

THE UNIVERSITY OF MANITOBA

INFLUENCE OF SOIL WATER CONTENT ON SOIL REDOX  
POTENTIAL (Eh), pH AND CONCENTRATION AND PLANT  
AVAILABILITY OF IRON AND MANGANESE IN SOIL SOLUTIONS

by

Michael O. Olomu

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## ABSTRACT

The changes in Eh, pH and concentrations of Fe and Mn in six Manitoba soils saturated with water were studied. The concentrations of Fe and Mn in soil solution increased as Eh and/or pH decreased; the soils containing large amounts of clay and/or organic matter showed a noticeable delay in the release of Fe and Mn into solution following soil reduction. Increase in Mn concentration preceded that of Fe after the initiation of saturation and Mn remained at a higher concentration than Fe for the entire duration of saturation. The two most strongly reduced soils had the lowest contents of  $\text{NO}_3\text{-N}$ , relatively high amounts of organic matter and released the largest amounts of Fe and Mn. The less reduced soils either had relatively high contents of  $\text{NO}_3\text{-N}$  or relatively low amounts of organic matter. Eh-pH diagrams indicated that  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{MnCO}_3$  were the compounds in equilibrium with Fe and Mn ions in soil solution.  $E^\circ$  values calculated from experimentally measured Eh, pH and  $\log(\text{Fe})$  or  $\log(\text{Mn})$  further indicated the presence of the  $\text{Mn}_2\text{O}_3\text{-Mn}^{2+}$  redox system but not that of the  $\text{Fe}_2\text{O}_3\text{-Fe}^{2+}$  redox system. Measurements of both Eh and pH accounted for more of the variation in the concentrations of Fe and Mn in soil solution than did Eh or pH alone. Concentrations of Fe, calculated from experimentally measured Eh and pH, were several fold lower than the concentrations of Fe measured

in soil solution. The concentrations of Mn, similarly calculated, came to within  $\pm 50\%$  of measured concentrations in about 33% of the instances.

The data indicated that almost all the Fe in soil solution was complexed with organic matter. Mn was either not complexed or only weakly complexed. The metal-organic matter complexes were negatively charged. The soil solutions had a greater affinity for Fe than did  $10^{-4}$ M EDTA. Calculations based on the assumption that the relative stability constants of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  with soil organic matter are the same as those with EDTA, indicated that the Fe in the Fe-organic matter complexes was probably  $\text{Fe}^{\text{III}}$ . The very high degree of complexing of Fe in soil solution was most probably responsible for the failure to obtain the theoretical  $E^\circ$  values for the  $\text{Fe}_2\text{O}_3\text{-Fe}^{2+}$  redox system from the experimental data.

The utilization of Fe and Mn by flax and oat plants grown under varying water regimes was also studied. Flax plants became chlorotic on four of the six soils when they were grown at 150% of field capacity moisture content. Oat plants developed normally on all the soils under all water levels. Chlorotic flax plants had lower yields, contained less Fe and more Mn than did the non-chlorotic plants. The ratio of Mn to Fe in chlorotic flax plants was four or greater; the non-chlorotic plants had lower Mn:Fe ratios. Yields of flax, measured after 35 days of growth, decreased with increases in the Mn content and Mn:Fe ratio of the plants. The  $r^2$  values for the relationships of yield and Mn

content and yield and Mn:Fe ratio were 0.54 and 0.59, respectively. The yields of flax increased with increases in the Fe content of the plants ( $r^2 = 0.33$ ). Contents of Fe and Mn and Mn:Fe ratio in oat tops were lower than those for flax. Mn content of oats increased with increasing soil moisture content but was not present in toxic amounts.

Irrespective of soil moisture regime, exceedingly large amounts of Fe and only small amounts of Mn accumulated in flax roots. Absorption or translocation of Fe by flax plants was unrelated to oxygen supply in the soil. In two of the soils in which bicarbonate content was measured, the bicarbonate ion concentrations were negatively correlated with Fe in the tops of flax grown on the two soils. Complexing of Fe as  $\text{Fe}^{\text{III}}$  by organic matter in soil solution and the accumulation of bicarbonate in saturated soils may be partly responsible for the decreased utilisation of Fe by flax plants under increased soil moisture conditions.

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## CHAPTER I

### INTRODUCTION

Flax plants afflicted with chlorosis or yellowing are a common feature in most Manitoba farm fields during the spring and early summer when most of the soils are wet or water-logged. Attempts to correct this chlorosis by applications of nitrogen and/or phosphorus fertilisers have not been successful. It has also been observed that cereal crops grown on plots adjacent to the chlorotic flax plots, have developed normally without becoming chlorotic.

Chlorotic flax plants growing on wet soils have also been reported in the two American states, Minnesota and North Dakota, which have common borders with Manitoba (46,81). Flor (46) reported that local areas bearing chlorotic plants are a conspicuous feature of many flax fields in the Red River Valley of North Dakota and Minnesota during the early summer. Flor described the abnormal condition of the flax plants as chlorotic dieback. As a result of the favourable responses shown to phosphate fertilisation by some of the chlorotic plants, he suggested that the chlorosis of the flax plants was caused, at least in part, by deficiency or unavailability of essential minerals, especially phosphate, in the highly calcareous alkaline soil.

King et al. (81) reported chlorosis of flax plants

in the upper Red River Valley of Minnesota. They showed that this chlorosis could not be corrected by application of fertilisers and soil amendments; correction was however obtained by spraying the plants with solutions containing iron.

In the cases and studies reported above, the soil and plant factors which must have resulted in the development of chlorosis were not investigated.

Since chlorosis generally results in reduced plant growth (especially where an annual plant does not recover from the condition throughout the growing season) with consequent reduction in yields, effective methods of correcting it would be of practical and economic significance. A knowledge of the soil and plant factors that induce chlorosis in flax would also aid in developing methods of correcting this undesirable condition in flax.

The objective of the present study was, therefore, the investigation of some of the soil and plant factors that induce chlorosis in flax plants grown in some Manitoba soils.

Specific approaches to the problem were as follows:-

(a) An investigation of chemical changes that occur in soils continuously saturated with water. The chemical changes studied included oxidation-reduction (redox) potential (Eh), pH and the concentrations of Fe and Mn in soil solution. Fe and Mn were chosen for study because they undergo oxidation and reduction in the soil by virtue of their multivalent nature and since their concentrations

and/or physiology in plants have often been associated with chlorosis.

(b) An investigation of the concentrations of Fe and Mn in flax and oat plants grown under different water regimes in the greenhouse.

(c) A study of the uptake patterns of Fe and Mn by flax plants subjected to different levels of aeration.

(d) A study of the  $\text{HCO}_3^-$  ion contents of soils at different water regimes and levels of aeration, since this ion has been implicated as a causative factor in lime-induced chlorosis in calcareous soils.

The chemical studies were supplemented by studies of the quantitative relationships between Eh, pH and the concentrations of Fe and Mn in the soil solutions and the factors that affect these relationships. The identification of the stable Fe and Mn compounds in the soils was also attempted by use of Eh-pH diagrams.

## CHAPTER II

### REVIEW OF LITERATURE

#### A. IRON AND MANGANESE IN SOILS

##### 1. Occurrence:

Iron, Fe, forms about 5.6% of the earth's crust or lithosphere and thus ranks fourth in abundance among the chemical elements in the earth's crust, after oxygen, silicon, and aluminum (67,82,149). Iron combines readily with other chemical elements and is a common constituent of many hundreds of minerals among which are the oxides such as hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ), ferrous carbonate or siderite ( $\text{FeCO}_3$ ), ferric carbonate ( $\text{Fe}_2(\text{CO}_3)_3$ ) and the sulfide or pyrite ( $\text{FeS}_2$ ). Limonite ( $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) may be formed through hydration and oxidation of siderite (149). Magnetite, a magnetic oxide of iron, can be regarded as a mixed oxide of iron (II) and iron (III):  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ .

Iron is present in many primary minerals such as hornblende, biotite and chlorite which are decomposed by physical and chemical weathering reactions to secondary minerals, such as oxides and hydroxides.

The element Fe is very abundant in soils, the amount ranging from 0.02% to at least 10%. The soils termed "ferruginous" contain a high percentage of Fe, which gives the soils a reddish colour. The Fe content of soils is

usually reported as iron oxide ( $\text{Fe}_2\text{O}_3$ ) soluble in hydrochloric acid;  $\text{Fe}_2\text{O}_3$  contains 70% Fe. According to Sauchelli (149), rarely do soils contain less than 2% iron oxide (equivalent to 1.4% Fe).

Manganese, Mn, forms about 0.095% of the earth's crust; thus ranking twelfth in abundance among the chemical elements in the earth's crust (67,82,149). Manganese occurs in a number of minerals, the most important being pyrolusite ( $\text{MnO}_2$ ) braunite ( $\text{Mn}_2\text{O}_3$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ ), manganite ( $\text{MnO}(\text{OH})$ ) and rhodochrosite ( $\text{MnCO}_3$ ). It also occurs as a trace constituent in some of the primary minerals, hornblende, olivine, biotite, garnet and augite (149). The manganese minerals are generally associated with iron.

The total amount of Mn in soils varies widely from a trace to more than 7%. Some soils in the Hawaiian Islands contain as much as 15% MnO, equivalent to 11.6% Mn (149). Sauchelli (149) reported values of 0.01 to 0.5% Mn for most arable soils in the United States, 0.02% Mn for some soils in Scotland and 0.01 to 0.13% Mn for soils in different parts of India. Reid and Webster (137) reported a range of 0.12 to 0.28% total Mn for a number of Alberta and Ontario soils.

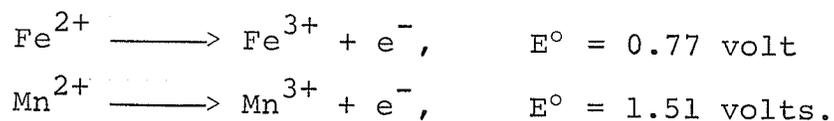
Hodgson (67), in a review of the chemistry of the micronutrient elements in soils, listed five general ways in which an element could be bound in soils: (i) it could be associated with soil surfaces, either in organic or in inorganic forms; (ii) it could become occluded during development of new solid phases in which it is not a principal

constituent; (iii) it could precipitate with other soil components, forming a new phase; (iv) it could occupy sites in soil minerals either as an original constituent or by entering the crystal lattice through solid state diffusion; or (v) it could become incorporated in biological systems and their residues in the soil. A knowledge of the reaction predominating and controlling the distribution of elements between soil matrix and soil solution is fundamental to an understanding of the soil chemistry of all nutrients. Unfortunately, the distinction between these forms is not always possible. The differentiation between surface adsorption and precipitation reactions, for example, is extremely difficult. According to Hodgson (67), Fe and Mn under conditions of satisfactory aeration are bound principally as precipitates of oxides and phosphates in most soils.

## 2. General Chemical Properties

Fe and Mn belong to the subgroups of elements collectively referred to as the transition elements in the periodic classification of the elements. Fe has an atomic number of 26 while Mn has an atomic number of 25 (153). Fe and Mn have electronic configurations of  $3d^64s^2$  and  $3d^54s^2$ , respectively, beyond the argon core (92). Fe shows a maximal oxidation state of +6, but generally only the +2 and +3 states are common. Mn shows oxidation states of +2, +3, +4, +6 and +7 (85,92,153). In the +2 state, Fe exists as the ferrous ion ( $Fe^{2+}$ ) while Mn exists as the manganous ion

(Mn<sup>2+</sup>) (67,149). The equations for the oxidation of the +2 to the +3 state, for the two elements are as follows (82,85):-



where:

$e^{-}$  = electron and

$E^{\circ}$  = standard electrode potential for the half-cell.

The standard potentials show that it is much easier to oxidise Fe<sup>2+</sup> than Mn<sup>2+</sup>.

In soil solutions and natural waters, the Fe<sup>3+</sup> ion appears in solution only in the lower range of the pH scale except where it is complexed with organic matter or present as various hydroxylated Fe ions and polymeric forms of Fe. Garrels and Christ (49) state that the Fe<sup>3+</sup> ion concentration is negligible above pH values of about 2, and is low at pH values of 1. Thus, the role of ferric ion as an important species in nature may have been overplayed since natural waters rarely have a pH of 2 or less (49). Mn can exist as manganic ion (Mn<sup>3+</sup>) only in solids and complex ions (149).

### 3. The Theory of pH Measurement

$$\text{pH} = -\log (\text{H}^+)$$

The above definition, although exact, is a purely formal one, since it involves the activity of a single ion, a quantity that cannot be measured directly. As a result of this, measured pH is defined in terms of an operational procedure (49).

