text{SO}_4$ retarded oxidation of Mn by depressing the Mn-oxidizing organisms (Timonin, 1950; 1965). On the other hand, application of organic N sources such as asparagine or urea increased Mn oxidation by enhancing the activity of the Mn oxidizing organisms.

Mn Uptake

Manganese is taken up as Mn^{2+} in a metabolic process requiring the expenditure of energy. Manganese concentration in tomato stem exudate was found to be two to five times ambient solution Mn concentration implying active uptake against a concentration gradient (Tiffin, 1967). Moore (1972) reviewed the literature dealing with active ion uptake and concluded that the best experimental evidence favored the carrier theory of ion uptake. The basic aspects of Mn uptake over time by five-day

old barley roots were found to be similar to other metabolically absorbed cations (Maas et al., 1968). There was an initial rapid uptake phase thought to be non-metabolic followed by a slower, metabolic uptake phase. The metabolic phase of the uptake could be inhibited by chemicals which uncouple oxidative phosphorylation such as dinitrophenol or azide (Maas et al., 1969). Cold temperatures also reduced active Mn uptake (Bowen, 1969). Manganese uptake by four-week old oat roots was also biphasic but both phases were non-metabolic (Page and Dainty, 1964). However, the roots they used were stunted and possibly damaged or diseased, thus their results are open to question.

Low pH in the ambient solution reduced Mn uptake by barley roots (Maas et al., 1969; Munns et al., 1963b) and optimum Mn uptake occurred around pH 6 (Bowen, 1969; Maas et al., 1968). Calcium (Ca) has been shown to overcome the inhibition of Mn uptake at low pH (Bowen, 1969). Magnesium (Mg) or Mg plus Ca inhibited Mn uptake but Ca alone slightly enhanced Mn uptake (Maas et al., 1969). These results are consistent with cation induced conformational changes in a carrier molecule (Maas et al., 1969).

The form of nitrogen (N) supplied in the nutrient solution also affects Mn uptake. Nitrate-N in the nutrient solution was found to favor Mn uptake while ammonium-N depressed Mn uptake (Sideris and Young, 1949). Mengel and Kirkby (1979) attribute this difference to plant maintenance of the cation-anion balance.

Munns et al. (1963a, 1963b) using ^{54}Mn , separated root Mn into three categories: replaceable, labile, and non-labile. Replaceable Mn was in the root free space; it could be rapidly washed out with CaCl_2 . Labile Mn was readily translocated to the shoots while non-labile Mn was translocated to the shoots slowly unless solution Mn was depleted. Labile Mn equilibrated more rapidly than non-labile Mn with the solution Mn.

Using electrophoresis, Tiffin (1967) showed that Mn is translocated as the uncomplexed divalent cation and that translocation occurs in the xylem. Some foliar applied Mn is translocated via the phloem but foliar applied Mn is only partially mobile within the plant (Wittwer and Teubner, 1959).

CHAPTER ONE

EFFECTS OF N FERTILIZATION ON Mn CONCENTRATION
AND YIELD OF BARLEY AND OATS

INTRODUCTION

Lower Klamath Lake was drained about 1920 and agricultural production began soon after. Soils on the lakebed are alkaline (pH 7.5 to 9.0) with organic matter contents ranging from 15 to 90% depending on the parent material and past management practices. In a review of early micronutrient research, Hodgson (1963) presented evidence that these two factors are major causes of manganese (Mn) deficiencies. Unpublished data (Halvorsen, Klamath Experiment Station Annual Reports) has shown that Cu, Zn, and Mn deficiencies can limit production of cereal crops on soils in the Lower Klamath Lake.

During the 1977 growing season, oats grown on the Lower Klamath Lake had symptoms characteristic of "grey speck" disease or Mn deficiency (Gerretson, 1949). Leaf samples were collected and plant analysis revealed Mn concentrations ranging from 8 to 15 $\mu\text{g/g}$. This is well below the critical level of 30 $\mu\text{g/g}$ suggested by Hammes and Berger (1960) in oat leaves collected at the boot stage.

Application of acid forming nitrogen (N) or phosphorus (P) fertilizers has been shown to increase the availability and uptake of Mn. The pH in a band of monocalcium phosphate (MCP) is less than pH 2 (Lindsey and Stephenson, 1959a) and as the wetting front moves out from the band, Mn is dissolved (Lehr et al., 1959; Lindsey and Stephenson, 1959a, 1959b). As the wetting front advances into the soil the pH rises and Mn availability is reduced.

In an experiment conducted in Klamath County on calcareous mineral soils Jackson and Carter (1976) found that band application of ammonium sulfate (AmS) and MCP without Mn increased both Mn concentration in potato petioles and tuber yields more than broadcast application of AmS and MCP with a band application of Mn. Band application of AmS plus Mn or MCP plus Mn increased Mn concentration in the petioles but the highest Mn concentration resulted from band application of all three materials--AmS, MCP, and Mn.

Band application of AmS plus MCP resulted in greater H_3PO_4 -extractable Mn as well as larger Mn concentrations in sugarbeet seedlings compared to band application of urea plus MCP (Voth and Christenson, 1980). With either N source, both the H_3PO_4 -extractable Mn and the Mn concentration in sugarbeet seedlings were greater when the MCP was banded rather than mixed with the soil.

Application of chloride (Cl) has also been shown to increase the availability and uptake of Mn. Application of Cl as KCl or $CaCl_2$ increased the leaf Mn concentration in both bush beans and sweet corn grown on acid soils; the increased uptake was such that Mn toxicity was evident on the bush beans (Jackson et al., 1966). Stewart and Leonard (1963) also found $CaCl_2$ application resulted in large increases in citrus leaf Mn levels. Application of KCl resulted in greater increases in $Mg(NO_3)_2$ -extractable Mn than did K_2SO_4 (Westermann et al., 1971). The increase in extractable Mn was attributed to an oxidation-reduction couple involving Mn and Cl.

The objectives of this research were to (1) evaluate the effects of band application of different N sources with and without Mn on the Mn concentration and yield of barley and oats, (2) compare the effects of band versus broadcast application of fertilizers on the Mn concentration and yield of barley and oats, and (3) determine the Mn critical level for barley and oats.

MATERIALS AND METHODS

Experiments were established on 23 and 24 May 1978 at Tulana Farm and Henzel Farm south field and on 3 and 4 May 1979, and 14 and 15 May 1980 at Henzel Farm north and south fields. Within each field the experiments were moved each year to prevent residual carryover of nutrient variables applied. Manganese deficiency symptoms on oats had been observed at each location in previous years. Chemical analysis of soil samples (Table 1) was performed using the procedures of Oregon State University Soil Testing Laboratory (Berg and Gardner, 1978). Yield responses to P fertilization are common on soils of Lower Klamath Lake but response to K fertilization has not been observed. All fields had less than 3.5 mmhos/cm conductivity except Henzel Farm north field; however, barley is relatively salt tolerant and no yield reduction would be expected at 7.3 mmhos/cm conductivity (Bernstein, 1970).

Table 1.1. Selected chemical properties of soils at sites used.

Location	pH	P	K	Ca	Mg	Na	Salt	Organic matter	DTPA Mn
		---ppm---		--meq/100	gm--	mmhos/cm		%	ppm
Tulana Farm	8.3	20	324	51	20	3.7	1.6	19	9.44
Henzel Farm									
North	7.8	39	464	48	25	10.7	7.3	17	0.84
South	7.6	9	355	48	23	3.7	3.4	18	0.88

The soil at all locations was classified as a Tulana variant; the morphology was that of the Tulana series (medial, nonacid, mesic, mollic, andequept), but the underlying horizons were moderately alkaline as in the Algoma series (medial over sandy or sandy skeletal, mixed [calcareous], mesic, mollic, halaquept) which is also common in the area.

'Cayuse' oats (Avena sativa L.) were planted at 110 kg/ha at the Tulana Farm plots in 1978 and at the Henzel Farm south field plots in 1978 and 1979; 'Cayuse' oats are known to be a Mn-inefficient variety (Murray and Benson, 1976) and thus are an effective indicator crop. 'Steptoe' barley (Hordeum vulgare L.) was planted at 110 kg/ha at the Henzel Farm south field plots in 1978 and at the north and south field plots in 1979 and 1980. All locations were either rained on or irrigated within 24 hours after planting and received adequate moisture, either rainfall or irrigation, throughout the growing season.

Nitrogen was applied at 0, 22, or 45 kg/ha as $(\text{NH}_4)_2\text{SO}_4$ (AmS), NH_4Cl (AmCl), urea (Ur), granular urea-phosphate (UP 17-44), a urea-phosphoric acid solution (UP pH 3), or a urea-phosphate solution made from the granular urea-phosphate (UP). All solutions were 6% N and 7% P. Phosphorus was applied at 19 kg/ha as MCP or at 25 kg/ha in the urea-phosphate solutions and Mn was applied at 0 or 5.6 kg/ha as MnSO_4 . Copper (Cu) was applied at 0 or 2.2 kg/ha as CuSO_4 banded with the seed at planting in 1978. In 1979 and 1980 Cu was applied at 5.6 kg/ha as a spray before planting. The granular N, P, and Mn fertilizers were either banded with the seed at planting or broadcast before planting. The urea phosphate solutions were applied in a stream with the seed at planting. All fertilizer materials except AmCl were supplied by the TVA. Fertilizer treatments were arranged in a randomized block design with four replications; individual plots were 1.5 m wide and 6.3 m long. Plots consisted of six rows with 25 cm between rows; the center four rows were harvested using a plot combine on 20 Sept. 1978, 19 Sept. 1979 and 17 Sept. 1980.

Leaf samples consisting of the upper half of the youngest fully expanded leaf were collected when the plants were at early- to mid-tillering on 6 July 1978, 5 July 1979, and 23 June 1980. Leaf samples were also collected on 19 June 1979 and 10 June 1980 when the plants were in the 3-4 leaf stage. Samples were dried at 70°C in a forced draft oven, ground to pass a 20 mesh screen, and stored in coin envelopes. One-half gram samples were digested in $\text{HNO}_3:\text{HClO}_4$

and Mn and Cu were measured using a Perkin-Elmer Model 4000 atomic absorption spectrophotometer. Samples collected in 1978 were analyzed for P using the vanadomolybdophosphoric acid method (Jackson, 1958). Samples collected in 1979 and 1980 were analyzed for P using a Scientific Instruments Model CFA 200 Auto-Analyzer. Standard statistical procedures were used to analyze the data.

RESULTS

1978 Growing Season

The leaf Mn, Cu, and P concentration and yield of barley grown at Henzel Farm south field and oats grown at Tulana Farm and Henzel Farm south field are shown in Tables 2, 3, and 4, respectively. The same treatments were applied in each experiment and the results will be discussed concurrently.