Measurement of pH is accomplished by the use of an EMF cell that consists of a glass electrode and a reference electrode (e.g., calomel). The reference electrode has a constant potential while the potential of the glass electrode varies with hydrogen ion activity. The overall voltage is a function of the hydrogen ion activity. This cell may be written

Ag, AgCl; solution of known pH; glass; solution of unknown pH, KCl (sat.); Hg<sub>2</sub>Cl<sub>2</sub>, Hg.

The half-cell potential of a hydrogen ion sensitive glass electrode for a solution having hydrogen ion activity (H<sup>+</sup>)<sub>x</sub> is given by:

$$E'_x = C_H + \frac{2.303RT}{F} \log (H^+)_x$$

i.e. 
$$E'_x = C_H - \frac{2.303RT}{F} \text{pH}$$

where:

$E'_x$  = half-cell potential of glass electrode

$C_H$  = asymmetry potential

$F$  = the Faraday = 23.06Kcal/mole-volt

$R$  = the gas constant = 1.98726 cal/deg mole

$T$  = absolute temperature; °K

If "liquid junction potentials" are neglected, the overall potential of the cell is given by the difference between the two half-cell potentials:

$$E_x = E'_x - E_{\text{ref}} = C_H - \frac{2.303RT}{F} \text{pH} - E_{\text{ref}}$$

where:

$E_x$  = overall potential of the cell

$E_{ref}$  = half-cell potential of the reference electrode.

Thus, if a given experimental arrangement, represented by the cell above, is used first to determine the EMF developed by a solution whose pH is to be measured and then the test solution is replaced by a standard reference solution of assigned pH value,  $pH_s$ , and the new EMF measured (at the same temperature), the relationships could be represented as follows:

$$E_t = C_H - \frac{2.303RT}{F} pH_t - E_{ref} \quad . . . (i)$$

and 
$$E_s = C_H - \frac{2.303RT}{F} pH_s - E_{ref} \quad . . . (ii)$$

(where:

$E_t$  = EMF of the test solution,

$pH_t$  = pH of the test solution and

$E_s$  = EMF of the standard solution of known pH.)

Subtracting (ii) from (i), and rearranging the equation, the following relationship is obtained:

$$pH_t = pH_s - \frac{F (E_t - E_s)}{2.303RT} \quad . . (iii)$$

This last equation (iii) is the basis for the modern operational definition of pH.

A "liquid junction potential" arises at the interface of the solution of unknown pH and KCl(sat.). The use of the saturated KCl bridge helps to minimize this potential. If the unknown and standard solutions are nearly alike in

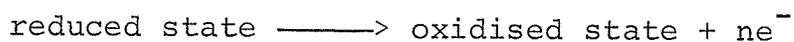
composition and concentration, then the liquid junction potential will be the same for each solution and need not be considered.

#### 4. The Theory of Eh Measurement

The oxidation reduction potential, Eh, is defined as the potential of a half-cell, referred to the standard hydrogen half-cell, the EMF of the standard hydrogen half-cell being taken as zero at all temperatures (49).

Oxidation reduction potential is measured with an electrode pair consisting of an inert electrode (e.g. platinum) and a reference electrode. The inert electrode acts as an electron acceptor or donor to the ions in the measured solution. When connected to the calomel electrode, the platinum electrode can accept electrons from dissolved ionic species, or it can furnish electrons, depending on whether the potential of the half-cell containing the dissolved species is greater or less than that of the reference electrode.

The half-reaction for every oxidation-reduction system can be written as:



and the corresponding half-cell potential as:

$$E_h = E^{\circ} + \frac{RT}{nF} \ln \frac{(\text{oxidised state})}{(\text{reduced state})}$$

where:

n = number of electrons involved in the reaction.

The above equation is normally referred to as the Nernst equation.  $E^\circ$  could be evaluated from the following relationships:

$$\Delta G^\circ = -nE^\circ F = -RT \ln K$$

where:

$\Delta G^\circ$  = standard free energy change of the reaction

and  $K$  = equilibrium constant.

The overall cell EMF is given by

$$EMF_{\text{cell}} = E_{\text{h, reduced state, oxidised state}} - E_{\text{h, ref}}$$

In order to obtain the activity ratio of dissolved ionic species by applying the experimental Eh value and the Nernst equation, the following assumptions are generally made:

(i) All species involved in the oxidation-reduction system are in equilibrium. In general, this assumption is satisfactory for simple dissolved species, with the notable exceptions for inorganic ions, of sulfate or bisulfate ions and dissolved oxygen.

(ii) The platinum electrode functions as an inert electrode. In some solutions the platinum may react and become coated with another substance, in which case the readings are useless for calculations involving dissolved species.

##### 5. Oxidation and Reduction of Fe and Mn in Soils and the Chemical Changes in Waterlogged Soils

Fe and Mn participate in oxidation and reduction reactions because they can change their oxidation states.

They tend to exist in oxidised forms in weathered soils. Some reduced Fe and Mn are present in all soils, particularly water-logged soils but they revert easily to the oxidised condition on aeration (98).

Redox potential, Eh, is a quantitative measure of the intensity of oxidation or reduction (49,85,98,124,133).

Since a number of studies (72,128) have clearly demonstrated that redox and other chemical changes that take place in soils are the same for saturated (water-logged) and flooded (submerged) soils, the terms, water-logged, saturated, flooded and submerged are used interchangeably in this review.

In recent years, the greatest interest in the study of redox reactions of Fe and Mn in soil has been shown in tropical and semi-tropical parts of the world where rice is grown under water-logged culture. These studies have also received some interest in areas of temperate climate, especially in areas where some soils get sufficiently wet or water-logged during the spring and summer to produce highly reducing conditions. In such instances, some micronutrient ions (especially Mn) may accumulate in amounts toxic to crops. Harter and McLean (57), working in Ohio, showed that soils could be drastically reduced at water levels just above field capacity and that toxic amounts of micronutrients could come into solution under such conditions.

Apart from the redox potential, the pH of the soil is also known to affect the chemistry of Fe and Mn in the soil

(45,67,121). Organic matter and micro-organisms also affect the chemistry of soil Fe and Mn in various ways, notably by complex formation and alteration of the Eh or pH of the soil (1,8,55,67,70,97,105,156,159). According to Hodgson (67), the most important microbiological effects on the availability of micronutrients involve the oxidation and reduction of Fe and Mn.

The sequence of chemical changes that take place in flooded soils has been studied and reviewed by a number of workers (72,124,128,142). In studies conducted at the International Rice Research Institute (IRRI) in the Philippines (72) and in a review by Ponnampereuma (128), the sequence of chemical changes was given as follows: depletion of oxygen, accumulation of carbon dioxide, denitrification, accumulation of ammonium ions, anaerobic decomposition of organic matter, reduction of Mn compounds and the reduction of Fe compounds. Flooding a soil cuts off the oxygen supply of the soil micro-organisms (128). The aerobic organisms use up the oxygen present in the soil and become quiescent or die. In the absence of oxygen, anaerobes utilise oxidised soil components such as  $\text{NO}_3^-$ , manganic oxides (95), ferric oxide, sulfate, phosphate and dissimilation products of organic matter as electron acceptors in their respiration, and thus reduce the soil.

The occurrence of large amounts of reduced Fe and Mn in water-logged soils has been reported by many workers (34, 38,57,70,74,93,97,106,109,111,129,136,141,163). Most of

these reports have emphasised the importance of micro-organisms and organic matter in enhancing the amounts of reduced Fe and Mn released. It has also been generally observed that the release of reduced Mn precedes that of reduced Fe.

6. Environmental Factors Affecting Redox Potential (Eh) and pH Values in Soils and Soil Solutions

Eh and pH, as quantitative measures of geochemical environments, are the consequence of an overall chemical balance of the entire chemical substances present, and not vice versa (148). An assumption is involved in this method of describing a geochemical environment, namely, the Eh and pH values of a geochemical system are largely controlled by the chemical properties and relative amounts of predominant reactive substances present, and can be treated as fixed quantities so long as those substances remain dominant or constantly supplied to the system (148). Other substances present in minor amounts are expected to stay conformable with fixed Eh and pH. Thus, the chemical balance of a system or environment (e.g. soil or soil solution) will determine the magnitudes of its Eh and pH.

Bass Becking et al. (2) also state that the substances formed and utilised in microbial reactions determine both the hydrogen-ion concentration (pH) and the electrode potential (Eh) of their environment. These authors stress that measurements of Eh and pH may often indicate the

ecology of an environment since living systems play a major role in controlling the aqueous milieu. Quispel (135) showed that the redox potential of well-aerated soils, in the absence of reducing substances, will be determined primarily by oxygen while, in more reduced soils, it will be determined by the concentration of soluble reversible redox-systems. Merkle (98) has suggested that dissolved oxygen in the soil solution is responsible for a part of the potential measured.

Rodrigo (142) reported that the factors which influence the redox potentials of soils are the degree of aeration, the content of readily decomposable organic matter and the base status of the soil. Good aeration, absence of excessive microbiological activity and a low base status are conducive to high potentials. The opposite conditions are favourable for low redox potentials. Peech and Boynton (125), showed that water-logging caused a marked drop in potential only in soils containing readily oxidisable organic matter and attempted to correlate susceptibility to reduction on water-logging to their C:N ratio. Pearsall (124) showed that this ratio must exceed 20 for a marked drop of potential to occur on water-logging. The association between organic matter and redox potentials suggests that microbial activity is involved.

In a study of redox potential trends in a submerged rice soil, Kalpage (78) reported that the Eh values were not significantly affected by different levels of added fresh

organic matter, but were depressed by cropping during the period of intensive vegetative growth due to oxygen consumption by the roots.

Bonner and Ralston (8) studied the redox potential of saturated forest soils and observed that large decreases in redox potentials over a 25-day incubation period were favoured by high temperature and the addition of sucrose or tree litter. The addition of a complete nutrient solution had no effect in soils incubated with sucrose, but it reduced the drop in potential in soils incubated with tree litter at 21 to 27° C. From these observations the authors stressed the need for care when evaluating soil aeration by means of redox potentials and also the dominant role of soil microorganisms in activating redox systems.

Baas Becking et al. (2), in a survey of the limits of the natural environment in terms of pH and Eh, found that variation in the molecular oxygen content of water appeared to have no direct influence on Eh, except at very low oxygen tensions. The presence of small amounts of oxidisable matter, both organic and inorganic will, however, be reacted on by molecular oxygen, thus generally poisoning the system at a lower Eh.

Turner and Patrick (163) studied the relation between soil oxygen content and redox potential in 10 Louisiana soils maintained at  $\frac{1}{3}$  bar moisture percentage and showed that decreasing oxygen content had little effect on redox potential until an oxygen content below 4% was reached.

They showed that, below 4% oxygen, a marked change in redox potential occurred, with an average redox potential at zero oxygen of  $332 \pm 5$  millivolts.

Krauskopf (82) and Garrels and Christ (49) have discussed the role of oxygen in the determination of the magnitude of redox potentials in natural media. They stated that redox potentials measured in oxygen-containing environments are generally lower than equilibrium values and there is no simple way to apply a correction factor. The lower potential which is measured is due to the fact that most reactions in which oxygen plays a role take place by a series of steps, and one of the steps is very slow. Sato (148) attributes the sluggishness of oxygen reactions, at room temperature, partly to the initial difficulty in breaking the bond between the two oxygen atoms. According to him, the faster reactions of oxygen are those in which the bond remains unbroken. Garrels and Christ (49) further state that the effect of the oxygen of the atmosphere is to provide a relatively mild oxidizing effect, with an Eh of about 0.650 to 0.700 volt at pH = 0, and of 0.300 to 0.350 volt at pH = 8. Although this effect is far less than theoretical, admission of air into systems of originally low Eh is followed by rapid reaction to the "irreversible" potential. Also, there seems to be some tendency for direct action of dissolved oxygen on the platinum electrode, so that the potential observed in systems containing dissolved air is to a certain extent independent of the oxidation

state of the dissolved components. Thus, systems exposed to the air show potentials (in volts, at 25° C) according to the approximate relation (49):

$$Eh = 0.70 - 0.06 \text{ pH.}$$

This is in contrast to the expected value at equilibrium of:

$$Eh = 1.23 - 0.06 \text{ pH.}$$

According to Garrels and Christ (49), it is difficult to measure natural systems out of equilibrium with air because of the problem of introducing electrodes without simultaneously introducing air.

The pH of a redox system affects the degree of ionisation and hence will alter the redox potentials. The Eh increases in many systems by about 0.060 volt for each unit lowering of the pH value of the system. That is, the same system will have lower Eh values in the alkaline range than in the acid range (98). The change in redox potential with pH can alter the relative position of a system on the redox scale and thus has great significance in the interpretation of redox potentials in soils (142). Jeffery (77), however, takes the view that there is little point in adjusting Eh measurements, in the field, for pH change since such measurements involve large errors.

In a study of the chemistry of water-logged soils, Rodrigo and Pollard (143) observed that when normally dry soils were submerged in water, the pH increased and Eh decreased in both soil and supernatant liquid, equilibrium values being attained in 80 days.

Redman and Patrick (136) studied the effect of submergence on several biological and chemical soil properties and reported that redox potential was closely related to soil pH. Generally, pH of acid soils increased and that of alkaline soils decreased after submergence.

Fairly detailed studies of the influence of several environmental factors on the pH and Eh of water-logged soils have been conducted at the IRRI (71,72) and reported by Ponnampereuma (128) and Ponnampereuma *et al.* (132). These studies showed that the pH values of acid soils increased on flooding while those of calcareous soils decreased. It was also found that carbon dioxide content of soils had a marked influence on the pH values of flooded soils. This was demonstrated by stirring the soil solution from a flooded latosolic soil in an atmosphere of nitrogen; after 30 minutes of gentle magnetic stirring, the pH increased from 6.60 to 7.80 and the Eh decreased from + 40 mv to - 320 mv. The nitrogen gas displaced the carbon dioxide in the soil solution. The effect of the carbon dioxide was seen to be more pronounced at low than at high partial pressures of  $\text{CO}_2$  ( $p\text{CO}_2$ ). The rate of pH increase was highest in the soils that rapidly underwent reduction and lowest in soils whose reduction was retarded by the presence of nitrate or insufficient organic matter. Ponnampereuma *et al.* (132) have derived some quantitative relationships between redox potential, partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) and pH of flooded soils. They showed the increase in soil solution pH of the acid soils to be

quantitatively related to the potential of the  $\text{Fe}(\text{OH})_3 - \text{Fe}^{++}$  system; the decrease in pH of the alkali soils to be defined by  $\text{pCO}_2$  through the  $\text{Na}_2\text{CO}_3 - \text{H}_2\text{O} - \text{CO}_2$  system and the decrease in the pH of calcareous soils to be defined by  $\text{pCO}_2$  through the  $\text{CaCO}_3 - \text{H}_2\text{O} - \text{CO}_2$  system. According to Ponnampereuma (128) the course of Eh changes, in a soil, on flooding, is determined by the initial aerobic potential, the temperature, the content of organic matter and the nature and content of electron acceptors present in the soil. The higher the initial aerobic potential, the steeper the decline on flooding. Temperatures below  $35^\circ \text{C}$  retard fall in Eh; above  $35^\circ \text{C}$ , temperature has no significant effect up to  $60^\circ \text{C}$ . The overriding factors controlling Eh kinetics, according to Ponnampereuma (128), are the nature and amount of organic matter and the kind and content of oxidised soil components.

In a more recent study of the influence of temperature on the chemical reactions in flooded soils, Ponnampereuma and Loy (130) reported that soil reduction and accompanying chemical changes generally were slowest at  $15^\circ \text{C}$ , fastest at  $25^\circ$  and  $35^\circ \text{C}$ , and intermediate at  $45^\circ \text{C}$ .

In an IRRI study (71) of the changes in Eh of thirty-one rice soils, it was observed that (a) soils low in organic matter (less than 1.5%) or high in active Mn (Mn more than 0.2%) maintained positive Eh values for almost six months; (b) active ferric Fe at a concentration of 4.5% Fe did not retard the decline of Eh until the potentials had

fallen to about - 50 mv; (c) soils low in active Fe and Mn (coarse textured soils) with more than 3.0% organic matter showed the steepest declines in Eh and attained Eh values lower than -200 mv within two weeks of submergence.

7. Eh-pH Diagrams and the Applications of Thermodynamics to Redox Equilibria in Soils and Soil Solutions with Particular Reference to Fe and Mn

Under conditions of chemical equilibrium in a solution containing ferric and ferrous Fe or manganic and manganous Mn, the redox potential is a function of the relative activities of the oxidised and reduced forms of Fe and Mn that are present. Also, under equilibrium conditions, the degree of dissociation of oxidised and reduced Fe and Mn compounds is a function of the hydrogen-ion concentration or pH of the solution (2,49,64,82,148).

A convenient means of representing these relationships is the stability field (Eh-pH) diagram. This diagram is a plot of pH values (abscissas) versus Eh values (ordinates) on which areas may be designated by thermodynamic computations to show the conditions under which specific ionic species dominate. Conventions and methods for constructing Eh-pH diagrams have been discussed in detail by a number of authors (2,49,64,82,148).

A review of the literature shows that work on the applications of Eh-pH diagrams and thermodynamic principles to the study of natural waters and solutions has been largely pioneered by geologists (2,49,61,62,63,64,148). It

is only in recent years that soil scientists have started applying these methods and principles to the studies of soils and soil solutions (5,6,9,35,36,72,73,107,131,133).

The fundamental relationship which fixes the position of the line dividing oxidised from reduced species is the Nernst equation. All the stable or metastable phases or ion species depicted in an Eh-pH diagram are within the upper and lower stability limits of water (49) since all the transformations from one phase to the other take place in water. Garrels and Christ (49) stipulate the upper limit of water stability as the equilibrium between water and oxygen at one atmosphere and the lower limit as the equilibrium between water and hydrogen at one atmosphere. The range of Eh and pH that must be considered in constructing diagrams is determined by the limits of values observed in nature (49).

Baas Becking et al. (2) have summarised all the Eh and pH measurements available in the literature. These investigators discussed in detail the factors that control Eh and pH, with emphasis on biologic aspects, and presented a comprehensive bibliography. Their investigations showed that Eh measurements on most aerated surface waters fall along a line well below, but roughly parallel to, the upper boundary of water stability. This line is the "irreversible oxygen potential," and has been explained by Sato (148) as being the  $H_2O_2 - O_2$  stability boundary on the basis that oxidation by oxygen has to go through a rate-controlling hydrogen peroxide step.

Eh-pH diagrams are also used for plotting the fields of stability for specific Fe and Mn minerals. This is done by writing the equations for the reactions relating the minerals of interest and calculating  $E^\circ$  from  $\Delta G^\circ$  (the standard free energy change) for the reactions (49,64,82). For minerals which are in the form of carbonates, an extra variable ( $p\text{CO}_2$  or total dissolved  $\text{CO}_3^{=}$ ) is required in addition to Eh and pH for determining and plotting the fields of stability. The partial pressure of  $\text{CO}_2$ , however, is usually fixed at a certain value and the Eh-pH diagram constructed, using only pH and Eh as variables. Since free energy of formation values are available for numerous ionic species, it is possible to calculate the activities of these species in equilibrium with the solid Fe and Mn minerals (49,82).

The use of Eh-pH diagrams is subject to the usual limitations encountered in applying quantitative chemistry to natural systems (82). Limitations are imposed by (i) the greater number of variables in natural situations and (ii) assumption of equilibrium. Another limitation is the arbitrary choice of  $p\text{CO}_2$  and total  $\text{CO}_3^{=}$  concentration in systems involving carbonate species. The relative stability of some minerals is evidently dependent on the activity of the water in which they occur; however, the activity of water is not usually taken into account in delineating the stability fields. The stability fields shown on the Eh-pH diagrams are for pure Fe or Mn compounds. Isomorphous substitution of other metals for Fe, for example, is common,

particularly magnesium and manganese in siderite and magnetite, and these impurities will change the field boundaries. Changes from one mineral to another are slow; a compound might therefore occasionally persist metastably under conditions where the equilibrium relations shown on the Eh-pH diagram would not permit.

The thermodynamics of flooded soils have been extensively studied at the IRRI (72,73) and by Ponnampereuma et al. (131,133). The problems involved in the quantitative treatment of redox equilibria in flooded soils and how they may be partly overcome have been reviewed by Ponnampereuma et al. (133). Studies conducted at the IRRI (72,73) established that the clear soil solution, drawn out by gravity from the flooded soil, may be considered the equilibrium soil solution and the thermodynamically meaningful phase. In these studies, it was found that the potentials of soil solutions were highly reproducible, of the right order of magnitude and reflected the changes in activities of the ions participating in redox equilibria. Potentials measured in soils varied markedly with the location of the electrodes and were far too low in terms of the inorganic redox systems operating in flooded soils. In general, Eh and pH determinations of the soil solution are more reliable because of lower liquid junction and carbon dioxide errors, as compared to measurements in soil.

The iron hydroxide and manganese oxide systems were

studied by Ponnampereuma et al. (131,133). In these studies, Fe and Mn redox systems were postulated and from  $\Delta G^\circ$  values,  $E^\circ$  values were calculated for the redox systems. The presence of a postulated redox system in a flooded soil was suggested on the basis of the conformity of the measured  $E^\circ$  value to the theoretical  $E^\circ$  value. The measured  $E^\circ$  values were obtained by substituting measured Eh, pH and Fe or Mn activity values into the Nernst relationships derived for the respective (postulated) redox systems. The presence of the following Fe redox systems were indicated: (a)  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$ , (b)  $\text{Fe}_3(\text{OH})_8 - \text{Fe}^{2+}$ , (c)  $\text{Fe}(\text{OH})_3 - \text{Fe}_3(\text{OH})_8$ . Measured values for system (a) were remarkably close to theoretical values during the entire period of flooding for 32 soils sampled weekly for 17 weeks. Good conformation was obtained for systems (b) and (c) only after the peak of water soluble Fe had occurred. The measured  $E^\circ$  values for the postulated Mn redox systems were remarkably lower than the theoretical values calculated for the ideal Mn oxides and varied with the soil and intensity of reduction. These marked variations were explained by the hypothesis that the Mn oxides involved in redox equilibria in soils that undergo seasonal oxidation-reduction are complex non-stoichiometric oxides of variable composition whose apparent standard free energies of formation are considerably less than those of their ideal counterparts (131).  $\text{MnCO}_3$  was also implicated as having a possible role in causing non-ideal behaviour of Mn oxides in flooded soils.

The literature shows that other workers outside the IRRI have not been very successful in attempts to apply thermodynamics to the study of redox equilibria in soil suspensions and solutions. Bohn (5) unsuccessfully attempted to relate the Eh measured by platinum electrodes ( $E_{Pt}$ ) in soil suspensions to the redox couples in the soil and concluded that  $E_{Pt}$  was a mixed potential whose major components were the  $O_2 - H_2O$  couple in aerated suspensions or the  $H^+ - H_2$  couple in anaerobic suspensions, but whose value was not related to the Nernst equation for oxidised and reduced species. Bohn thus concluded that  $E_{Pt}$  was only a qualitative measure of the oxidation-reduction conditions in the soil and that it had no quantitative significance. In another study, Bohn (6) reported that adding iron (II) sulphate to soil suspensions resulted in  $E_{Pt}/pH$  slopes which were unrelated to the reaction taking place since  $E_{Pt}$  was a mixed potential. He derived an equation for mixed potentials of electrodes to explain this non-Nernstian behaviour in dilute solutions and at nonequilibrium conditions. The studies of Bohn (5,6) were, however, conducted in soil suspensions and not in soil solutions and air was not excluded during the Eh and pH measurements.

Breemen (9) determined Eh, pH and  $Fe^{2+}$  activity in the interstitial solution of two flooded soils (an illitic clay soil from the Netherlands and a reddish brown soil from Kenya) and observed that the equilibria between  $Fe^{2+}$  and  $Fe^{3+}$  were governed largely by ill-defined ferric oxides

intermediate between amorphous  $(\text{Fe}(\text{OH})_3$  and  $\alpha\text{-FeOOH}$  (goethite).

Collins and Buol (35,36) recently conducted studies to examine the physico-chemical behaviour of Fe and Mn in terms of pH and Eh. These studies were conducted in pure Fe and/or Mn solutions and in sand culture. In all mono-elemental systems, the observed occurrences and measurements coincided closely with theoretically-predicted conditions. However, when both  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  were present, the precipitation of Fe at Eh-pH values lower than those generally necessary to precipitate Mn interfered with  $\text{Mn}^{2+}$  still in solution. The removal of  $\text{Mn}^{2+}$  from solution was thought to be due to both occlusion and sorption by the solid Fe precipitate. They also found that where mass-flow led to rapid rates of ion movement and where conditions of slow oxidation prevailed, the results disagreed with the theoretical equilibrium predictions. Under acid or slightly acid conditions the oxidation of both  $\text{Fe}^{2+}$  and particularly  $\text{Mn}^{2+}$  was slow.