All fertilizer treatments were band applied with the seed at planting unless otherwise specified. Application of 22 or 45 kg N/ha as AmS with P and Cu (trts 2 and 4) increased leaf Mn levels at all locations and increased barley yields at Henzel Farm south field and oat yields at Tulana Farm. A severe weed infestation limited oat production at Henzel Farm south field, particularly when Mn deficiency resulted in reduced seedling vigor. Because of the limited yield data statistical analysis was not performed on data from the oat experiment. In contrast to AmS, application of 22 kg N/ha as Ur with P and Cu (trt 3) was ineffective at increasing either leaf Mn levels or yield. When Mn was included in the fertilizer band, similar leaf Mn levels and yields resulted at 22 kg N/ha with both Ur and AmS. Manganese fertilization increased mean leaf Mn levels from 18 to 26 $\mu\text{g/g}$ in oats at Tulana Farm, and from 17 to 30 $\mu\text{g/g}$ in oats at Henzel Farm south field. These increases were significant at the 5% probability level. Application of Mn with 45 kg N/ha (trt 7) further increased the barley yield as well as increasing oat leaf Mn levels. Broadcast application of fertilizer (trt 14) was ineffective at increasing either leaf Mn concentration or yields.

Leaf Cu levels were above the critical level of 4.0 $\mu\text{g/g}$ suggested by Kresge (1977) and yield increases from Cu application were not evident. The mean leaf Cu concentration was increased from 5 to 5.6 $\mu\text{g/g}$ in oats at Tulana Farm and from 6.4 to 7.6 $\mu\text{g/g}$ in oats at Henzel Farm south field by Cu fertilization.

Table 1.2. Leaf Mn, Cu, and P concentration and yield of barley grown at Henzel Farm south field, 1978.

No.	Treatments				Concentration			Yield kg/ha
	N [†]	P [‡]	Mn [§]	Cu [¶]	P	Mn	Cu	
	-----kg/ha-----				%	---µg/g---		
1	---	--	---	---	0.46	11	7.8	3240
2	22 AmS	19	---	2.2	0.47	19	---	5420
3	22 Ur	19	---	2.2	0.49	12	---	3520
4	45 AmS	19	---	2.2	0.47	18	---	5360
5	22 AmS	19	5.6	2.2	0.44	17	7.3	5280
6	22 Ur	19	5.6	2.2	0.45	17	7.6	5060
7	45 AmS	19	5.6	2.2	0.46	20	8.1	6420
8	22 AmS	--	5.6	---	0.42	20	---	4760
9	22 Ur	--	5.6	---	0.45	17	---	4960
10	45 AmS	--	5.6	---	0.41	21	---	5160
11	22 AmS	19	5.6	---	0.47	18	7.3	5720
12	22 Ur	19	5.6	---	0.45	17	7.3	6630
13	45 AmS	19	5.6	---	0.42	25	7.1	5510
14#	45 AmS	19	---	2.2	0.45	11	---	2960
	LSD _(0.05)				0.04	3	n.s.	1450

[†]AmS = $(\text{NH}_4)_2\text{SO}_4$ and Ur = urea.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

[§]Mn applied as MnSO_4 .

[¶]Cu applied as CuSO_4 .

[#]Broadcast before planting.

Table 1.3. Leaf Mn, Cu, and P concentration and yield of oats grown at Tulana Farm, 1978.

No.	Treatments				Concentration			Yield
	N [†]	P [‡]	Mn [§]	Cu [¶]	P	Mn	Cu	
	-----kg/ha-----				%	----µg/g----		kg/ha
1	---	--	---	---	0.30	15	6.1	1670
2	22 AmS	19	---	2.2	0.26	19	---	2560
3	22 Ur	19	---	2.2	0.30	16	---	1810
4	45 AmS	19	---	2.2	0.30	20	---	2600
5	22 AmS	19	5.6	2.2	0.29	21	5.8	3000
6	22 Ur	19	5.6	2.2	0.28	30	5.1	2930
7	45 AmS	19	5.6	2.2	0.27	27	6.1	3060
8	22 AmS	--	5.6	---	0.26	22	---	2350
9	22 Ur	--	5.6	---	0.25	23	---	1950
10	45 AmS	--	5.6	---	0.23	25	---	2600
11	22 AmS	19	5.6	---	0.24	33	4.8	3150
12	22 Ur	19	5.6	---	0.24	22	4.8	2940
13	45 AmS	19	5.6	---	0.26	35	5.4	3250
14#	45 AmS	19	---	2.2	0.30	16	---	1780
	LSD _(0.05)				0.05	6	0.7	270

[†]AmS = $(\text{NH}_4)_2\text{SO}_4$ and Ur = urea.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

[§]Mn applied as MnSO_4 .

[¶]Cu applied as CuSO_4 .

[#]Broadcast before planting.

Table 1.4. Leaf Mn, Cu, and P concentration and yield of oats grown at Henzel Farm south field, 1978.

No.	Treatments				Concentration			Yield kg/ha
	N [†]	P [‡]	Mn [§]	Cu [¶]	P	Mn	Cu	
	-----kg/ha-----				%	---µg/g---		
1	--	--	---	---	0.41	10	6.1	----
2	22 AmS	19	---	2.2	0.42	16	---	----
3	22 Ur	19	---	2.2	0.42	12	---	----
4	45 AmS	19	---	2.2	0.41	22	---	----
5	22 AmS	19	5.6	2.2	0.35	28	7.5	2100
6	22 Ur	19	5.6	2.2	0.34	28	8.1	2230
7	45 AmS	19	5.6	2.2	0.37	35	7.1	2560
8	22 AmS	--	5.6	---	0.33	27	---	1510
9	22 Ur	--	5.6	---	0.34	27	---	----
10	45 AmS	--	5.6	---	0.31	40	---	1770
11	22 AmS	19	5.6	---	0.38	24	6.4	1800
12	22 Ur	19	5.6	---	0.36	23	6.2	1940
13	45 AmS	19	5.6	---	0.36	41	6.5	2730
14#	45 AmS	19	---	2.2	0.41	10	---	----
	LSD _(0.05)				0.03	6	n.s.	----

[†]AmS = $(\text{NH}_4)_2\text{SO}_4$ and Ur = urea.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

[§]Mn applied as MnSO_4 .

[¶]Cu applied as CuSO_4 .

[#]Broadcast before planting.

Phosphorus fertilization increased mean barley yields from 4960 to 5950 kg/ha, comparing only treatments with a P variable; barley leaf P levels were less responsive to P fertilization. Oat yields at Tulana Farm were consistently increased by P fertilization but differences in leaf P levels were not evident. Oat leaf P levels were increased by P fertilization at Henzel Farm south field and some evidence of a yield response is present but the limited data preclude statistical comparisons. Phosphorus fertilization comparisons can be made without Cu fertilization since Cu yield responses were not evident. The tendency for leaf P levels to decrease on plots fertilized with N, P, or Mn is probably a dilution effect.

1979 Growing Season

Oat and barley experiments had different treatments applied and will be discussed separately.

Barley. The leaf Mn and P concentration and yield of barley at Henzel Farm north and south fields are shown in Tables 5 and 6, respectively. Application of 22 kg N/ha as AmS, AmCl, or Ur with P (trts 4, 11, and 15) increased leaf Mn levels at both locations. Yields were increased from all N sources but yields from application of Ur at the north field and UP (17-44) at the south field were significantly less than from other the N sources at their respective locations. Application of 45 kg N/ha as AmS did not increase yields over 22 kg N/ha, but 45 kg N/ha as AmCl did increase yield at the south field.

Application of 5.6 kg Mn/ha with AmS or AmCl and P further increased the leaf Mn concentration but did not significantly increase the yield; Mn application did increase the yield of the Ur treatments at the north field and the UP (17-44) treatment at the south field. Broadcast application of fertilizer (trt 19) was ineffective at increasing leaf Mn levels but did increase yields; however, the yields were less than those resulting from band application of the same fertilizer.

Table 1.5. Leaf Mn and P concentration and yield of barley at Henzel Farm north field, 1979.

No.	Treatments			Concentration		Yield kg/ha
	N [†]	P [‡]	Mn [§]	Mn µg/g	P %	
-----kg/ha-----						
1	--	--	---	12	0.34	3480
2	22 AmS	--	---	15	0.33	5300
3	--	19	---	13	0.43	4190
4	22 AmS	19	---	16	0.42	5400
5	--	--	5.6	14	0.32	5290
6	22 AmS	--	5.6	22	0.33	5870
7	--	19	5.6	18	0.40	6020
8	22 AmS	19	5.6	22	0.40	5830
9	45 AmS	19	---	20	0.42	6270
10	45 AmS	19	5.6	27	0.43	5680
11	22 AmCl	19	---	18	0.42	6000
12	45 AmCl	19	---	18	0.42	5470
13	22 AmCl	19	5.6	20	0.39	5970
14	45 AmCl	19	5.6	24	0.41	5730
15	22 Ur	19	---	16	0.43	4180
16	22 Ur	19	5.6	19	0.40	5760
17	22 UP(17-44)	25	---	13	0.38	5940
18	22 UP(17-44)	25	5.6	13	0.39	5830
19¶	45 AmS	19	5.6	13	0.33	4650
LSD _(0.05)				3	0.02	1090

[†]AmS = $(\text{NH}_4)_2\text{SO}_4$, AmCl = NH_4Cl , Ur = urea, and UP(17-44) = granular urea-phosphate.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in treatments 3, 4, 7 through 16, and 19.

[§]Mn applied as MnSO_4 .

[¶]Broadcast before planting.

Table 1.6. Leaf Mn and P concentration and yield of barley at Henzel Farm south field, 1979.

No.	Treatments			Mn conc. µg/g	P concentration		Yield kg/ha
	N [†]	P [‡]	Mn [§]		3-4 leaf	Early- tillering to mid-	
-----kg/ha-----					-----%-----		
1	--	--	---	8	0.38	0.42	740
2	22 AmS	--	---	11	----	0.42	3830
3	--	19	---	10	----	0.42	4520
4	22 AmS	19	---	13	----	0.39	5250
5	--	--	5.6	11	----	0.39	3420
6	22 AmS	--	5.6	15	0.28	0.39	4000
7	--	19	5.6	12	----	0.42	4660
8	22 AmS	19	5.6	16	0.48	0.40	6050
9	45 AmS	19	---	15	----	0.38	5600
10	45 AmS	19	5.6	19	0.57	0.38	5870
11	22 AmCl	19	---	12	----	0.39	4900
12	45 AmCl	19	---	16	----	0.39	5980
13	22 AmCl	19	5.6	16	----	0.37	5590
14	45 AmCl	19	5.6	16	----	0.37	6080
15	22 Ur	19	---	13	----	0.36	5380
16	22 Ur	19	5.6	11	----	0.39	4820
17	22 UP(17-44)	25	---	8	----	0.37	3580
18	22 UP(17-44)	25	5.6	10	0.45	0.42	4650
19#	45 AmS	19	5.6	10	----	0.39	3190
LSD _(0.05)				4	0.06	0.03	840

[†] AmS = $(\text{NH}_4)_2\text{SO}_4$, AmCl = NH_4Cl , and Ur = urea.

[‡] P applied as $\text{Ca}(\text{H}_2\text{PO}_4)$ in treatments 3, 4, and 7 through 16.