In a survey of ferrous-ferric chemical equilibria and redox potentials, Hem and Cropper (64) concluded that the Nernst equation was effective for defining an Fe system in a natural water provided that certain rather restrictive conditions were met. The system must be stable under the conditions in which the properties of the water are being measured, so that the Fe system will be in equilibrium; complicating factors including complexing or chelation and deviations from assumed activity coefficients, must be

insignificant or known. The Eh, to be measured accurately, must be set by a reversible electrode system. Many natural waters do not fit these conditions (64). These workers also stated that the amounts of Fe that theoretically could be present in solution are mostly below 0.01 ppm if the pH is between 5 and 8, and Eh between 0.30v and 0.50v. However, they found in their investigations that the content of Fe could exceed 100 ppm at pH 5 and Eh of 0.30v. They attributed this disparity to the fact that measurable amounts of Fe in water may not be truly in solution or may be combined in complex ions.

In a study of the chemistry of submerged soils, Ponnampereuma et al. (129) also postulated that the actual concentration of Fe in soil solution may be considerably in excess of that permitted by ionic equilibria, owing to the formation of soluble organic complexes by Fe and the products of anaerobic decomposition of organic matter.

According to Martell and Calvin (96), the formation of a metal chelate or complex is accompanied by a decrease in ionic activity of the metal and hence a modification in its oxidation potential occurs. These authors also state that, in a qualitative sense, chelate formation of metal ions with amino acids and with the acid form of other chelating agents results in a pH drop.

Hem (62) studied complexes of  $Fe^{2+}$  with tannic acid and observed that a ferrous complex formed at a pH of more than 5 in a solution containing 500 ppm of tannic acid. This

complex was oxidised at a slow rate and some  $\text{Fe}^{2+}$  remained in solution after a month of storage in contact with air. Uncomplexed  $\text{Fe}^{2+}$  was oxidised and precipitated from solution in a few hours or less at pH levels of more than 5. Complexed  $\text{Fe}^{++}$  is known to be fairly stable so that it cannot be readily oxidised. In another investigation, Hem (61) studied restraints on dissolved  $\text{Fe}^{2+}$  imposed by  $\text{HCO}_3^-$ , Eh and pH and reported that, at equilibrium, pH and Fe provided a basis for estimating the Eh of ground water. If much  $\text{HCO}_3^-$  was present, however, the amount of Fe dissolved did not change with change in Eh. Hem (61) stated that the  $\text{HCO}_3^-$  effect was twofold because it fixed the pH of the water and also restricted the solubility of  $\text{Fe}^{2+}$ . The amount of  $\text{Fe}^{3+}$  that can be retained in solution is a function of the third power of  $\text{H}^+$  activity; hence, in systems where  $\text{Fe}(\text{OH})_3$  is present, a change in pH can produce a large change in the  $\text{Fe}^{3+} - \text{Fe}^{2+}$  ratio, and a considerably different equilibrium value for Eh can result.

Hem (63) also studied chemical equilibria and rates of Mn oxidation and found that Mn formed soluble complexes with  $\text{HCO}_3^-$  and  $\text{SO}_4^{=}$ . He determined the association constant for the  $\text{MnHCO}_3^+$  ion to be 63. He found that the solubility of Mn in natural water, especially that which contains large amounts of  $\text{HCO}_3^-$  or  $\text{SO}_4^{=}$ , is influenced by complexing. He found that, in a solution where the total dissolved Mn was 1.0 ppm, the concentration of  $\text{SO}_4^{=}$  250 ppm, and  $\text{HCO}_3^-$  concentration 470 ppm, half the Mn present will be in the complexed

form. He also found that the rate at which  $Mn^{2+}$  was oxidised and precipitated from aerated solutions was sharply increased by increasing the pH; the rate of oxidation diminished when  $SO_4^{=}$  and  $HCO_3^{-}$  ions were present.

#### 8. Iron and Manganese Complexes in Soil and Soil Solution

When a metal ion combines with an electron donor, the resulting substance is said to be a complex, or co-ordination compound. If the substance which combines with the metal contains two or more donor groups so that one or more rings are formed, the resulting structure is said to be a chelate compound, or metal chelate, and the donor is said to be a chelating agent. The electron-pair bonds formed between the electron-accepting metal and the electron-donating complexing or chelating agent may be "essentially ionic" or "essentially covalent" depending on the metals and donor atoms involved (96).

Complexes and chelates are formed by nearly all metals of the periodic table but complex-ion formation is particularly characteristic of the transition elements of which Fe and Mn are examples (153). The tendency for complex formation with donor molecules may be interpreted as the tendency for metal ions to fill up unoccupied orbitals and thereby approach the electronic configuration of an inert gas (96). The transition elements have vacant orbitals hence their great tendency to form complexes (153). Methods for detecting the presence or formation of complexes and

chelates have been discussed by Martell and Calvin (96).

In literature on soils, the terms, complex and chelate have been used rather loosely or interchangeably since the chemical structure of soil organic matter is unknown.

Bremner et al. (10) were among the first to detect the presence of metallo-organic complexes in the soil. They extracted soils with a number of compounds and observed that those compounds which were good polyvalent-metal extractants were also good organic matter extractants. The extractants were also known to form co-ordinating complexes with polyvalent metals. The authors thus suggested that some of the polyvalent metals in soils existed as an insoluble metallo-organic complex and that, if the polyvalent metal could be removed from the complex by a suitable reagent solution (such as pyrophosphate), the organic matter became soluble. They also postulated that metals in the metallo-organic complexes were not in the exchangeable form. After the pioneering work of Bremner and his co-workers, several other workers (11,37,41,42,50,59,60,62,66,68,80,99,174) later confirmed, by various methods, the presence or formation of metallo-organic complexes in soils.

Hem (62) suggested that the charge of most Fe complexes was positive and that neutral and anionic complexes also existed.

Several workers (41,42,59,66,80,104,174) have attempted to characterize and identify the ligands involved

in the formation of metal-organic matter complexes. Polycarboxylic acids, hydroxycarboxylic acids, acidic polysaccharide, carboxyl groups, non-carboxylic hydroxyl groups and amide groups have been suggested as possible ligands by the various workers.

Soil scientists have shown considerable interest in determining the magnitude or degree of binding between the soil organic matter ligands and the metals with which they form complexes. This degree of binding has been usually referred to as the stability constant (66).

The following equilibrium, as discussed by Himes and Barber (66), is usually employed in the calculation of stability constants:



where:

M is the metal ion

x is the number of moles of the chelating agent Ch, which combines with one metal ion to form the metal chelate compound.

The equilibrium constant is:

$$K = \frac{(MCh_x)}{(M) (Ch)^x}$$

where: the brackets indicate activities.

Log K = stability constant

= log MCh<sub>x</sub> - log M - xlog Ch.

The solution to this equation and the methods for circumventing the difficult problem of determining the

concentration of a chelating agent in the soil are discussed by Himes and Barber (66).

Several workers have determined the relative stability constants of complexes formed between soil organic matter and a number of metals but only the work of Schnitzer and Skinner (151) and Schnitzer and Hansen (150) will be cited since they show the relative stability constants for Fe and Mn.

Schnitzer and Skinner (151) determined the stability constants of complexes formed between fulvic acid and nine divalent metal ions and found their stability constants to decrease in the order:  $\text{Cu}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$  at pH 3.5; the order was  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+} \approx \text{Co}^{2+} > \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+}$  at pH 5.0. In a more recent study, Schnitzer and Hansen (150) showed that the stability constants of metals with fulvic acid increased with increases in pH. The order of stabilities at low pH was:  $\text{Fe}^{2+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+} = \text{Ca}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$ . It is thus evident that, in general, the stability constant of Fe-organic matter complex is considerably greater than that of the Mn-organic matter complex.

Some workers (37,59,157,166) take the view that the involvement of a metal in a complex with organic matter increases the availability of the metal to plants but Miller and Ohlrogge (100) take the opposite view. It has been suggested that chelating agents without metals often compete

with roots and soil for metal ions (157,166).

## B. Fe AND Mn IN PLANTS

### 1. Physiological Roles of Fe and Mn in Plants

It is generally believed that Fe is an essential activator for one or more enzymes catalyzing reactions involved in chlorophyll synthesis. Most of these reactions have not been investigated thoroughly. Fe forms a necessary part of certain pigment molecules, the cytochromes, which act as electron carriers in photosynthesis and in respiration. It also is an essential part of another photosynthetic electron carrier called ferredoxin and perhaps of nitrate reductase, one of the enzymes participating in the reduction of nitrate to ammonium ions. In the cytochromes and ferredoxin, the Fe becomes alternately reduced and oxidised from the ferric to the ferrous state, and this may prove to be true in nitrate reductase. Peroxidase and catalase enzymes which are responsible for removing  $H_2O_2$  produced in metabolic reactions, are Fe-containing enzymes, the Fe being bound to a porphyrin group. In each case, only the  $Fe^{3+}$  ion occurs (146).

Mn is known to activate many enzymes, several of which are also activated by magnesium. Manganese activates one or more enzymes involved in fatty acid synthesis, those responsible for deoxyribonucleic acid and ribonucleic acid formation and a respiratory enzyme of the Krebs' cycle that decarboxylates and oxidises isocitric acid. It is also

involved directly in photosynthesis, participating in a reaction by which water is split and oxygen is released. Mn also plays a structural role in the chloroplast membrane system (146).

## 2. Methods of Measuring the Availabilities of Fe and Mn in Soils

Numerous methods have been employed in attempts to assess the plant availability of Fe in soils but no one method has received wide usage or become accepted as a standard (4,149). Common extractants that have been used to measure available Fe include 0.74M NaOAc of pH 4.8 (126), 1NNH<sub>4</sub>OAc of pH 4.8 (114), 1NNH<sub>4</sub>OAc of pH 3.0 (75) and diethylenetriamine pentaacetic acid-triethanolamine (DTPA-TEA) solution (91). Lindsay and Norvell (91) have successfully employed the DTPA-TEA test in diagnosing Zn and Fe deficiencies in 77 Colorado soils.

A solution of 1NNH<sub>4</sub>OAc plus 2% hydroquinone has been most widely used to measure soil available Mn (86). Leeper (86) found that soils containing greater than 100 ppm of quinol-soluble Mn usually produced healthy crops. In a recent study of the Mn status of Alberta soils, Reid and Webster (137) found that those soils that had produced oats with Mn deficiency symptoms or had given substantial responses to applications of Mn generally had low levels of quinol-soluble Mn.

Recently, Browman et al. (14) evaluated eight soil

Mn tests for their ability to predict Mn uptake by maize (Zea mays L.) on 63 soils collected from various parts of the United States. Regression equations were derived by comparing Mn uptake with each test in combination with pH. The best prediction of Mn uptake was provided by a combination of  $\text{NH}_4\text{OAc}$ -extractable Mn and pH; 52.9% of the variability in Mn uptake was accounted for by these two variables. EDTA and  $\text{H}_3\text{PO}_4$ -extractable Mn were superior to the other soil Mn tests in predicting Mn uptake. These workers (14) also studied the effect of soil properties on the extractibility of soil Mn by each extractant and found that only with quinol-extractable Mn did soil variables account for a major portion of the variability in the Mn test.

### 3. Factors Affecting Fe Availability

Hodgson (67), in a review of the chemistry of micronutrient elements in soils, has discussed the factors that affect the availability of micronutrients in soils. These include pH, organic matter, microbiological activity, oxidation and reduction, seasonal variation and the rhizosphere. The pH of the soil affects Fe availability through its effect on Fe solubility.  $\text{Fe}^{2+}$  ions are regarded as the more readily available forms of Fe to the plants.

Olson (113) reported that the amount of Fe dissolved by  $\text{NH}_4\text{OAc}$  (pH 4.8) tended to increase rapidly with decreases in soil pH in soils more acid than pH 6.5. Such a condition indicated a difference in the amount or form of Fe in acid

soils as compared to neutral or alkaline soils. He also observed that soil pH was not the only factor determining the solubility of Fe in soils and the ability of soils to supply Fe to plants; one other factor, was the amount of free iron oxides in soils.

Wallace and Lunt (167) state that the solubility of  $\text{Fe}^{3+}$  at pH 4 is about 3 ppb and decreases by a factor of 1000 for each pH unit increase. The same authors state that  $\text{Fe}^{2+}$  which is soluble to the extent of about 100 ppm up to about pH 8 is readily oxidised to  $\text{Fe}^{3+}$  in aqueous solutions in the presence of  $\text{O}_2$ .

The presence of organic matter may promote Fe availability by supplying soluble complexing agents that will interfere with fixation (67,89).

Where soil reduction has been caused by increased or excessive moisture in the soil, the  $\text{Fe}^{2+}$  ions that come into solution as a consequence might not be fully available to the plant especially in calcareous soils (27,138). The increased Fe solubility might be accompanied by increased solubility of other ions which might interfere with Fe absorption (23, 167) or metabolism (26,44,167).

Iron deficiency usually expresses itself by an inter-veinal chlorosis developing in expanding new leaves. The area between the veins becomes light green, then yellow as the deficiency advances. The veins remain green except with extremely severe deficiency where the entire leaf may become nearly white (167).