[§] Mn applied as MnSO_4 .

[¶] Broadcast before planting.

Phosphorus fertilization increased leaf P levels in samples collected at early-to-mid tillering from the north field and at the 3-4 leaf stage from the south field. Leaf P levels were similar whether Ur plus P or UP (17-44) was applied. A yield response to P fertilization occurred at the south field location. When Mn was applied, the yields were similar from application of Ur plus P or UP (17-44).

Oats. The leaf Mn concentration and yield of oats grown at Henzel Farm south field are shown in Table 7. All plots received 19 kg P/ha and 5.6 kg Cu/ha. Application of Mn resulted in significant increases in leaf Mn and yield. Application of 22 kg N/ha as either AmS or AmCl increased leaf Mn more than Mn application but the yields were similar. Further increases in leaf Mn and yield occurred when both N and Mn were applied.

1980 Growing Season

In contrast with previous years, the barley planted at Henzel Farm north and south fields had different treatments applied and the results from each location will be discussed separately.

North Field. The Mn and P concentration and yield of barley are shown in Table 8. Leaf Mn concentration was increased by band application of 22 kg N/ha as AmS, AmS plus P or UP but not by application of UP (pH 3). The three N-P sources increased yields a similar amount. Manganese fertilization further increased leaf Mn concentration; the highest Mn concentration was found when Mn was applied with AmS. Additional yield increases were not evident from Mn fertilization.

Application of P as MCP, UP (pH 3), or UP resulted in increased leaf P concentration at both the 3-4 leaf stage and early- to mid-tillering. A large but non-significant yield increase resulted from P fertilization.

South Field. The Mn and P concentration and yield of barley grown at Henzel Farm south field are shown in Table 9. The

Table 1.7. Leaf Mn concentration and yield of oats at Henzel Farm south field, 1979.

No.	Treatments		Mn conc.	Yield
	N [†]	Mn [‡]		
	-----kg/ha-----		µg/g	kg/ha
1	---	---	13	930
2	---	5.6	16	2390
3	22 AmS	---	20	2420
4	22 AmS	5.6	24	3090
5	22 AmCl	---	19	2420
6	22 AmCl	5.6	23	3030
	LSD _(0.05)		3	820

[†]AmS = $(\text{NH}_4)_2\text{SO}_4$ and AmCl = NH_4Cl .

[‡]Mn applied as MnSO_4 .

Table 1.8. Leaf Mn and P concentration and yield of barley at Henzel Farm north field, 1980.

No.	Treatments			Concentration			Yield kg/ha
	N [†]	P [‡]	Mn [§]	Mn	P		
	-----kg/ha-----			µg/g	3-4 leaf	Early- to mid- tillering	
					-----%-----		
1	--	--	---	16	----	0.36	2300
2	22 AmS	--	---	24	----	0.30	3400
3	22 AmS	19	---	27	----	0.48	4670
4	22 AmS	--	5.6	35	0.37	0.32	4220
5	22 AmS	19	5.6	42	0.60	0.46	5120
6	45 AmS	19	5.6	49	----	0.48	4610
7	22 UP (pH 3)	25	---	18	----	0.43	4130
8	22 UP (pH 3)	25	2.8	22	----	0.43	3950
9	22 UP (pH 3)	25	5.6	27	0.54	0.44	4780
10	22 UP	25	---	20	----	0.46	4560
	LSD (0.05)			4	0.08	0.07	1060

[†]AmS = $(\text{NH}_4)_2\text{SO}_4$, UP (pH 3) = urea-phosphoric acid solution, and
UP = urea-phosphate solution made from granular urea-phosphate.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in treatments 3, 5, and 6.

[§]Mn applied as MnSO_4 .

Table 1.9. Leaf Mn and P concentration and yield of barley at Henzel Farm south field, 1980.

No.	Treatments			Concentration			Yield kg/ha
	N [†]	P [‡]	Mn [§]	Mn	P		
	-----kg/ha-----			µg/g	3-4 leaf	Early- to mid- tillering	
					-----%-----		
1	--	--	---	16	----	0.45	2700
2	22 AmS	--	---	25	----	0.36	5300
3	22 AmS	19	---	25	----	0.54	5880
4	22 AmS	--	5.6	31	0.34	0.34	5120
5	22 AmS	19	5.6	31	0.65	0.53	6380
6	45 AmS	19	5.6	50	----	0.55	6600
7	22 Ur	19	---	17	----	0.58	4840
8	22 Ur	19	5.6	25	----	0.52	5770
9	22 UP (pH 3)	25	---	20	----	0.59	4950
10	22 UP (pH 3)	25	5.6	25	0.58	0.52	5170
11	22 UP	25	---	20	----	0.60	4960
12	22 UP	25	5.6	29	0.66	0.49	5170
	LSD _(0.05)			8	0.12	0.07	670

[†]AmS = $(\text{NH}_4)_2\text{SO}_4$, Ur = urea, UP (pH 3) = urea-phosphoric acid solution, and UP = urea-phosphate solution made from granular urea-phosphate.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in treatments 3 and 5 through 8.

[§]Mn applied as MnSO_4 .

application of 22 kg N/ha as AmS plus P increased leaf Mn concentration but application of Ur plus P, UP (pH 3), or UP was ineffective at increasing leaf Mn levels. These treatments all increased yields but the yield from AmS was significantly greater than from other N sources. Application of Mn tended to increase leaf Mn concentration but the only significant increase occurred when N was applied as Ur. The greatest yield, 6600 kg/ha, resulted from application of 45 kg N/ha as AmS plus P and Mn.

Application of P as MCP (trt 5), UP (pH 3), or UP increased leaf P concentration at both the 3-4 leaf stage and at early-to-mid tillering. When N was applied as AmS, a significant yield increase resulted from P fertilization. The decreased leaf P levels resulting from Mn fertilization are probably a dilution effect resulting from more vigorous early growth. However, in a companion laboratory experiment (Chapter Two of this thesis), it was found that Mn application consistently lowered soil solution P concentration.

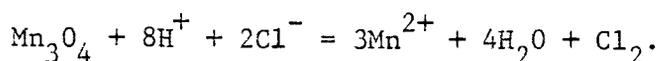
DISCUSSION AND CONCLUSIONS

The pH of soils used in these experiments ranged from 7.6 to 8.3 and the organic matter content ranged from 17 to 19%; these conditions are known to reduce the availability of Mn. Band application of an acidic N fertilizer such as AmS or AmCl was more effective than other N sources at increasing the Mn concentration and correcting the Mn deficiency. Hammes and Berger (1960) also found band application of an acidic fertilizer to be more effective than a neutral fertilizer at correcting Mn deficiency and increasing oat yields on an alkaline soil. Decreasing soil pH has also been shown to enhance the conversion of reducible Mn to water soluble plus exchangeable Mn (Gotoh and Patrick, 1972). The latter fraction of soil Mn is available for plant uptake. In a companion laboratory experiment, (Chapter Two of this thesis) it was found that band application of AmS or AmCl decreased the pH in the fertilizer band and increased the Mn concentration in the soil solution whereas Ur increased the pH in the fertilizer band and did not increase soil solution Mn.

The lack of yield responses from Ur may have been due to NH_3 toxicity; band application of Ur has been shown to reduce seedling emergence (Stephen and Waid, 1963) and root growth (Creamer and Fox, 1980). The effect would be expected to be more striking if the potential for Mn deficiency were also present. Reduced root growth would limit uptake of Mn, increasing the possibility of Mn deficiency. Application of Mn corrected the Mn deficiency and adequate irrigation throughout the growing season would have enabled the plants to overcome the initial growth retardation.

There is ample evidence in the literature that Cl application can enhance the availability and uptake of Mn (Hamilton, 1966; Jackson et al., 1967; Stewart and Leonard, 1963; Westermann et al., 1971). The most dramatic increases in Mn concentration have occurred on acid soils; responses on alkaline soils have been much less pronounced (Sherman et al., 1943; Stewart and Leonard, 1963). A

thermodynamically feasible mechanism proposed by Westermann et al. (1971) is the reaction



Chloride acts as an electron donor reducing the Mn to Mn^{2+} which results in the evolution of Cl_2 gas. The reaction requires H^+ ions which would be present at low concentrations in an alkaline soil; thus, this reaction is of less importance in alkaline soils than in acid soils. The increased leaf Mn concentration resulting from application of AmCl is probably a pH effect similar to that found with AmS.

Application of either liquid or granular UP fertilizers was generally less effective than AmS plus MCP at increasing leaf Mn concentration and yield. The UP fertilizers were as effective at increasing leaf P concentrations as MCP.

Application of MCP increased leaf P levels and yields but did not increase leaf Mn concentration. The reduced pH in a band of MCP dissolves Mn (Lindsey and Stephenson, 1959a, 1959b) which then precipitates as the wetting front moves outward and the pH rises. The MCP is converted to dicalcium phosphate (DCP) which is relatively insoluble and has little effect on the pH or Mn concentration. The high calcium concentration of these soils would rapidly neutralize the acidity in the MCP band and enhance the conversion of MCP to DCP. This would reduce the amount of Mn brought into solution by the MCP.

Band application of the fertilizer was necessary to increase Mn concentration and yield; broadcast application was ineffective at increasing leaf Mn levels and only moderately effective at increasing yields. Band application of fertilizer reduces soil-fertilizer contact and concentrates the acidity developed in a relatively small volume. The decreased pH increases the Mn availability and slows the oxidation of Mn to less available compounds.

The relationship between leaf Mn concentration at early- to mid-tillering and yield of barley and oats is shown in Figs. 1 and 2, respectively. Assuming the critical level to be the Mn concentration at 90% of optimum yield, the Mn critical level for barley is 18 $\mu\text{g/g}$ and for oats it is 25 $\mu\text{g/g}$. These values are in close agreement with Melsted et al. (1969) who suggest a Mn critical level of 30 $\mu\text{g/g}$ in whole wheat plants collected at the boot stage and Mammes and Berger (1960) who suggest 30 $\mu\text{g/g}$ in oat flag leaf samples collected at the boot stage.

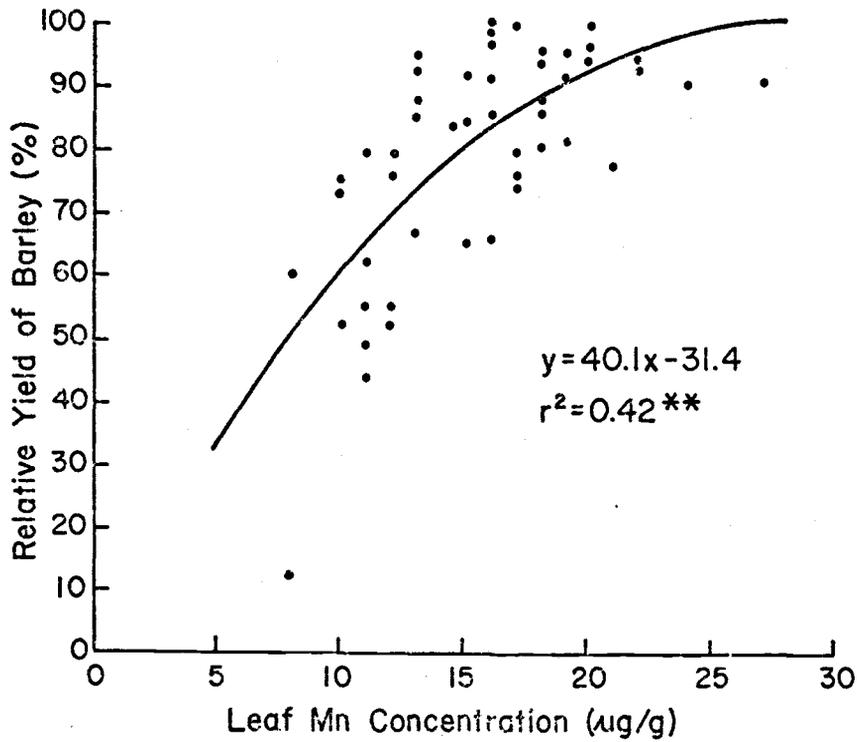


Fig. 1.1. Relationship of barley leaf Mn concentration at early-to-mid tillering to relative grain yield.

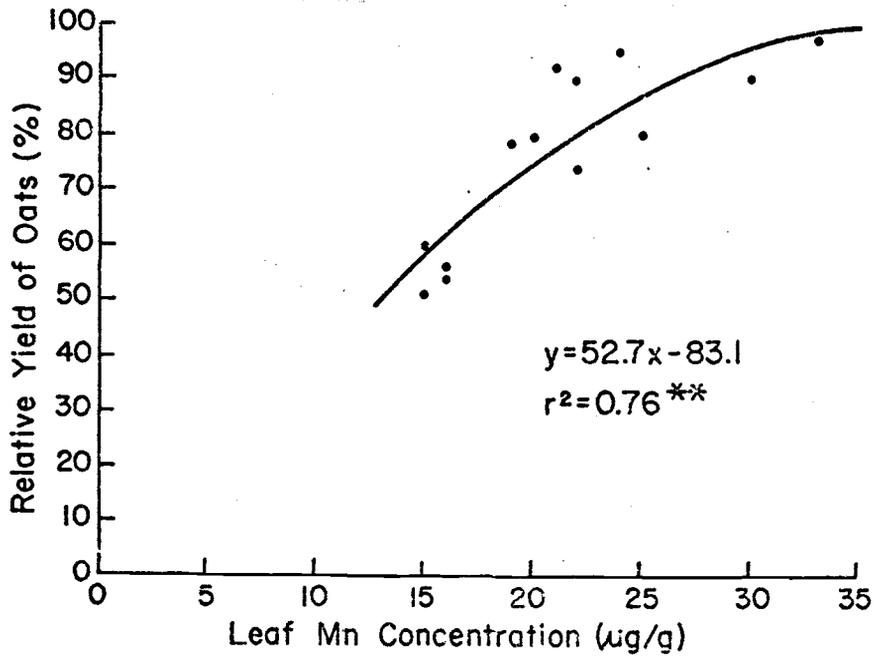


Fig. 1.2. Relationship of oat leaf Mn concentration at early-to mid tillering to relative grain yield.

CHAPTER TWO
EFFECTS OF FERTILIZATION ON SOIL SOLUTION pH
AND Mn AND P CONCENTRATION

INTRODUCTION

There are numerous reports in the literature of manganese (Mn) deficiency of small grains, particularly on alkaline soils. Nevertheless, virtually all soils contain sufficient Mn for optimum plant growth and development; deficiencies arise when soil conditions limit Mn availability. Fertilizers are applied to increase the quantity of available Mn by (1) supplying additional Mn^{2+} or (2) reducing the pH to enhance the availability of native soil Mn.

The most common inorganic Mn fertilizer is $MnSO_4$ (Murphy and Walsh, 1972). It has proven effective at correcting Mn deficiency of small grains grown on both acid and alkaline soils. Lowering the soil pH in a localized zone by band application of acid-forming nitrogen (N) or phosphorus (P) fertilizers has also resulted in increased Mn uptake and yields (Hammes and Berger, 1960; Jackson and Carter, 1976; Mortvedt and Giordano, 1975). Increased levels of ammonium acetate-extractable Mn have also resulted from application of acidic N or P fertilizers (Sims and Atkinson, 1974; Voth and Christenson, 1980). However, little research has been done on the effects of fertilizers on the soil solution Mn concentration.

The soil solution is defined by the Soil Science Society of America (1979) as "the aqueous liquid phase of the soil and its solutes." Virtually all soil chemical reactions occur in the soil solution or at the soil solution-gaseous phase or soil solution-solid phase interfaces. With the exception of foliar applied Mn fertilizers, all plant Mn is taken up from the soil solution. Thus, the soil solution Mn concentration is a prime factor in evaluating the effectiveness of fertilizer treatments at correcting Mn deficiency.

A companion field experiment (Chapter One of this thesis) clearly showed that band application of acid forming fertilizers was necessary to correct the Mn deficiency and produce maximum barley and oat yields. The objectives of this research were to determine the effects of different fertilizers on the soil solution pH and Mn and P

concentration in the fertilizer band and 2.5 cm from the fertilizer band.

MATERIALS AND METHODS

Soil from the upper 15 cm of the profile was collected adjacent to the Henzel Farm south field plots, mixed thoroughly, and stored in an air dry condition until used. The soil was classified as a Tulana silt loam variant; the morphology was characteristic of the Tulana series but the underlying horizons were alkaline, not acidic. The soil test values were: pH, 7.6; P, 9 $\mu\text{g/g}$; K, 355 $\mu\text{g/g}$; Ca, 48 meq/100 gm; Mg, 23 meq/100 gm; Na, 3.7 meq/100 gm, salt, 3.4 mmhos/cm; DTPA-extractable Mn, 0.88 $\mu\text{g/g}$; and organic matter, 18% with the procedures used by Oregon State University Soil Testing Laboratory (Berg and Gardner, 1978).

The air dry soil was placed in plastic-lined wooden boxes which were 60 cm x 80 cm x 12.5 cm deep. One end was removable to allow removal of soil samples. Water purified by reverse osmosis was added to bring the soil to 0.1 bar moisture tension at which time the gravimetric water content was 160%. The soil was incubated for ten days to allow moisture equilibration. Simulated fertilizer bands were placed 3.75 cm deep and marked with washed silica sand. Nitrogen was applied at 0 or 22 kg/ha as $(\text{NH}_4)_2\text{SO}_4$ (AmS), NH_4Cl (AmCl), urea (Ur), or a granular urea-phosphate, UP(17-44), which had the formulation 17-44-0. Phosphorus was applied at 0 or 19 kg/ha as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (MCP) or at 25 kg/ha as UP. Manganese was applied at 0 or 5.6 kg/ha as MnSO_4 . All fertilizer rates were based on 25 cm row spacing and all fertilizers except AmCl were provided by TVA. The soil was covered with 2.5 cm of perlite and the boxes were loosely covered with plastic to reduce evaporation but maintain aerobic conditions. No additional water was added to the soil during the course of the experiment. The boxes were stored in the dark at 15°C in a constant temperature room.

Prior to sample collection, the end of the box was removed and 2.5 cm of soil was removed and discarded. A 5.0 cm thick slab of soil was removed and used for sample collection. A lucite tube with

1.25 cm inside diameter was used to collect soil samples in the fertilizer band and 2.5 cm from the fertilizer band at 7, 14, and 28 days after the fertilizer was added. The soil solution was removed by centrifugation as described fully in Chapter Three of this thesis, "Soil Solution Removal by Centrifugation." The pH of the soil solution was measured immediately and the solution was transferred to 20 ml capped vials and stored frozen until analyzed. The soil solution was analyzed for Mn using a Perkin-Elmer Model 4000 atomic absorption spectrophotometer. Phosphorus was measured using a Scientific Instruments Model CFA 200 Auto-Analyzer.

RESULTS

Experiment One. Application of N fertilizers with MCP significantly lowered the soil solution pH in the fertilizer band at 7, 14, and 28 days after fertilization (Table 1). Application of AmS or MCP alone lowered the soil solution pH somewhat but the combination of AmS and MCP generally resulted in a lower soil solution pH. The soil solution pH in the Ur and UP(17-44) bands was reduced initially, but tended to rise throughout the course of the experiment while the soil solution pH in the AmS and AmCl bands tended to remain depressed. The application of Mn had no consistent effect on the soil solution pH.

The N or P fertilizers had little effect on the soil solution pH 2.5 cm from the fertilizer band (Table 2). The pH reductions resulting from fertilizer application were consistent at all sampling times but significant only at 28 days after fertilization. Application of MCP lowered the soil solution pH and further lowered the soil solution pH in the AmS band; both of these effects were also evident in the fertilizer band. Application of Mn had no consistent effects on soil solution pH.

There were distinct differences in the soil solution Mn concentration in the fertilizer band resulting from application of different N fertilizers (Table 3). The upper LSD value is valid for comparing all treatments with the check while the lower LSD value is valid only for comparing treatments which did not receive Mn with the check treatment. In bands not receiving Mn, the soil solution Mn concentration was consistently lower in the Ur band; the Mn concentration in the band was not significantly different than the check band at 14 and 28 days after fertilization. Other N sources applied with MCP significantly increased soil solution Mn concentration at 14 and 28 days after fertilization.

Application of AmS or MCP did not increase the soil solution Mn concentration at 14 or 28 days after fertilization; however,

Table 2.1. Effect of fertilizers on the soil solution pH in the fertilizer band; experiment one.

No.	Treatment			Incubation time (days)		
	N [†]	P [‡]	Mn [§]	7	14	28
	Source [¶]	---kg/ha---		-----pH-----		
1	--	--	---	8.12	7.98	8.05
2	AmS	--	---	7.30	7.06	7.05
3	--	19	---	6.91	7.08	7.39
4	AmS	19	---	7.01	6.69	6.67
5	AmS	19	5.6	6.37	6.34	6.60
6	AmCl	19	---	6.49	6.29	6.54
7	AmCl	19	5.6	6.43	7.03	6.65
8	Ur	19	---	6.84	6.24	7.10
9	Ur	19	5.6	6.73	6.99	7.37
10	UP(17-44)	25	---	6.22	6.45	6.55
11	UP(17-44)	25	5.6	5.52	6.64	6.89
	LSD	(.05)		0.88	0.84	0.49

[†]All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in treatments 3 through 9.

[§]Mn applied as MnSO_4 .

[¶]AmS = $(\text{NH}_4)_2\text{SO}_4$, AmCl = NH_4Cl , Ur = urea, and UP(17-44) = granular urea phosphate.

Table 2.2. Effect of fertilizers on the soil solution pH
2.5 cm from the fertilizer band; experiment one.