A number of authors have reviewed the work on the chlorosis problem (15,16,167). Wallace and Lunt (167) stated that the following factors, singly or in partial combination, contribute directly or indirectly to the onset of chlorosis: (a) low Fe supply, (b)  $\text{CaCO}_3$  in soil, (c)  $\text{HCO}_3^-$  in soil or irrigation water, (d) over-irrigation or high water condition, (e) high phosphate, (f) high levels of heavy metals such as Mn, Cu, Zn, (g) low or high temperatures, (h) high light intensities, (i) high levels of  $\text{NO}_3\text{-N}$ , (j) unbalanced cation ratios, (k) poor aeration, (l) certain organic matter additions to the soil, (m) viruses and (n) root damage by nematodes.

The literature shows that chlorosis or lack of chlorophyll might not always be associated with lower levels of Fe in the plant. Some workers (44,115) have shown chlorotic plants to have the same level of total Fe as the normal green plants while others (56,76,81,101,154,169,176) have shown chlorotic plants to have lower levels of Fe than the normal green plants. Oserkowsky (115) was one of the first workers to attempt to correlate the amount of Fe in pear leaves with their chlorophyll content. He successfully correlated chlorophyll content with Fe extracted with  $1.0\text{NHCl}$  from dried leaves; he referred to this Fe fraction as "active iron". Elgala and Maier (44) have correlated "active iron" but not total plant Fe with chlorosis. Jacobson (76), while confirming Oserkowsky's concept of active iron in relation to chlorophyll content of corn,

tobacco and pear leaves, also proved that a proportionality existed between total Fe and chlorophyll content in the leaves of plants. Jacobson (76), as well as others (154, 169) who have correlated total plant Fe with chlorosis or chlorophyll content, emphasise that thorough washing of the leaves with dilute acid or detergent was a prerequisite for valid quantitative analyses of Fe.

Considerable evidence has been provided in support of the view that the  $\text{HCO}_3^-$  ion is a factor which contributes to the development of Fe chlorosis. Impetus to  $\text{HCO}_3^-$  investigations was provided by the observations of Harley and Linder (56). They found that the application of irrigation waters relatively high in  $\text{HCO}_3^-$  ion induced Fe chlorosis in apple and pear trees. Subsequent irrigation with water low in  $\text{HCO}_3^-$  ion tended to alleviate the Fe chlorosis. A number of workers (39,90,134,145,165,170) later reported reduced Fe accumulation in the shoots of plants when grown in nutrient solutions containing  $\text{HCO}_3^-$ . Brown et al. (25) used the split medium technique to study the effect of  $\text{HCO}_3^-$  in inducing Fe chlorosis in plants. Plant roots were extended from a soil medium through an air gap and into a solution culture. Fe was supplied in the soil and  $\text{HCO}_3^-$  in the nutrient culture. The separation of Fe prevented precipitation or competitive effects which might occur in the nutrient solution. High levels of  $\text{HCO}_3^-$  in the nutrient solution did not result in chlorosis of the chlorosis-susceptible soybean variety. In contrast, those plants

grown on complete nutrient solution plus  $\text{HCO}_3^-$  developed severe chlorosis. Chlorosis developed in the susceptible variety of soybeans grown on the split medium technique with  $\text{HCO}_3^-$  if the concentration of phosphate was high in the nutrient solution. From these results, the effect of  $\text{HCO}_3^-$  on chlorosis was believed to be indirect rather than direct.

According to Brown (15), very few data are available which compare the  $\text{HCO}_3^-$  content of soils producing chlorotic and nonchlorotic plants. Most of the results published involve solution cultures using  $\text{NaHCO}_3$ . This, according to Brown, leaves a great deal to be done as far as soils are concerned.

Rutland (145) induced Fe deficiency in plants by growing them in nutrient solution high in lime but could not obtain the same results in soil culture. Wallihan and Garber (172), using soil in pot culture, showed that addition of  $\text{CaCO}_3$  to the soil markedly reduced the efficiency of sweet orange roots in the uptake of Fe but affected that of sour orange roots only slightly.

Lindsay and Thorne (90) concluded from their aeration- $\text{HCO}_3^-$  studies that chlorosis was aggravated by high  $\text{O}_2$  levels. At low  $\text{O}_2$  levels, chlorosis was less prevalent. They concluded that chlorosis associated with poor aeration could not be attributed to low  $\text{O}_2$  levels in the growth media. Increasing levels of  $\text{CO}_2$  at the roots of plants growing in a  $\text{HCO}_3^-$  medium contributed to the chlorotic condition by raising the  $\text{HCO}_3^-$  level. They also observed that the  $\text{HCO}_3^-$

ion reduced movement of radio-iron into the leaves and stems and accentuated its accumulation in the roots. DeKock (39) confirmed the work of Lindsay and Thorne using mustard (Sinapsis alba).

Wallihan et al. (173) studied the effect of soil O<sub>2</sub> deficit on Fe nutrition of orange seedlings and observed that plants in calcareous soils at low O<sub>2</sub> level developed strong typical Fe chlorosis whereas all other plants were normal in appearance. Leaf analysis showed significant reduction in the concentrations of Fe and Mn resulting from both low O<sub>2</sub> and added CaCO<sub>3</sub>. The effects of the two factors (O<sub>2</sub> and CaCO<sub>3</sub>) were additive in their adverse effects on Fe and Mn nutrition.

Mandal (94) grew rice plants in water-logged soils and maintained O<sub>2</sub> concentration above the water surface at 0 - 30% by volume. He found that dry weight and Fe and Mn contents of plants were highest in soils kept under an atmosphere of 10% O<sub>2</sub>.

Elgala and Maier (44) grew soybean plants in soils in the greenhouse under two moisture levels (75% and 120% of moisture equivalent) and induced chlorosis in the plants grown at the higher moisture level. They did not measure the aeration status of the soils and they attributed chlorosis at the higher moisture level to an increase in free Ca ions in the wetter soils.

Plant varieties have been shown to differ in the concentration of available Fe required in the growth media

to prevent Fe chlorosis (19). Brown et al. (22) showed the genotype of rootstocks to be a controlling factor in the uptake of Fe by two soybean varieties that differed in their susceptibility to chlorosis. Hawkeye (non-susceptible) soybean rootstocks were more efficient than PI-54619-5-1 (chlorosis-susceptible) soybean rootstocks in the sorption of Fe, at low concentrations of Fe. PI- and HA-tops were non-chlorotic on HA-rootstocks but developed chlorosis on PI-rootstocks in calcareous soil. Brown (17) and Brown et al. (24) later accounted for the difference in the chlorosis-susceptibility of the PI and HA soybeans by showing that HA roots had greater reductive capacity, than PI roots, for Fe compounds in the growth medium and that translocation of Fe in HA was greater than that for PI. They also suggested that the PI variety seemed to lack the chelation-type reaction reducing  $Fe^{3+}$  to  $Fe^{2+}$  and making Fe available for translocation.

Dronzek (43) worked with HA and PI soybeans in Manitoba and showed that  $Fe^{59}$  fed as  $Fe^{59}$  chelates was absorbed into the roots and translocated to the tops at equal rates for both varieties. When Fe was supplied as  $Fe^{59}Cl_3$ , the movement of Fe occurred at slow rates for both varieties, although HA translocated twice as much Fe to the tops as PI in a 24 hour period.

Brown (18), Brown and Bell (20) and Brown and Ambler (21) have also studied two corn genotypes that differed in their efficiencies in the use of Fe. Plant factors recognised

as favouring Fe transport were (i) ability of roots to lower the pH of their growth medium, (ii) efflux of material by the root that reduces  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , (iii) increase of citrate in root sap, and (iv) decrease of P in root sap.

Phosphorus has been shown to internally inactivate or at least increase the requirement for Fe (26,103,112,145). Thorne et al. (163), however, do not fully support this view. Brown et al. (23) considered high P to be a major contributing factor to chlorosis development in a Millville soil. DeKock (39) has suggested the use of the P/Fe ratio as a means of making an assessment of the Fe status of plants.

An abnormally high concentration of one, several, or all of the micronutrients, except Fe, usually causes an induced Fe deficiency chlorosis (15). It is generally believed that a very high concentration of heavy metals in relation to Fe induces Fe deficiency or chlorosis in the plant. Somers and Shive (155) originally indicated that a high concentration of soluble Mn in plant tissues was invariably associated with low concentrations of Fe and vice versa. That is, symptoms of Fe toxicity correspond to those of Mn deficiency, and symptoms of Mn toxicity correspond to those of Fe deficiency. Somers and Shive (155) suggested that the ratio of Fe:Mn in both the growth medium and the plant tissue should be around 2 for good growth and development of plants free from pathological symptoms.

Several workers (40,79,112,116,160,164) have confirmed the original findings of Somers and Shive (155) while

others (29,65,118,162) failed to do so. O'Sullivan (116) studied Fe chlorosis in two grasses and concluded that the Ca/K and Fe/Mn ratios appeared to be the most reliable methods of identifying Fe deficiency in both grasses. Both ratios were low in chlorotic plants but increased with the Fe status of the plant. A relatively high K level in plant tissues has been suggested as capable of inducing chlorosis (88).

Wallace and Thorne (161) provided evidence which indicated that soil and plant conditions associated with chlorosis were more conducive to the maintenance of Fe in insoluble ferric compounds than were conditions in both soils and plants associated with normal leaf development.

Temperature may affect the uptake of Fe by influencing the rate of growth of the plants and the activities of the microflora in the soil (15). Millikan (101) noted that cool temperatures enhanced chlorosis of flax while Gingrich (52) reported that chlorosis was induced in sorghum plants grown at 100° F as a result of increased uptake of applied P at 100° F.

There is very little evidence that iron toxicity occurs under natural conditions. It has been observed in plants which have received soluble Fe salts in excessive amounts, either as sprays or as soil amendments, and first appears in the form of necrotic spots (171).

#### 4. Factors Affecting Mn Availability

The same general factors that affect the availability of Fe also affect that of Mn (67) but several authors (14, 30, 67, 83, 108, 139, 144, 149) have reported the predominant influence of soil pH on the availability of Mn to the plant. Christensen et al. (33) found that liming a soil from pH 4.6 to 6.5 decreased the exchangeable Mn 20 to 50 times. Fujimoto and Sherman (48) observed nearly as great a variation in exchangeable Mn upon the addition of four tons of lime to certain Hawaiian soils.

Several workers (54, 69, 102, 107, 117, 119, 120, 122, 123, 140, 144, 152, 175) have reported the increased solubility and availability of Mn with increasing acidity in the soil or growth medium. Most of these reports showed that increasing soil acidity results in increased accumulation of Mn in the plants while lowering soil acidity by liming reduced Mn uptake by plants. Increased Mn accumulation in plants generally resulted in Mn toxicity symptoms and marked decreases in yield. Visual symptoms of toxicity were bronzing, scorching, severe crinkling of leaves, necrotic spotting, interveinal chlorosis and malformation of pods.

According to Russell (144), Mn differs from the other trace elements for it is the only one that can accumulate in plant tissues in quantities far higher than are necessary for optimum growth. Robinson and Edington (140) reported that certain pasture herbage growing on very acid soil in Sweden had an MnO content exceeding 700 ppm (about 560 ppm Mn).

Bailey and Anderson (3) found tobacco plants containing as high as 2,262 ppm of Mn for certain plants grown in Connecticut. Gupta et al. (54) reported that carrots grown on an acid sphagnum peat soil showed bronze-coloured symptoms on their leaves when the Mn content of tops was more than 2,600 ppm. The bronzing symptoms were associated with lower yields when the Mn content of tops ranged from about 7,100 to 9,600 ppm. The Mn content of the carrot roots varied from 133 to 236 ppm.

Foy et al. (47) have reported differences in tolerance of cotton varieties, adapted to various regions of the Cotton Belt of the United States, to excess Mn in soils. They attributed the tolerance of some varieties to the fact that they or their ancestors were developed on high-Mn soils.

Cheng and Ouellette (31) recently studied the effect of various N fertilisers on Mn and Fe availability by incubation and soil culture methods. They found that, after two months of incubation, soils treated with inorganic N fertilizers contained more available Mn than those treated with organic sources, except for thiourea which increased available Mn very greatly. They attributed changes in Mn availability partly to pH changes and partly to the oxidation reduction influence of the N carriers.

Bolas and Portsmouth (7) found that a high concentration of CO<sub>2</sub> caused enough higher Mn oxide to dissolve to protect plants against Mn deficiency.

Heintze and Mann (58) suggested the theory that Mn

becomes non-available through the formation of complexes with organic matter. Page (121) has suggested that the formation of the complexes is controlled by pH and that the organic matter responsible for complex formation is not dissociated under acid conditions, but is completely dissociated at high pH.