No.	Treatment			Incubation time (days)		
	N [†]	P [‡]	Mn [§]	7	14	28
	Source [¶]	---kg/ha---		-----pH-----		
1	--	--	---	8.15	7.99	8.10
2	AmS	--	---	7.61	7.39	7.52
3	--	19	---	7.93	7.83	7.88
4	AmS	19	---	7.66	7.45	7.55
5	AmS	19	5.6	7.30	7.67	7.49
6	AmCl	19	---	7.59	7.65	7.65
7	AmCl	19	5.6	7.47	7.43	7.41
8	Ur	19	---	7.69	7.62	7.73
9	Ur	19	5.6	7.51	7.61	7.87
10	UP(17-44)	25	---	7.31	7.37	7.41
11	UP(17-44)	25	5.6	7.25	7.48	7.55
	LSD (.05)			0.43	NS	0.39

[†]All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in treatments 3 through 9.

[§]Mn applied as MnSO_4 .

[¶]AmS = $(\text{NH}_4)_2\text{SO}_4$, AmCl = NH_4Cl , Ur = urea, and UP(17-44) = granular urea-phosphate.

Table 2.3. Effect of fertilizers on the soil solution Mn concentration in the fertilizer band; experiment one.

No.	Treatment			Incubation time (days)		
	N [†]	P [‡]	Mn [§]	7	14	28
	Source [¶]	---kg/ha---		-----µg Mn/ml-----		
1	--	--	---	0.04	0.06	0.01
2	AmS	--	---	0.16	0.07	0.02
3	--	19	---	0.20	0.09	0.03
4	AmS	19	---	0.18	0.36	0.25
5	AmS	19	5.6	22.0	16.6	15.6
6	AmCl	19	---	0.32	0.33	0.23
7	AmCl	19	5.6	16.6	9.8	12.1
8	Ur	19	---	0.12	0.16	0.03
9	Ur	19	5.6	26.5	11.8	4.9
10	UP(17-44)	25	---	0.50	0.26	0.20
11	UP(17-44)	25	5.6	35.7	24.9	11.7
	LSD (.05)			14.2	8.3	7.2
				0.25	0.19	0.15

[†]All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[‡]P applied as Ca(H₂PO₄) in treatments 3 through 9.

[§]Mn applied as MnSO₄.

[¶]AmS = (NH₄)SO₄, AmCl = NH₄Cl, Ur = urea, and UP(17-44) = granular urea-phosphate.

[#]Valid for comparisons involving any treatments with check band.

^{††}Valid for comparisons involving treatments not receiving Mn with check band.

application of AmS and MCP together significantly increased Mn concentration at 14 and 28 days after fertilization. The combination of AmS and MCP also resulted in a lower soil solution pH than either AmS or MCP applied alone (Table 1).

Soil solution Mn concentration was markedly increased by Mn application at 7 and 14 days after fertilization regardless of N source. At 28 days after fertilization, the soil solution Mn concentration in the Ur band had fallen and was not significantly different than the check band while the Mn concentration was still elevated in the bands of the other N fertilizers.

Application of N or P fertilizers had little effect on the soil solution Mn concentration 2.5 cm from the fertilizer band (Table 4). There were consistent but non-significant increases in soil solution Mn concentration at 7 and 14 days after fertilization when Mn was applied in the fertilizer band. The Mn concentration was significantly increased at 28 days after fertilization when AmS or UP were applied. Soil solution Mn concentration fell rapidly when Ur was applied.

Soil solution P concentration in the fertilizer band was markedly increased by application of either MCP or UP (Table 5). Although more P was applied as UP(17-44), both P sources were equally effective at increasing the soil solution P concentration. Application of Mn had no effect on P concentration at 7 days after fertilization but consistently reduced P concentration at 14 and 28 days after fertilization.

The P concentration fell more rapidly when MCP was applied alone than when MCP was applied with AmS. The P concentration in the Ur band was lower than in the band of other N sources at the end of the experiment.

Soil solution P concentration 2.5 cm from the fertilizer band was less affected by P fertilization (Table 6). As in the fertilizer band, MCP with AmS resulted in larger P concentration than MCP alone at 28 days after fertilization. Urea was less effective than other N sources at maintaining elevated P levels in the soil solution.

Table 2.4. Effect of fertilizers on the soil solution Mn concentration 2.5 cm from the fertilizer band; experiment one.

No.	Treatment			Incubation time (days)		
	N [†]	P [‡]	Mn [§]	7	14	28
	Source [¶]	---kg/ha---		-----µg Mn/ml-----		
1	--	--	---	0.02	0.03	0.01
2	AmS	--	---	0.04	0.05	0.01
3	--	19	---	0.07	0.02	0.01
4	AmS	19	---	0.04	0.06	0.01
5	AmS	19	5.6	0.30	0.13	0.67
6	AmCl	19	---	0.08	0.06	0.02
7	AmCl	19	5.6	0.13	0.08	0.26
8	Ur	19	---	0.05	0.02	0.02
9	Ur	19	5.6	0.11	0.02	0.02
10	UP(17-44)	25	---	0.07	0.02	0.02
11	UP(17-44)	25	5.6	0.25	0.17	0.76
	LSD(.05)			NS	NS	0.44

[†]All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in treatments 3 through 9.

[§]Mn applied as MnSO_4 .

[¶]AmS = $(\text{NH}_4)_2\text{SO}_4$, AmCl = NH_4Cl , Ur = urea, and UP(17-44) = granular urea-phosphate.

Table 2.5. Effect of fertilizers on the soil solution P concentration in the fertilizer band; experiment one.

No.	Treatment			Incubation time (days)		
	N [†]	P [‡]	Mn [§]	7	14	28
	Source [¶]	---kg/ha---		-----µg P/ml-----		
1	--	--	---	2.2	3.0	2.3
2	AmS	--	---	2.1	3.2	1.7
3	--	19	---	77	40	13
4	AmS	19	---	72	105	55
5	AmS	19	5.6	137	68	47
6	AmCl	19	---	105	100	71
7	AmCl	19	5.6	61	24	37
8	Ur	19	---	52	79	31
9	Ur	19	5.6	86	43	11
10	UP(17-44)	25	---	130	86	56
11	UP(17-44)	25	5.6	83	86	25
	LSD (.05)			68	58	32

[†]All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in treatments 3 through 9.

[§]Mn applied as MnSO_4 .

[¶]AmS = $(\text{NH}_4)_2\text{SO}_4$, AmCl = NH_4Cl , Ur = urea, and UP(17-44) = granular urea-phosphate.

Table 2.6. Effect of fertilizer on the soil solution P concentration 2.5 cm from the fertilizer band, experiment one.

No.	Treatment			Incubation time (days)		
	N [†]	P [‡]	Mn [§]	7	14	28
	Source [¶]	---kg/ha---		-----µg P/ml-----		
1	--	--	---	1.8	2.9	2.3
2	AmS	--	---	2.1	2.7	1.7
3	--	19	---	8.5	7.3	3.4
4	AmS	19	---	6.8	6.6	8.2
5	AmS	19	5.6	13.8	15.7	7.1
6	AmCl	19	---	4.5	5.3	5.4
7	AmCl	19	5.6	4.8	9.4	7.1
8	Ur	19	---	3.6	3.1	3.4
9	Ur	19	5.6	3.7	6.7	2.0
10	UP(17-44)	25	---	23	16	10.0
11	UP(17-44)	25	5.6	9.5	4.3	9.0
	LSD(.05)			9.1	6.1	3.7

[†]All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[‡]P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$ in treatments 3 through 9.

[§]Mn applied as MnSO_4 .

[¶]AmS = $(\text{NH}_4)_2\text{SO}_4$, AmCl = NH_4Cl , Ur = urea, and UP(17-44) = granular urea-phosphate.

Application of Mn tended to increase P concentration at 14 and 28 days after fertilization.

Experiment Two. Application of MCP is known to reduce the pH and increase Mn concentration (Lindsey and Stephenson, 1959a, 1959b). To separate the effects of the N source from those of the MCP, AmCl and Ur were reapplied without MCP; AmS had been applied without MCP in experiment one. The soil had been stored in a moist state for several weeks and organic matter oxidation lowered the check band pH somewhat.

Application of AmCl lowered the soil solution pH while application of Ur increased the pH at 7 days after fertilization (Table 7). At 14 and 28 days after fertilization both AmCl and Ur reduced the pH but the pH in the band of AmCl was significantly lower than in the Ur band. Application of Mn did not affect soil solution pH.

At 2.5 cm from the fertilizer band application of AmCl lowered the soil solution pH at all sampling times while Ur application lowered the soil solution significantly only at 28 days after fertilization (Table 7). As in the fertilizer band, effects of Mn application on pH were not evident.

Soil solution Mn concentration in the fertilizer band increased only when Mn fertilizer was applied (Table 7); application of AmCl, Ur, or AmS (Table 3) without MCP was ineffective at increasing Mn concentration. Increases in soil solution Mn concentration were not evident 2.5 cm from the fertilizer band.

Table 2.7. Effect of fertilizers on the soil solution pH in the fertilizer band and 2.5 cm from the fertilizer band and Mn concentration in the fertilizer band; experiment two.

No.	Treatment		Incubation time (days)		
	N†	Mn‡	7	14	28
	Source§	kg/ha	----pH in the band----		
1	--	---	7.75	7.75	7.81
2	AmCl	---	7.21	7.07	7.04
3	Ur	---	8.01	7.43	7.47
4	--	5.6	7.63	7.72	7.70
	LSD (.05)		0.11	0.18	0.31
			--pH 2.5 cm from band--		
1	--	---	7.79	7.75	7.82
2	AmCl	---	7.32	7.13	7.29
3	Ur	---	7.81	7.66	7.58
4	--	5.6	7.73	7.86	7.90
	LSD (.05)		0.17	0.14	0.20
			---µg Mn/ml in band---		
1	--	---	0.02	0.02	0.02
2	AmCl	---	0.11	0.06	0.09
3	Ur	---	0.09	0.02	0.03
4	--	5.6	7.2	5.9	0.74
	LSD (.05)		3.8 [¶]	3.0	0.68
			0.05 [#]	0.03	0.07

† All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

‡ Mn applied as $MnSO_4$.

§ AmCl = NH_4Cl and Ur = urea.

¶ Valid for comparisons involving any treatment with the check band.

Valid for comparisons involving treatments not receiving Mn with the check band.

DISCUSSION

The results of these experiments are consistent with those obtained in three years of field experiments (Chapter One of this thesis). In the field studies, it was found that band application of an acid forming N fertilizer, such as AmS or AmCl, with MCP was more effective than Ur with MCP at increasing leaf Mn concentration and yield of barley and oats.

In the laboratory experiments, application of either AmS or AmCl alone lowered the soil solution pH throughout the course of the experiment and application of MCP with either N fertilizer further lowered the soil solution pH. Oxidation of NH_4^+ lowers the pH in a band of AmS or AmCl while the products of MCP dissolution also markedly depress the pH (Lindsey and Stephenson, 1959a). Over the course of the experiment the pH rose more slowly when MCP was applied with AmS or AmCl than when MCP was applied alone or with Ur. The high calcium (Ca) concentration in these soils probably resulted in the rapid conversion of MCP to dicalcium phosphate (DCP), a relatively insoluble mineral with little effect on the soil solution pH (Lindsey and Stephenson, 1959c). The acidity developed in the AmS or AmCl band slowed this process as indicated by the lower soil solution pH and greater P concentration when AmS or AmCl were included with MCP in the fertilizer band.

Application of Ur with MCP lowered the pH initially but the pH rose during the experiment due to a more rapid neutralization of the acidity resulting from MCP than occurred with AmS or AmCl. Soil solution P concentration also fell more rapidly when Ur was applied, presumably due to the conversion of MCP to DCP. The soil solution pH was increased when Ur was applied alone due to the initial hydrolysis reaction but fell over time. The decomposition of $(\text{NH}_4)_2\text{CO}_3$ released NH_4^+ which was oxidized resulting in the pH depression.

Significant increases in soil solution Mn concentration were not evident from application of N fertilizers or MCP alone whereas the Mn

concentration was increased by application of AmS or AmCl with MCP as well as UP. Lindsey and Stephenson (1959b) reported large increases in soluble Mn, as well as iron (Fe) and aluminum (Al), near a granule of MCP; after 27 days Fe-phosphates and Al-phosphates had precipitated and the Fe and Al concentration fell. The Mn concentration remained elevated and, in a separate study, evidence of a Mn-phosphate precipitate was not found after one year (Lindsey and Stephenson, 1959c). The inability of MCP alone or Ur with MCP to increase soil solution Mn concentration suggests that the acidity in the fertilizer band is an important factor in maintaining elevated Mn concentrations.

Chloride (Cl) application has resulted in increased plant tissue Mn concentration (Jackson et al., 1967; Steward and Leonard, 1963) and extractable soil Mn (Westermann et al., 1971). The mechanism proposed by Westermann et al. (1971) is a Mn-Cl redox couple which requires the presence of H^+ ions. The Cl effect is much less dramatic on alkaline soils (Stewart and Leonard, 1963). The leaf Mn concentration was increased a similar amount by AmS or AmCl in field experiments (Chapter One of this thesis) and soil solution Mn concentration increases were similar from either N source. Thus, the increased soil solution Mn concentration resulting from AmCl application was probably solely a pH effect comparable to the effect of AmS.

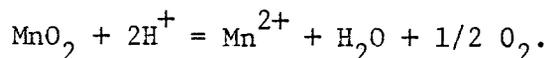
The N source may also alter the soil solution Mn concentration through changes in the microbial population. Timonin (1950, 1965) found that organic forms of N such as Ur or asparagine favored the growth of Mn oxidizing microorganisms which would decrease soluble Mn. In contrast, inorganic N forms such as AmS or $Ca(NO_3)_2$ favored the growth of Mn reducing microorganisms which would increase the soil solution Mn concentration.

The soil solution P concentration was markedly increased by P application as MCP or UP. Application of Mn consistently lowered the P concentration in the fertilizer band at 14 and 28 days after fertilization. Explanations for this are not obvious; Lindsey and

Stephenson (1959c) concluded that Mn was not associated with P removal from solution by precipitation. The formation of a Mn-P complex (Hem, 1963a) may have increased P solubility and diffusion away from the fertilizer band as there was a tendency for P concentration to increase 2.5 cm from the fertilizer band when Mn was applied.

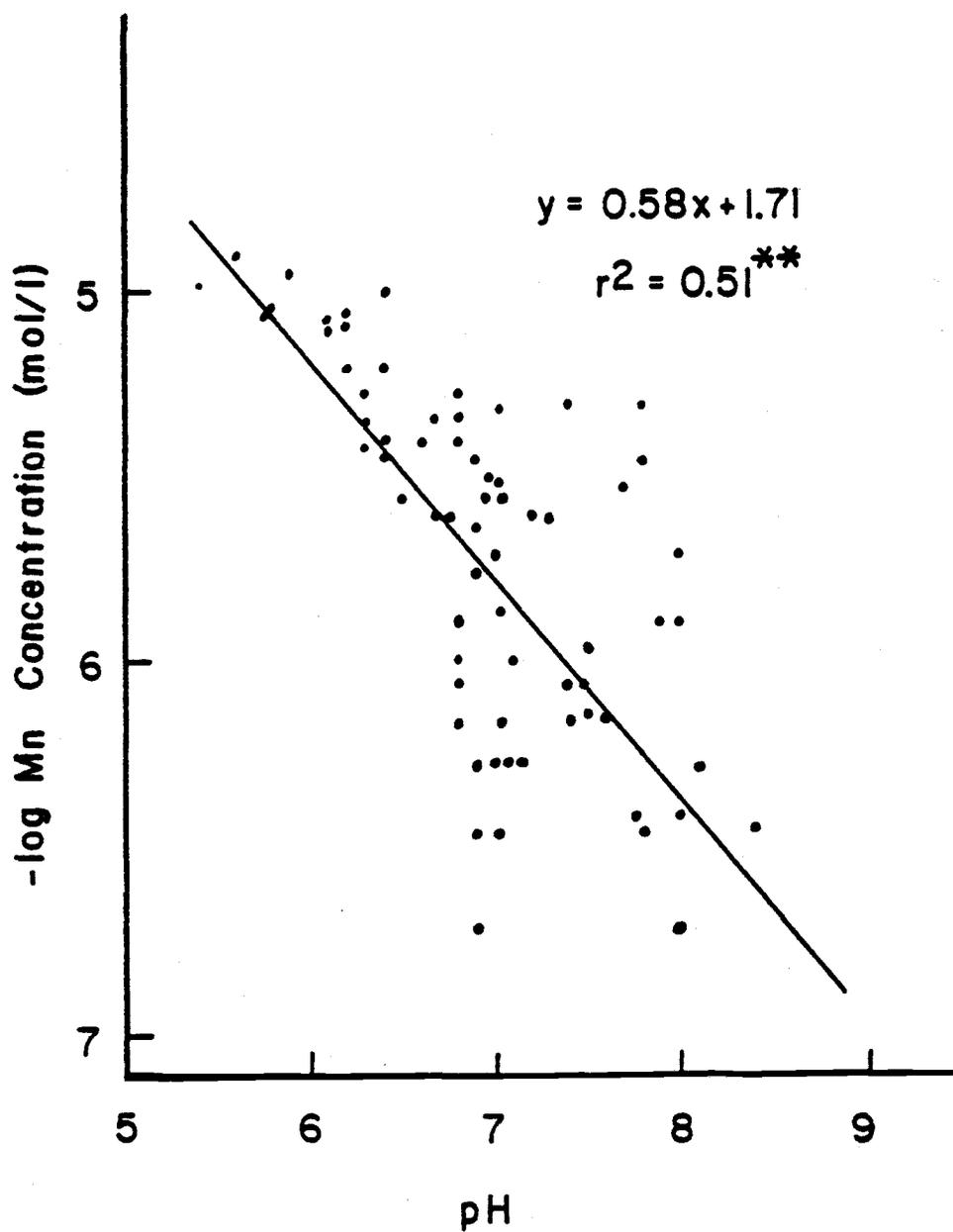
There was a highly significant correlation between the soil solution pH and the Mn concentration in the fertilizer band of treatments not receiving Mn (Fig. 1). At pH 6, 7, and 8 the Mn concentration calculated from the regression equation was 6.46×10^{-6} , 1.7×10^{-6} , and 4.46×10^{-7} mol/l, respectively; the Mn concentration decreased 3.8-fold for each one unit pH increase.

Pyrolusite (MnO_2) is commonly considered the solid phase controlling Mn solubility (Lindsey, 1972); the solubility of Mn^{2+} is given by the equation



The equilibrium constant for this reaction was calculated from the data of Robie and Waldbaum (1968). The resulting Mn concentrations at pH 6, 7, and 8 are 2.7×10^{-13} , 2.7×10^{-15} , and 2.7×10^{-17} mol/l, respectively. The Mn concentration decreases 100-fold for each one unit pH increase. The pronounced differences between the observed and calculated Mn concentrations are not unusual. Bohn (1970) has reported similar discrepancies between calculated and measured Mn concentrations in soil-water extracts. The substantial disagreements between calculated and measured Mn concentration may be due to (1) the absence of MnO_2 in the soil or (2) the activity of certain microorganisms.

In a study of 26 clay-sized nodules from Australian soils Taylor et al. (1964) found only one example of pure pyrolusite. The other nodules were complex secondary minerals and Mn was often found in two oxidation states in one mineral. The solubility of these other minerals may differ markedly from that of pyrolusite. Heintze (1958) was unable to find evidence of Mn^{4+} in alkaline organic soils in



England and speculated that a Mn-organic matter complex controlled the solubility of Mn.

Microbial activity also has a major impact on Mn solubility. Certain microorganisms are able to utilize higher oxides of Mn as electron acceptors when gaseous O_2 is unavailable (Hochster and Quastel, 1952). This mechanism was thought to be responsible for most of the reduction of Mn that occurred under anaerobic conditions. As discussed previously the source of N may also effect Mn solubility by alteration of the microbial population (Timonin, 1950, 1965).

CHAPTER THREE
SOIL SOLUTION REMOVAL BY CENTRIFUGATION

Soil Solution Removal by Centrifugation

The soil solution is defined by the Soil Science Society of America (1979) as "the aqueous liquid phase of the soil and its solutes." Virtually all soil chemical reactions occur in the soil solution or at the soil solution-solid phase or soil solution-gaseous phase interfaces. With the exception of foliar applied fertilizers, virtually all plant nutrients are taken up from the soil solution. Thus, evaluating the concentration of solutes in the soil solution is of prime importance in much of soil chemistry and soil fertility/plant nutrition research.

Various methods have been proposed for removing the soil solution in an unaltered state. Displacement of the soil solution with another liquid was proposed by Parker (1921) and has been shown to remove the soil solution unaltered by Adams (1971) and Burd and Martin (1923). However, this method required at least 80 grams of moist soil and 8 hours to complete. The pressure membrane technique developed by Richards (1941) has proven successful for determining soil moisture retention curves but Adams (1971) has raised several objections to its use in soil solution composition research. These include alteration of the pH due to changes in the partial pressure of CO_2 as gas pressure in the chamber changes and possible adsorption of phosphorus on the porous plate or membrane. The immiscible displacement centrifugation technique of Murabak and Olsen (1976) is rapid and simple but the bulk density of the soil must be greater than one. The technique does not alter the natural pH of the soil solution or the equilibrium of BaSO_4 (Murabak and Olsen, 1976a, 1976b). However, substantial but variable amounts of Cu, Cd, Mn, and Zn exist in organic complexes in the soil solution (Geering et al., 1969; Hodgson et al., 1965) and may be partitioned between the organic solvent and the soil solution during removal. A method of removing the soil solution by centrifugation was developed by Davies and Davies (1963) but was unable to remove any soil solution when the

soil contained less than 32% moisture. This may have been due to the limited velocity, 4000 rpm, of their centrifuge. This note reports on a rapid and simple centrifuge technique which effectively removes the soil solution from small quantities of moist soil.