Bromfield (12,13) reported that root washings were capable of dissolving  $MnO_2$ . He demonstrated the solubilizing effect of root exudates on insoluble  $MnO_2$  and was able to separate chromatographically the complexed from uncomplexed  $Mn^{2+}$ . He was unable to find any complexes formed when the exudate was added to  $Mn^{2+}$ . Possibly, weaker complexes were formed with  $Mn^{2+}$  which dissociated in the acid chromatographic solvent used. The stronger complexes with Mn of higher oxidation states were probably responsible for the dissolution of solid  $MnO_2$ .

Plants especially sensitive to Mn deficiency are oats, potatoes, apple, cherry, citrus, peas and to a lesser extent beans and sugar beets (83,144). Oats suffer from grey-speck disease, sugar-beet from yellows and peas from marsh spot when Mn is deficient (144). Grey-speck of oats resulting from Mn deficiency has been reported in Alberta (137).

Gerrestsen (51) suggested that the grey speck disease of oats was not caused by Mn deficiency alone. The appearance of the typical deficiency symptoms also depended on the presence of certain bacteria which attacked the roots

of the plants.

It appears from the review of literature that many factors control the amounts of Fe and Mn in soil solutions. Eh, pH and the forms of iron and manganese compounds in soils are only some of the factors shown to affect Fe and Mn solubility. Yet the relationship between amounts of Fe and Mn in soil solutions and Eh and pH has not been thoroughly investigated. The ability of plants to utilize Fe and Mn in soil solutions has received considerable attention. Many of these reports, however, are contradictory and inconclusive and thus more information is required on the factors controlling the absorption of Fe and Mn from soils by plants.

## CHAPTER III

### MATERIALS AND METHODS

#### Soils

Six Manitoba soils, varying in texture and carbonate content, were selected for study. A subgroup designation and characteristics of the soils selected are given in Tables 1 and 2, respectively. Soil samples obtained from the 0 to 3-inch depth were used in the study.

TABLE 1  
Subgroup Designation of Soils Selected

Soil Series	Subgroup
Red River	Gleyed Rego Black
Tarno	Carbonated Rego Humic Gleysol
Lakeland	Gleyed Carbonated Rego Black
Newdale	Orthic Black
Stockton	Orthic Black
Plum Ridge	Gleyed Carbonated Rego Black

#### Laboratory Methods

The methods employed in characterising the soils and the analytical procedures employed in the laboratory and greenhouse are described below. Specific methods for

TABLE 2  
SOME CHARACTERISTICS OF THE SOILS STUDIED

Characteristic	Red River	Tarno	Lakeland	Newdale	Stockton	Plum Ridge
pH	7.40	7.70	7.90	7.50	6.40	7.80
Texture	C	C	SiCL	CL	LVFS	VFSL
C.E.C.* (meq/100 g.)	49	39	29	34	19	19
Exchangeable Cations (meq/100 g.)						
Calcium	26	30	32	24	28	28
Magnesium	22	22	14	8	6	8
Water at Field Capacity (%)	49	39	30	30	28	22
Water at Saturation (%)	100	77	64	71	60	52
Inorganic CO <sub>3</sub> (%)	0.40	18.00	18.00	1.00	0.40	19.00
Organic Matter (%)	10.0	7.0	5.7	6.7	4.4	4.3
NaHCO <sub>3</sub> Extractable P (ppm)	16	23	9	16	10	14
NO <sub>3</sub> - N (ppm)	13	18	2	1	7	3
NH <sub>4</sub> OAc Extractable K (ppm)	535	390	190	315	550	140
Fe <sub>2</sub> O <sub>3</sub> (%)	0.63	0.44	0.22	0.83	0.24	0.24
Active Mn (%)	0.02	0.01	0.008	0.02	0.02	0.006
Total Fe (%)	2.50	2.30	1.70	2.20	2.00	1.30
Total Mn (%)	0.07	0.05	0.04	0.07	0.07	0.04

\*Cation Exchange Capacity.

individual experiments are described along with the results obtained under the various subsections since several individual studies with different experimental procedures were conducted.

1. Moisture Holding Capacity of Soils: The field capacities (1/3 atmosphere moisture tension) of the soils were determined by the pressure membrane method. Saturated soil samples were placed in a pressure membrane chamber and subjected to 1/3 atmosphere pressure using compressed nitrogen gas. The soil samples were removed and their water contents determined when the water level in the outflow tube of the pressure membrane apparatus ceased moving.

The "saturation" moisture capacities of the soils were determined by the porous ceramic plate method. A soil sample was placed on a porous ceramic plate under which a negative head of water (1.0 cm of water below the plate) was maintained. The samples were weighed daily. The water contents of the samples were determined when the soils attained constant weight.

The hygroscopic moisture contents of the air-dry soils were determined by drying weighed samples at 110° C and determining the loss in weight.

2. Soil pH: The pH values of the soils were determined electrometrically by the use of the glass and calomel electrodes on an Orion Model 801 digital pH meter. A soil:water ratio of

1:1 (w:v) was used (75).

3. Soil Cation Exchange Capacity: Twenty-five grams of soil, placed in a Buchner funnel, were leached with 350 ml of neutral normal ammonium acetate. (The leachate was retained for analysis.) The ammonium was then displaced from the soil colloids by leaching the soil with 225 ml of 10% acidified NaCl. The ammonium content of the NaCl leachate was determined by the Kjeldahl method (4).

4. Exchangeable Cations: The calcium and magnesium contents of the 1N  $\text{NH}_4\text{OAc}$  leachate (obtained from the CEC determination) were determined by EDTA titration (4).

5. Carbonate Content: A one-gram soil sample was digested in 10% HCl for 10 minutes. The  $\text{CO}_2$  evolved was sucked through a drying and adsorption train, then adsorbed by Ascarite. The weight of  $\text{CO}_2$  absorbed was determined and expressed as percent  $\text{CO}_3$  (4).

6. Soil Organic Matter: The soil organic matter was oxidised using excess chromic acid; the unreacted chromic acid was titrated with ferrous sulfate (75).

7.  $\text{NaHCO}_3$  Extractable Phosphorus: The soils were shaken with 0.5M  $\text{NaHCO}_3$  solution for 30 minutes and then filtered. The extracted phosphorus was determined colorimetrically (75).

8. Soil Nitrate Nitrogen: Nitrate nitrogen was extracted using 0.5M  $\text{NaHCO}_3$  solution. The nitrate nitrogen in the extract was measured colorimetrically using the nitrophenol-disulfonic acid method (75).
9. Ammonium Acetate Extractable Potassium: This was extracted with 1N  $\text{NH}_4\text{OAc}$  solution of pH 7.0 and determined by the flame photometer (75).
10. Free Iron Oxides ( $\text{Fe}_2\text{O}_3$ ): Soil iron oxides were extracted with  $\text{Na}_2\text{S}_2\text{O}_4$  (4); the extracted iron was determined by titration with  $\text{K}_2\text{Cr}_2\text{O}_7$  after reduction to the ferrous state (4).
11. Total Fe and Mn: A one-tenth gram soil sample, passed through a 100-mesh sieve, was digested with 18N  $\text{H}_2\text{SO}_4$  and HF. The solution was filtered and the Fe and Mn contents of the filtrate determined by atomic absorption spectrophotometry (4).
12. Easily Reducible (Active) Mn Oxides: Easily reducible Mn was extracted with neutral 1N  $\text{NH}_4\text{OAc}$  containing 0.2% hydroquinone (75).
13. Fe and Mn in Solution: The Fe and Mn contents of soil extracts and plant digests were determined by atomic absorption spectrophotometry.
14. Use and Care of Electrodes: Glass, platinum and saturated calomel electrodes, purchased from the Fisher Scientific

Company were used. The platinum electrode (Fisher Cat. No. 13-639-102) had a flat circular bright platinum tip. The glass electrode (Fisher Cat. No. 13-639-3) had a rugged bulb. The calomel electrode (Fisher Cat. No. 13-639-51) had a porous ceramic junction.

The electrodes were used on an Orion digital pH meter, Model 801. The instrument directly read pH and Eh (millivolts). The glass and calomel electrodes were used for the measurement of pH and the platinum and calomel electrodes for the measurement of Eh.

Prior to making measurements, the operation of the glass electrode was checked using buffer solutions. The operation of the platinum electrode was checked using a solution consisting of 1/300M potassium ferrocyanide, 1/300M potassium ferricyanide, and 1/10M KCl. This solution which was originally introduced by ZoBell (177) has an Eh of 0.430 volt at 25° C.

Between successive readings, the electrodes were thoroughly rinsed with de-ionised water and wiped dry with Kleenex tissue. The platinum surface of the platinum electrode was wiped with emery paper to remove possible chemical coatings (49). The saturated KCl solution in the calomel electrode was replaced regularly to avoid contamination of the KCl solution with soil solution ions (49).

In all Eh measurements, the saturated calomel half-cell EMF of 0.246 volt was added to the measured EMF.

Greenhouse Procedures:

Prior to initiation of the greenhouse studies, all fixtures such as the fluorescent light tubes were thoroughly cleaned to prevent any contamination of the plants. The soils used for the greenhouse studies were air-dried, thoroughly mixed and crushed to pass through a 3mm sieve. Flax (Linum usitatissimum, L. "Noralta") and oats (Avena sativa L. "Harmon") were the crops used in the greenhouse experiments. The weights of soil placed into the pots and the numbers of plants grown per pot are given along with the results obtained for each individual experiment.

Nitrogen, in the form of  $\text{NH}_4\text{NO}_3$  was added to each pot to give 50 ppm N in the soil, allowance being made for the amount of  $\text{NO}_3\text{-N}$  present in the soil. Additional nitrogen, at a rate of 50 ppm N, was added at two-week intervals. Phosphorus, in the form of  $\text{KH}_2\text{PO}_4$  was supplied at a rate of 20 ppm.

Supplementary lighting, using cool-white fluorescent tubes, was used to give a 16-hour light period.

Each experiment was arranged in the greenhouse in a randomized complete block design. Pots were randomized within each block and the position of each block was relocated weekly. The numbers of replications used are given along with the individual experimental results.

The plants were harvested by cutting the stems at the surface of the soil with a stainless steel blade. The plants were then washed with de-ionised water, 0.1N HCl solution and

rinsed several times with de-ionised water (76,154,169,171). The washed plant materials were then cut into three-inch portions, placed in paper bags and allowed to air-dry in the greenhouse for about four days. The plant materials were then dried at 80° C for 60 hours and weighed (75,127).

The plant material was ground in a stainless steel grinder and 2.0 g. subsamples taken for digestion and analysis. The plant tissues were digested by wet oxidation using a  $\text{HNO}_3 - \text{H}_2\text{SO}_4 - \text{HClO}_4$  ternary acid mixture (72,127). A preliminary oxidation with  $\text{HNO}_3$  was conducted prior to addition of the ternary acid mixture (75). After digestion, the samples were brought to volume using de-ionised water. Blank determinations, containing all acids but no plant tissues were conducted for each set of digestions. The Fe and Mn contents of the solutions were determined using an atomic absorption spectrophotometer.

## CHAPTER IV

### PRESENTATION OF EXPERIMENTAL RESULTS

#### 1. LABORATORY STUDIES

##### (a) A Study of Chemical Changes in Saturated Soils

Many of the studies of chemical changes in saturated soils have not involved the simultaneous measurement of Eh, pH and concentrations of Fe and Mn in the soils or soil solutions. Eh and pH both influence the chemistry of Fe and Mn in soils. A simultaneous study of changes in Eh, pH and Fe and Mn concentrations in soils would thus give a fuller understanding of the chemical changes in saturated soils. Most studies reported to date have failed to show any quantitative relationship between Eh measured by the platinum electrode ( $E_{Pt}$ ), pH and the Fe and Mn redox systems in soil suspensions and/or solutions. An experiment was thus conducted to determine if  $E_{Pt}$  and pH could be quantitatively related to Fe and Mn redox systems in the solutions of a number of Manitoba soils.  $E_{Pt}$ , pH, concentrations of Fe and Mn were measured in extracted soil solutions since the soil solution has been shown to be the thermodynamically meaningful phase in studies of soil redox systems (72,73).

Four hundred grams of air-dry soil (crushed to pass a 2 mm sieve) were placed in 600 ml beakers of known weight, brought to saturation moisture content with de-ionised water,

covered with a watch glass, and allowed to stand in the laboratory. The soils were weighed daily and brought up to weight by the addition of de-ionised water.

The extraction of the soil solutions from the various samples were initiated three days after initiation of saturation. Extractions were also made one week after saturation and at weekly intervals for a period of ten weeks. Separate samples were used for each weekly extraction.