Two polycarbonate centrifuge tubes are used, a 12 ml tube with eight holes drilled in the bottom using a no. 63 drillbit and a 50 ml tube with a screw-on cap. Fiberglass wool is packed 1.5 cm thick in the bottom of the 12 ml tube and the moist soil is placed in the tube. The 12 ml tube is placed inside the 50 ml tube which is then capped. The tubes are placed in the centrifuge and spun; the soil solution is forced out of the soil in the 12 ml tube and collected in the 50 ml tube.

The technique was evaluated using two soils, a Tulana silt loam and a Chehalis silt loam. The Tulana and Chehalis soils had 18 and 3% organic matter, respectively, and the gravimetric water content at 0.3 bars was 156 and 31% and at 15 bars was 35 and 13%, respectively. Before centrifugation, the soils were brought to various moisture contents and allowed to equilibrate for at least 24 hours.

The effect of centrifugal force on the percentage of soil solution removed from soils at 0.3 bars moisture tension is shown in Fig. 1. All trials were conducted for 30 minutes. At 30,900 g 50 and 36% of the soil solution was removed from the Tulana and Chehalis soils, respectively. The 12 ml tubes failed frequently at 30,900 g so faster centrifuge velocities were not examined. All later trials were conducted at 17,400 g and tube failure occurred only rarely. Thirty minutes of centrifuge time were nearly as effective as two hours at removing the soil solution (Fig. 2). A maximum of 54 and 37% of the soil solution was removed from the Tulana and Chehalis soils, respectively.

The effect of soil moisture tension on the percentage of soil solution removed is shown in Fig. 3. Small amounts of soil solution could be removed from the Chehalis soil at 4 bars tension; this corresponds to 18% moisture. Soil solution could be removed from the

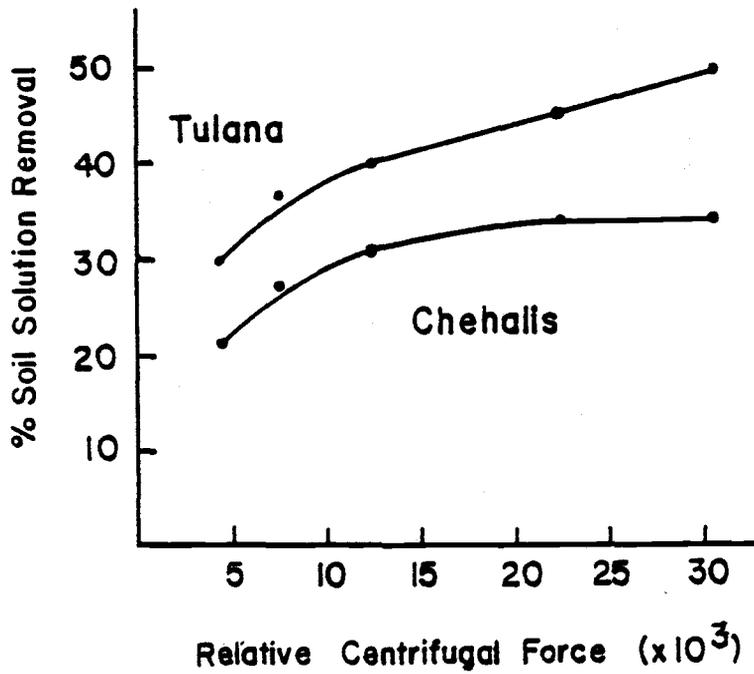


Fig. 3.1. Effect of relative centrifugal force on the percentage of soil solution removed.

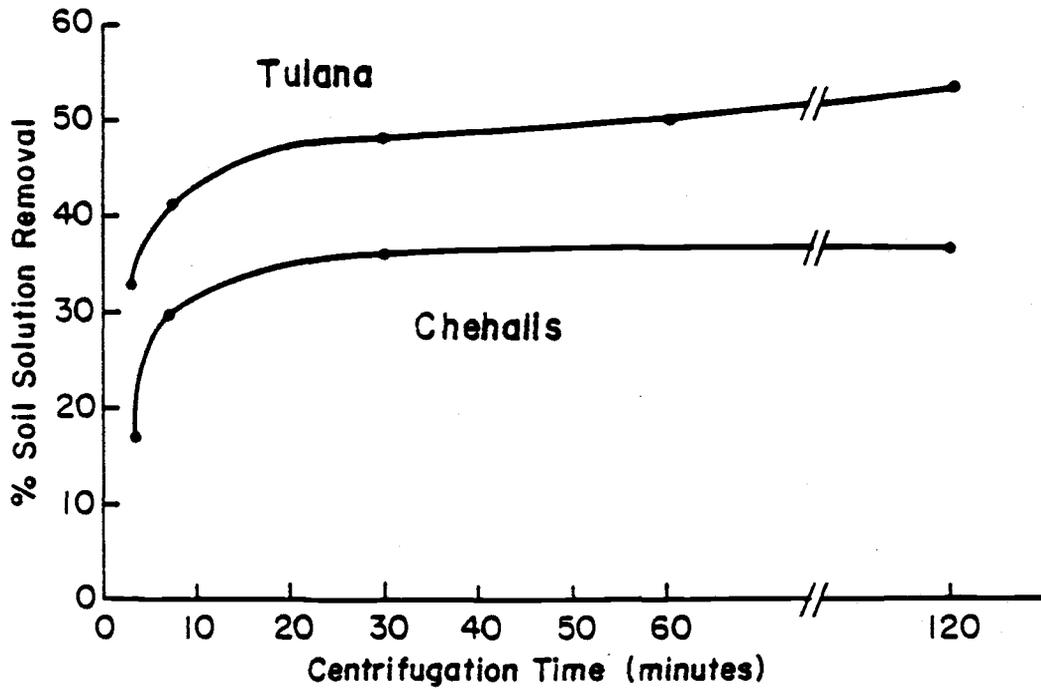


Fig. 3.2. Effect of centrifuge time on the percentage of soil solution removed.

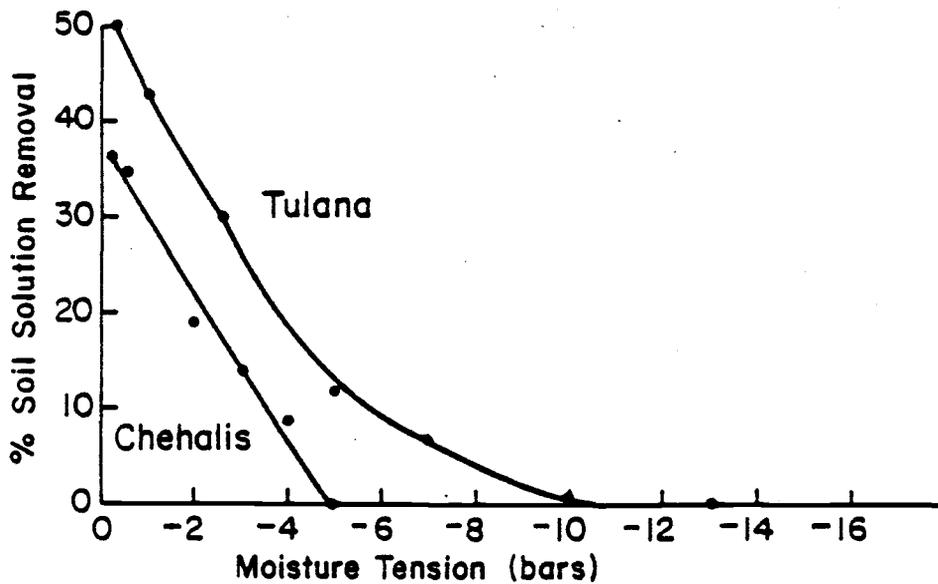


Fig. 3.3. Effect of soil moisture tension on the percentage of soil solution removed.

Tulana soil at a tension of 7 to 8 bars; this corresponds to approximately 55% moisture. The technique more effectively removed soil solution from the Tulana soil; the reasons for this are not known.

Removing the soil solution in an unaltered condition is important. However, there is no generally accepted technique for soil solution removal so establishing the validity of a technique is difficult. One method has been to evaluate the effects of a technique on the Ba^{2+} concentration in equilibrium with BaSO_4 (Murabak and Olsen, 1976). Five grams of reagent grade BaSO_4 were placed in 12 ml centrifuge tubes and deionized water added to bring the moisture content to 50, 100, or 150%. The tubes were then centrifuged as previously described and the Ba^{2+} concentration in the solutions was measured using a Perkin-Elmer Model 4000 atomic absorption spectrophotometer. The Ba^{2+} concentration in the solutions is shown in Table 1. The Ba^{2+} concentration was near the sensitivity limit of the instrument, hence the relatively larger error terms. The calculated Ba^{2+} concentration is 1.37 $\mu\text{g/g}$; centrifugation did not alter the equilibrium concentration from the calculated value. Thus, centrifugation does not alter the equilibrium, at least for this one mineral, and results in the removal of a representative sample of the equilibrium solution.

Limitations of other techniques used to remove or approximate the soil solution include alteration of equilibrium, adsorption or desorption effects, and dilution effects. The equilibrium of many reactions occurring in the soil solution may be altered by the increased gas pressure or vacuum used in some removal techniques. These alterations may in turn modify the composition of the soil solution. Techniques requiring the use of porous membranes, filter papers, or similar materials may alter the composition of the soil solution by selective adsorption or desorption. Effects of this nature were not evident. Dilution of the soil solution, as in saturation paste extracts, is known to alter the composition of the soil solution (Adams, 1971). Calculation of the dilution effect is

generally impossible. None of these limitations appear to apply to this technique.

Table 3.1. Ba^{2+} concentrations in solution removed from BaSO_4 by centrifugation.

Moisture Content	Concentration of Ba^{2+} in Solution
%	$\mu\text{g/g}$
50	2.0 ± 1
100	2.0 ± 1
150	1.6 ± 1
Calculated	1.37

SUMMARY

Soils of Lower Klamath Lake are alkaline (pH 7.5 to 9.0) and have from 15 to 90% organic matter depending on the parent material and past management practices. Widespread Mn deficiency was observed on small grains during the 1976 and 1977 growing seasons. Field experiments were conducted in 1978, 1979, and 1980 to evaluate the effects of N source, rate, and method of application on the Mn concentration and yield of barley and oats. Soils at locations used for these experiments were mildly alkaline (pH 7.6 to 8.3) with 17 to 19% organic matter.

Band application of 22 kg N/ha as AmS or AmCl was more effective than Ur at increasing leaf Mn concentration and yield. Granular or liquid UP materials were intermediate in effectiveness at increasing leaf Mn concentration and yield. When 5.6 kg Mn/ha was applied in the fertilizer band the leaf Mn concentration and yields were similar regardless of N source. There was a tendency for yields to increase when 45 kg N/ha was applied with 5.6 kg Mn/ha.

Phosphorus fertilization increased both leaf P levels and yields but the increases did not necessarily coincide. Leaf Cu levels were increased by Cu fertilization but all Cu concentrations were above the critical level of 4 $\mu\text{g/g}$ and yield responses from Cu were not measured.