The extraction of the soil solutions was conducted as follows: The soil was removed from the beaker and placed into the chamber of a stainless steel pressure plate moisture extractor obtained from the Soil Moisture Equipment Co., Santa Barbara, California (Figure 1). Nitrogen gas at a pressure of about  $1 \frac{1}{3}$  atmospheres was applied to the pressure plate chamber.

The soil solution extracted by the pressure plate was passed through tubing into a specially constructed cell filled with nitrogen gas and containing glass, platinum and saturated calomel electrodes (Figure 2). The nitrogen gas (99.995% pure) was passed into the cell to flush out oxygen from the cell chamber. The cell was made of plexiglass.

Each sample was extracted for 30 minutes to allow sufficient soil solution to collect in the cell. The tubing connecting the cell to the pressure plate was then disconnected and the inlet tube of the cell sealed with a small metal clip. The pH and Eh of the soil solution in the cell were then measured. The Eh readings were taken 5 to 10

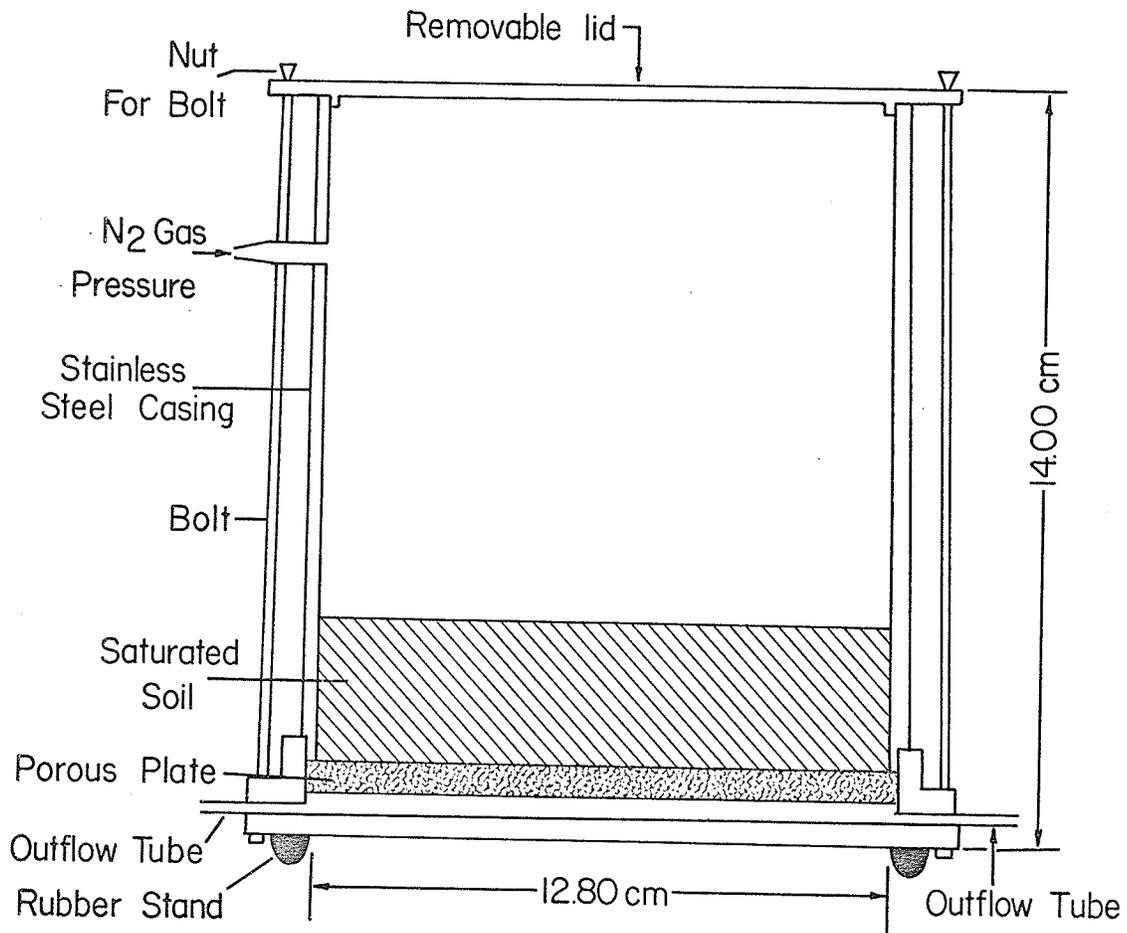


FIGURE 1. Pressure Plate Moisture Extractor

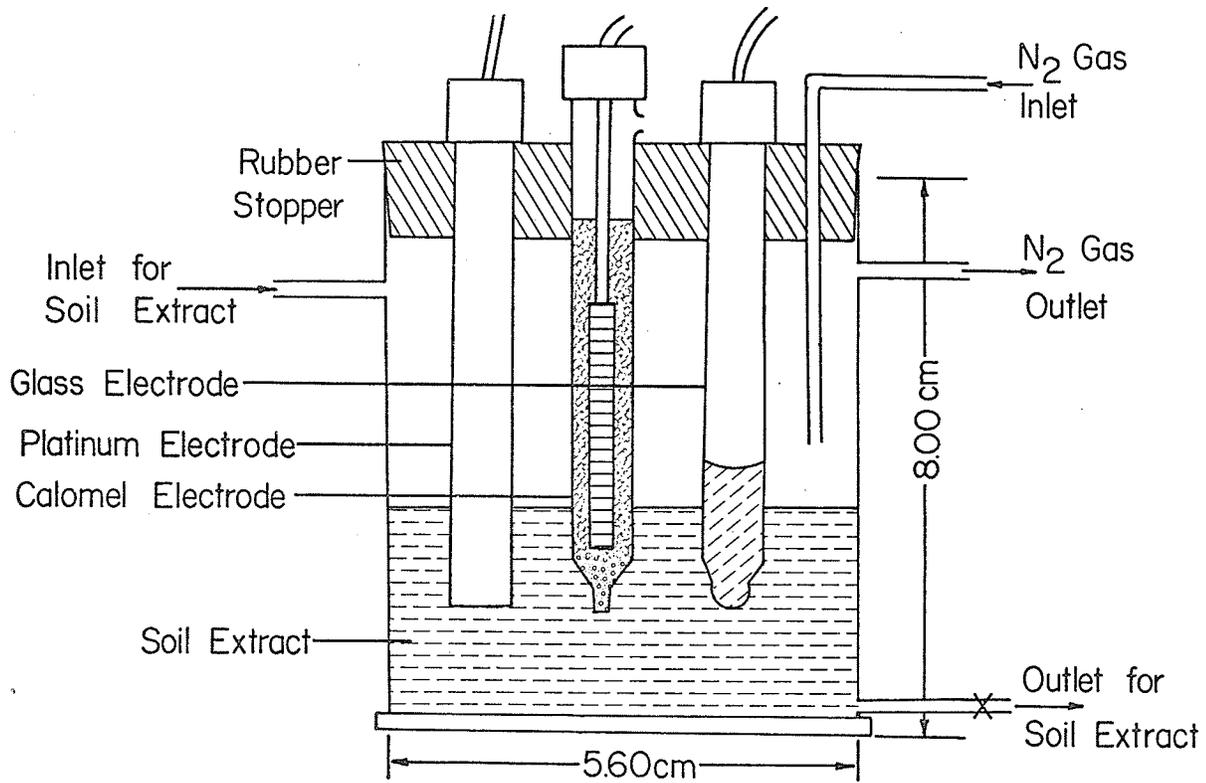


FIGURE 2. Cell Unit for Measurement of Eh and pH.

minutes after the connection of the platinum and calomel electrodes to the pH meter. Preliminary measurements showed that electrode poisoning was less prevalent and Eh readings more reproducible when the platinum electrode was inserted into the soil solution just prior to making the measurements. The following procedure was adopted in all measurements. As the soil solution collected in the cell, the opening in the cell for the insertion of the platinum electrode was stoppered with a small rubber stopper. When the Eh measurement was to be taken, the rubber stopper was removed and the platinum electrode immediately inserted into the solution through the opening.

After the measurement of Eh and pH, the soil solution was transferred into a conical flask and the concentrations of Fe and Mn in solution determined using an atomic absorption spectrophotometer.

The results obtained for the six soils are shown in Tables 3 to 8 and Figures 3 to 8. The totals of the concentrations of Fe and Mn measured on the third day and at weekly intervals for each soil are shown at the bottoms of Tables 3 to 8.

The pH of the soil extracts varied considerably with

TABLE 3  
 pH and Eh Values, and Fe and Mn  
 Concentrations (ppm) of Extracted Soil Solutions  
 of the Red River Soil at Varying Time  
 Intervals Following Saturation

Number of Days after Saturation	pH	Eh (v)	Fe (ppm)	Mn (ppm)
3	7.97	0.442	0.00	0.00
7	7.05	0.472	0.00	0.96
14	6.97	0.451	0.40	2.30
21	7.54	0.376	0.60	2.70
28	7.22	0.257	1.80	3.20
35	7.18	0.362	1.25	1.00
42	7.22	0.438	3.50	4.00
49	7.18	0.416	5.20	3.90
56	7.16	0.364	3.75	4.25
63	7.30	0.448	0.10	1.60
70	7.05	0.454	1.85	3.50
			Total = 18.45	27.41

TABLE 4  
 pH and Eh Values, and Fe<sup>2+</sup> and Mn<sup>2+</sup>  
 Concentrations (ppm) of Extracted Soil Solutions  
 of the Tarno Soil at Varying Time  
 Intervals Following Saturation

Number of Days after Saturation	pH	Eh (v)	Fe <sup>2+</sup> (ppm)	Mn <sup>2+</sup> (ppm)
3	7.54	0.437	0.00	0.12
7	7.34	0.468	0.00	1.55
14	7.33	0.414	0.25	2.44
21	7.76	0.370	1.00	3.90
28	7.23	0.289	2.50	4.30
35	7.37	0.401	3.75	1.95
42	7.40	0.392	5.00	6.20
49	7.21	0.398	7.50	6.10
56	7.24	0.403	4.75	4.75
63	7.36	0.474	0.20	3.00
70	7.20	0.445	4.00	5.30
			Total = 28.95	39.61

TABLE 5  
 pH and Eh Values, and Fe<sup>2+</sup> and Mn<sup>2+</sup>  
 Concentrations (ppm) of Extracted Soil Solutions  
 of the Lakeland Soil at Varying Time  
 Intervals Following Saturation

Number of Days after Saturation	pH	Eh (v)	Fe <sup>2+</sup> (ppm)	Mn <sup>2+</sup> (ppm)
3	7.04	0.468	0.10	0.20
7	7.19	0.462	0.00	3.55
14	7.31	0.299	2.20	5.15
21	7.69	0.221	4.30	8.30
28	7.27	0.130	6.80	10.50
35	7.37	0.158	12.20	7.40
42	7.37	0.331	6.80	8.40
49	7.31	0.345	11.10	10.10
56	7.43	0.295	10.75	10.90
63	7.20	0.423	9.40	8.05
70	7.25	0.413	6.00	7.65
			Total = 69.65	80.20

TABLE 6  
 pH and Eh Values, and Fe<sup>2+</sup> and Mn<sup>2+</sup>  
 Concentrations (ppm) of Extracted Soil Solutions  
 of the Newdale Soil at Varying Time  
 Intervals Following Saturation

Number of Days after Saturation	pH	Eh (v)	Fe <sup>2+</sup> (ppm)	Mn <sup>2+</sup> (ppm)
3	7.60	0.448	0.00	0.44
7	6.75	0.462	0.12	4.20
14	7.00	0.251	9.00	11.20
21	7.26	0.175	12.60	14.75
28	7.26	0.379	17.70	17.10
35	7.03	0.165	12.60	9.30
42	7.30	0.433	9.20	7.80
49	7.09	0.164	11.20	19.60
56	7.08	0.217	18.40	13.65
63	7.35	0.471	0.25	2.50
70	7.15	0.422	8.00	8.65
			Total = 99.07	109.19

TABLE 7  
 pH and Eh Values, and Fe<sup>2+</sup> and Mn<sup>2+</sup>  
 Concentrations (ppm) of Extracted Soil Solutions  
 of the Stockton Soil at Varying Time  
 Intervals Following Saturation

Number of Days after Saturation	pH	Eh (v)	Fe <sup>2+</sup> (ppm)	Mn <sup>2+</sup> (ppm)
3	7.67	0.465	0.00	0.22
7	6.99	0.454	0.00	0.67
14	7.00	0.432	3.10	7.50
21	7.56	0.393	0.00	1.90
28	7.28	0.422	2.40	4.90
35	7.17	0.340	0.50	3.15
42	7.46	0.439	0.00	1.20
49	7.22	0.406	0.90	3.50
56	7.26	0.416	0.50	2.75
63	7.29	0.441	3.15	6.40
70	7.40	0.464	0.10	1.50
			Total = 10.65	33.69