A centrifuge technique was developed for removing an unaltered sample of the soil solution. Laboratory experiments confirmed the value of band application of acidic N or P fertilizers. The soil solution pH in simulated fertilizer bands was lowered by the application of AmS or AmCl but Ur application raised the soil solution pH. When MCP was included in the fertilizer band the soil solution pH was lowered regardless of N source. The pH remained depressed in the AmS and AmCl bands but rose in the Ur band.

There was a significant correlation between soil solution pH and Mn concentration in the fertilizer band when Mn was not applied; Mn concentration increased 3.8-fold for each one unit pH drop. Soil solution Mn levels increased dramatically when Mn was applied but the Mn concentration fell rapidly in the Ur band.

Application of MCP markedly increased P concentration in the soil

solution. The P concentration decreased during the course of the experiment regardless of the treatment but fell more rapidly when Ur was applied than when AmS or AmCl were applied. Application of Mn lowered the P concentration in the fertilizer band and tended to increase the P levels 2.5 cm from the fertilizer band. Reasons for this are not clear but the formation of a Mn-P complex which diffused away from the fertilizer band is one plausible explanation.

The results of these experiments reinforce the concept that band application of an acid forming fertilizer is essential in the correction of Mn deficiency of annual crops on Lower Klamath Lake. Grower acceptance of band application of fertilizer has increased markedly since the beginning of these experiments.

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APPENDICES

APPENDIX TABLE 1. Leaf Mn and P concentration and yield of barley grown at Tulana Farm, 1978.

Treatments				Mn and P Concentration		Yield
N ⁺	P [†]	Mn*	Cu ⁺⁺	Mn	P	
----- kg/ha -----				µg/g	%	kg/ha
--	--	--	--	18	0.27	6790
22 AmS	19	--	2.2	18	0.25	6480
22 Ur	19	--	2.2	16	0.27	6910
45 AmS	19	--	2.2	18	0.27	6930
22 AmS	19	5.6	2.2	20	0.25	6190
22 Ur	19	5.6	2.2	23	0.26	6590
45 AmS	19	5.6	2.2	22	0.27	7360
22 AmS	--	5.6	--	23	0.25	6050
22 Ur	--	5.6	--	20	0.27	7760
45 AmS	--	5.6	--	22	0.24	5920
22 AmS	19	5.6	--	18	0.28	6330
22 Ur	19	5.6	--	19	0.28	6820
45 AmS	19	5.6	--	25	0.27	6860
45 AmS [#]	19	--	2.2	20	0.25	6110
LSD _(0.05)				4	NS	920

+AmS = $(\text{NH}_4)_2 \text{SO}_4$ and Ur = urea

†P applied as $\text{Ca}(\text{H}_2\text{PO}_4)_2$

*Mn applied as MnSO_4

++Cu applied as Cu SO_4

#Broadcast before planting

APPENDIX TABLE 2. Effects of fertilizer on the soil solution Cu concentration in the fertilizer band, experiment one.

Source ⁺⁺	Treatments		Incubation Time (Days)			
	N ⁺	P [†]	Mn [*]	7	14	28
	--kg/ha [#]			-----µg Cu/ml-----		
--	--	--	--	0.24	0.08	0.06
AmS	--	--	--	0.25	0.08	0.08
AmS	19	--	--	0.10	0.19	0.09
AmS	--	5.6	5.6	0.10	0.12	0.10
--	19	--	--	0.11	0.09	0.06
AmS	19	5.6	5.6	0.29	0.11	0.07
AmCl	19	--	--	0.14	0.16	0.06
AmCl	19	5.6	5.6	0.19	0.15	0.06
Ur	19	--	--	0.22	0.09	0.13
Ur	19	5.6	5.6	0.28	0.10	0.06
UP(17-44)	25	--	--	0.15	0.14	0.08
UP(17-44)	25	5.6	5.6	NA	0.08	0.13
UP(pH 3)	25	--	--	0.11	0.08	0.06
UP(pH 3)	25	5.6	5.6	0.10	0.07	0.15
UP	25	--	--	0.14	0.07	0.04
UP	25	5.6	5.6	0.11	0.07	0.21

⁺All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[†]P applied as Ca(H₂PO₄)₂ in treatments receiving 19 kg P/ha.

*Mn applied as MnSO₄.

⁺⁺AmS = (NH₄)₂ SO₄, AmCl = NH₄Cl, Ur = urea, UP (17-44) = granular urea-phosphate, UP (pH 3) = urea-phosphoric acid solution, and UP = urea-phosphate solution made from granular urea-phosphate.

[#]Based on 25 cm row spacing.

APPENDIX TABLE 3. Effects of fertilizers on the soil solution Cu concentration 2.5 cm from the fertilizer band, experiment one.

N ⁺	Treatments †		Incubation Time (Days)		
	P †	Mn *	7	14	28
Source ⁺⁺	--kg/ha #		----- µg Cu/ml -----		
--	--	--	0.18	0.06	0.05
AmS	--	--	0.10	0.12	0.06
AmS	19	--	0.14	0.15	0.07
AmS	--	5.6	0.13	0.14	0.08
--	19	--	0.18	0.09	0.04
AmS	19	5.6	0.13	0.10	0.03
AmCl	19	--	0.11	0.08	0.10
AmCl	19	5.6	0.13	0.14	0.07
Ur	19	--	0.28	0.06	0.07
Ur	19	5.6	0.10	0.07	0.07
UP(17-44)	25	--	0.23	0.09	0.07
UP(17-44)	25	5.6	0.15	0.10	0.06
UP(pH 3)	25	--	0.11	0.07	0.06
UP(pH 3)	25	5.6	0.21	0.14	0.06
UP	25	--			
UP	25	5.6	0.08	0.05	0.06
			0.20	0.07	0.08

⁺All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[†]P applied as Ca(H₂PO₄)₂ in treatments receiving 19 kg P/ha.

*Mn applied as MnSO₄.

⁺⁺AmS = (NH₄)₂ SO₄, AmCl = NH₄Cl, Ur = urea, UP (17-44) = granular urea-phosphate, UP (pH 3) = urea-phosphoric acid solution, and UP = urea-phosphate solution made from granular urea-phosphate.

[#]Based on 25 cm row spacing.

APPENDIX TABLE 4. Effects of fertilizers on the soil solution Cu concentration in the fertilizer band, experiment two.

Treatments			Incubation Time (Days)		
N ⁺	P	Mn [†]	7	14	28
Source*	-- kg/ha ⁺⁺ --		----- µg Cu/ml -----		
--	--	--	0.05	0.03	0.04
AmCl	--	--	0.06	0.06	0.04
Ur	--	--	0.07	0.04	<0.01
UP(17-44)	25	5.6	0.06	0.08	0.05
--	--	5.6	0.04	0.04	0.03

⁺ All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[†] Mn applied as MnSO₄

* AmCl = NH₄Cl, Ur = urea, and UP (17-44) = granular urea-phosphate.

⁺⁺ Based on 25 cm row spacing.

APPENDIX TABLE 5. Effects of fertilizers on the soil solution Cu concentration 2.5 cm from the fertilizer band, experiment two.

Treatments			Incubation Time (Days)		
N ⁺	P	Mn [†]	7	14	28
Source*	-- kg/ha ⁺⁺ --		----- µg Cu/ml -----		
--	--	--	0.06	0.03	0.05
AmCl	--	--	0.07	0.07	0.04
Ur	--	--	0.05	0.05	0.03
UP(17-44)	25	--	0.05	0.11	0.04
--	--	5.6	0.04	0.03	0.01

⁺ All N sources applied at 22 kg N/ha, based on 25 cm row spacing.

[†] Mn applied as MnSO₄

* AmCl = NH₄Cl, Ur = urea, and UP (17-44) = granular urea-phosphate.

⁺⁺ Based on 25 cm row spacing.

Appendix Table 6. Standard error of the mean and error degrees of freedom for nutrient concentrations and yields reported in chapter one.

Location	Parameter	SEM	error d.f.
Henzel Farm south field barley, 1978	P Conc.	0.0000427	39
	Mn Conc.	7.674	39
	Cu Conc.	0.358	18
	Yield	1486419	39
Tulana Farm oats, 1978	P Conc.	0.00136	39
	Mn Conc.	26.80	39
	Cu Conc.	0.339	18
	Yield	52284	39
Henzel Farm south field oats, 1978	P Conc.	0.00067	39
	Mn Conc.	21.364	39
	Cu Conc.	2.044	18
Henzel Farm north field barley, 1979	Mn Conc.	2.94	54
	P Conc.	0.00024	54
	Yield	846805	54
Henzel Farm south field barley, 1979	Mn Conc.	8.83	54
	P Conc.		
	3-4 leaf early to mid tillering	0.0022	12
		0.00052	54
	Yield	506529	54
Henzel Farm south field oats, 1979	Mn Conc.	2.873	15
	Yield	138499	10
Henzel Farm north field barley, 1980	Mn Conc.	10.4	27
	P Conc.		
	3-4 leaf early to mid tillering	0.0027	6
		0.008	27
	Yield	776716	27
Henzel Farm south field barley, 1980	Mn Conc.	41.37	33
	P Conc.		
	3-4 leaf early to mid tillering	0.0089	9
		0.0034	33
	Yield	309883	33

Appendix Table 7. Standard error of the mean and error degrees of freedom for pH, Mn, and P concentrations reported in chapter two.

Parameter	SEM			error d.f.		
	-----incubation time (days)-----					
	7	14	28	7	14	28
Soil solution pH in fertilizer band, exp't one.	0.398	0.364	0.121	22	22	22
Soil solution pH one inch from fertilizer band; exp't one.	0.0953	0.1188	0.0441	22	22	22
Soil solution Mn concentration in fertilizer band; exp't one.	102.941 ⁺ 0.0391 [‡]	35.256 ⁺ 0.0181 [‡]	26.185 ⁺ 0.0112 [‡]	22 ⁺ 14 [‡]	22 ⁺ 14 [‡]	22 ⁺ 14 [‡]
Soil solution Mn concentration one inch from fertilizer band; exp't two.	0.0191	0.0069	0.100	22	22	22
Soil solution P concentration in fertilizer band; exp't one.	2379.86	1722.87	526.07	22	22	22
Soil solution P concentration one inch from fertilizer band; exp't one.	41.48	18.68	6.981	22	22	22
Soil solution pH in the fertilizer band; exp't two.	0.0047	0.0137	0.0428	8	8	8
Soil solution pH one inch from fertilizer band; exp't two.	0.0125	0.0082	0.0182	8	8	8
Soil solution Mn concentration in fertilizer band; exp't two.	6.226 ⁺ 0.0011 [‡]	3.904 ⁺ 0.0004 [‡]	0.198 ⁺ 0.0018 [‡]	8 ⁺ 6 [‡]	8 ⁺ 6 [‡]	8 ⁺ 6 [‡]

⁺ Valid for comparisons involving any treatment with the check band.

[‡] Valid for comparisons involving treatments not receiving Mn with the check band.