TABLE 8

pH and Eh Values, and Fe<sup>2+</sup> and Mn<sup>2+</sup>  
Concentrations (ppm) of Extracted Soil Solutions  
of the Plum Ridge Soil at Varying Time  
Intervals Following Saturation

Number of Days after Saturation	pH	Eh (v)	Fe <sup>2+</sup> (ppm)	Mn (ppm)
3	7.60	0.452	0.00	0.45
7	8.39	0.396	0.00	0.10
14	8.01	0.412	0.00	0.20
21	8.10	0.242	0.00	0.80
28	7.93	0.414	0.00	0.70
35	7.06	0.276	3.30	10.55
42	7.66	0.426	0.00	1.00
49	8.04	0.424	0.10	1.80
56	8.14	0.364	0.15	1.25
63	7.54	0.434	1.40	3.25
70	7.70	0.391	0.00	1.50
Total =			4.95	21.60

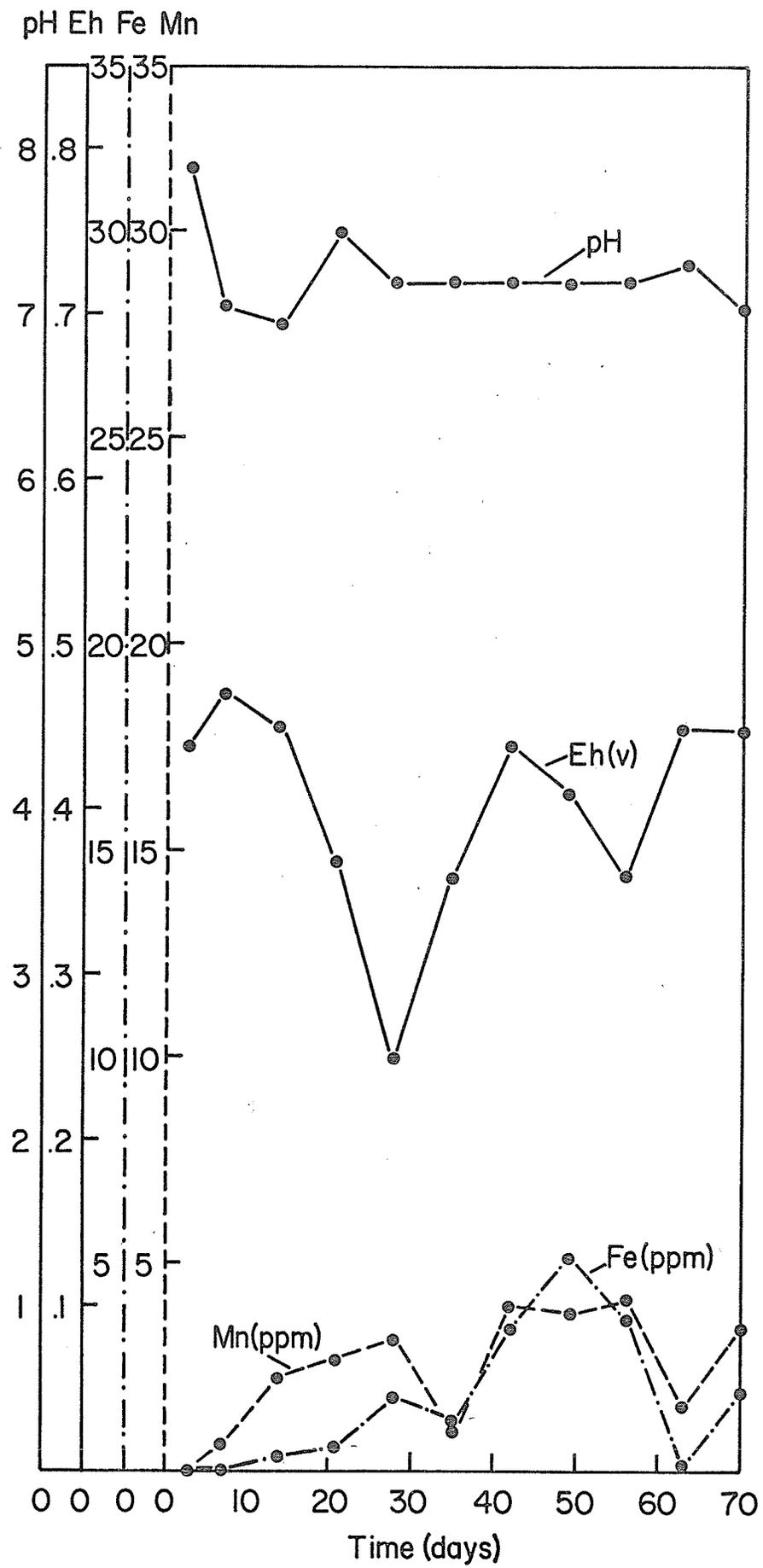


FIGURE 3. Influence of Time of Saturation on pH, Eh and Concentration of Fe and Mn in the Red River Soil.

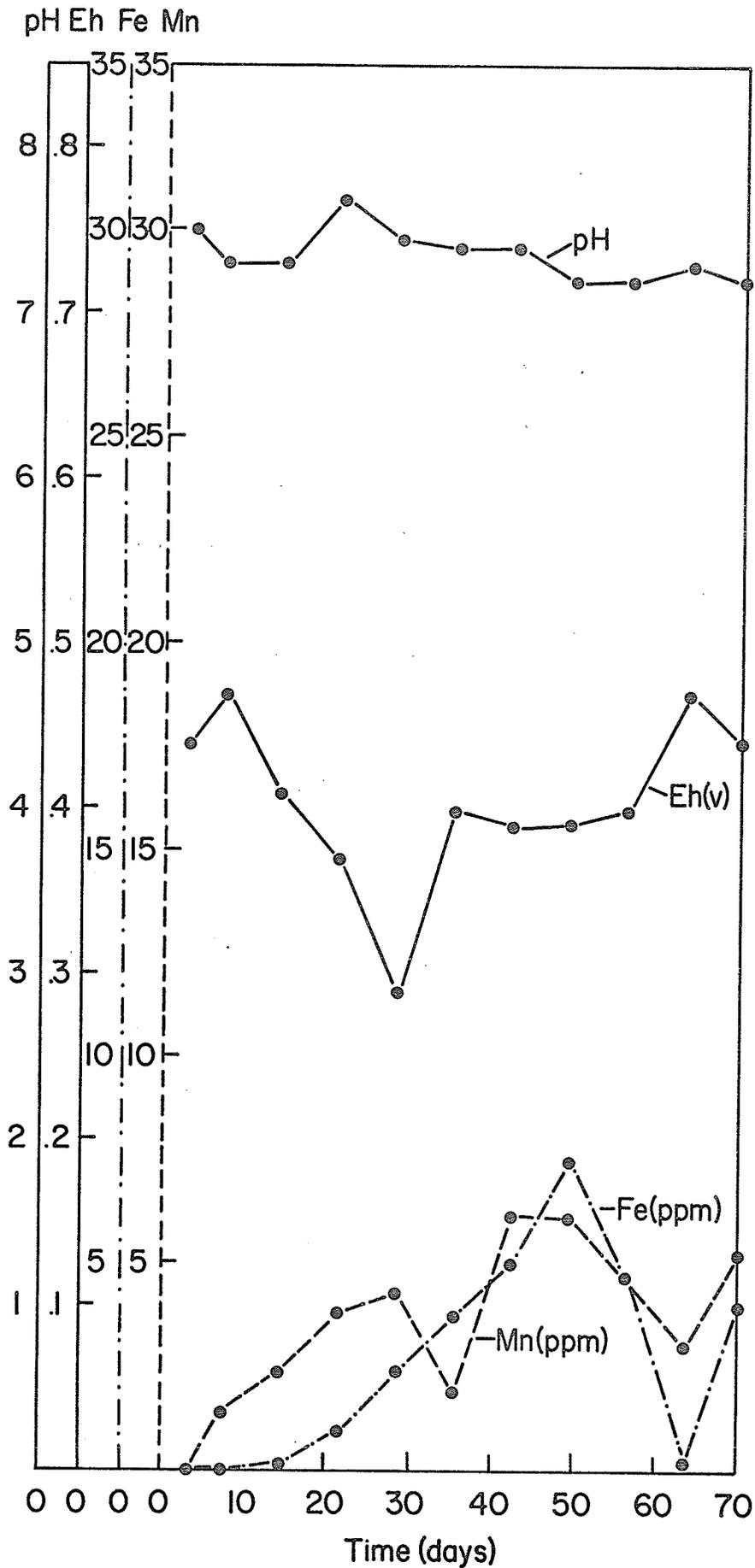


FIGURE 4. Influence of Time of Saturation on pH, Eh and Concentration of Fe and Mn in the Tarno Soil.

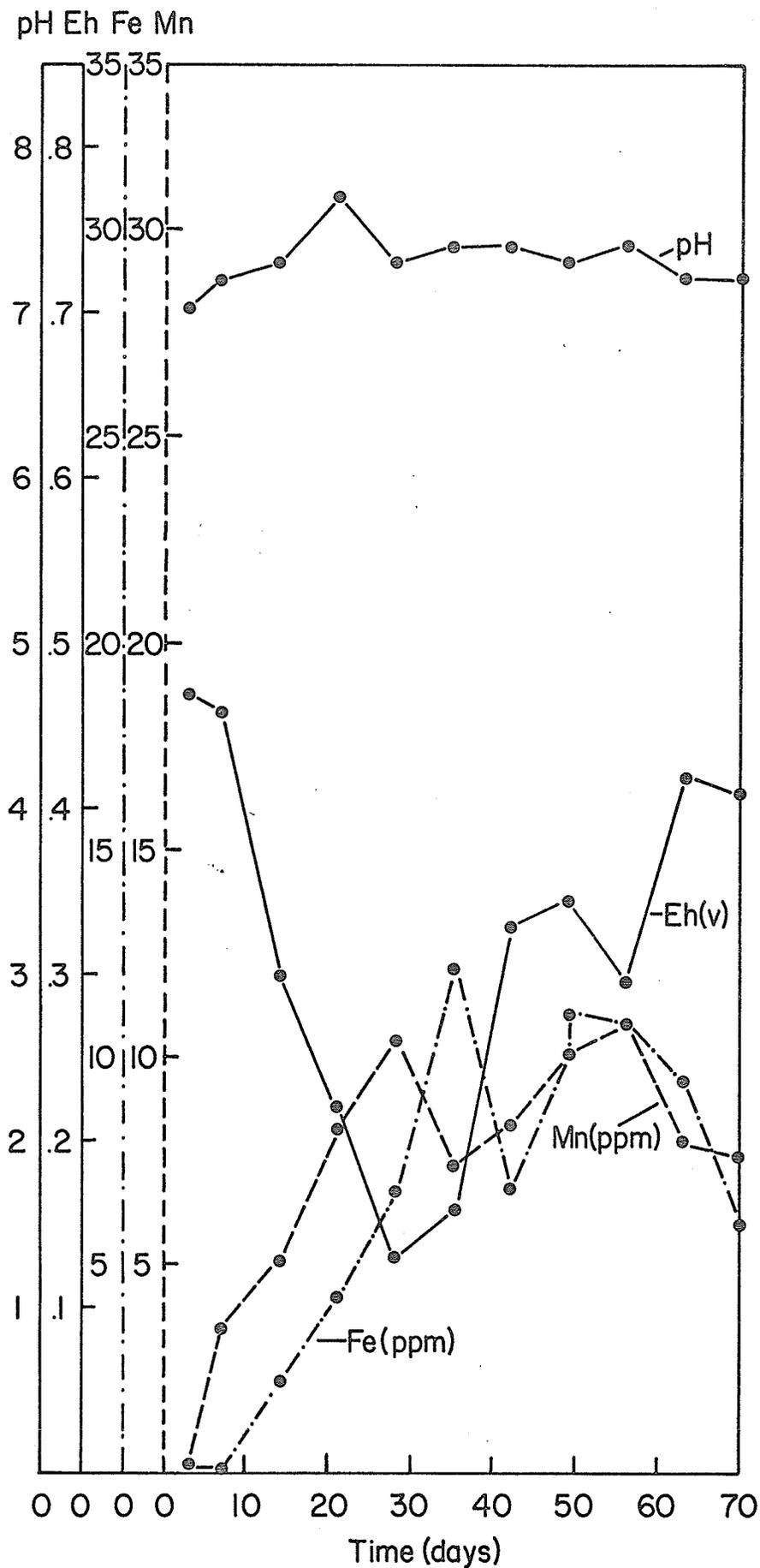


FIGURE 5. Influence of Time of Saturation on pH, Eh and Concentration of Fe and Mn in the Lakeland Soil.

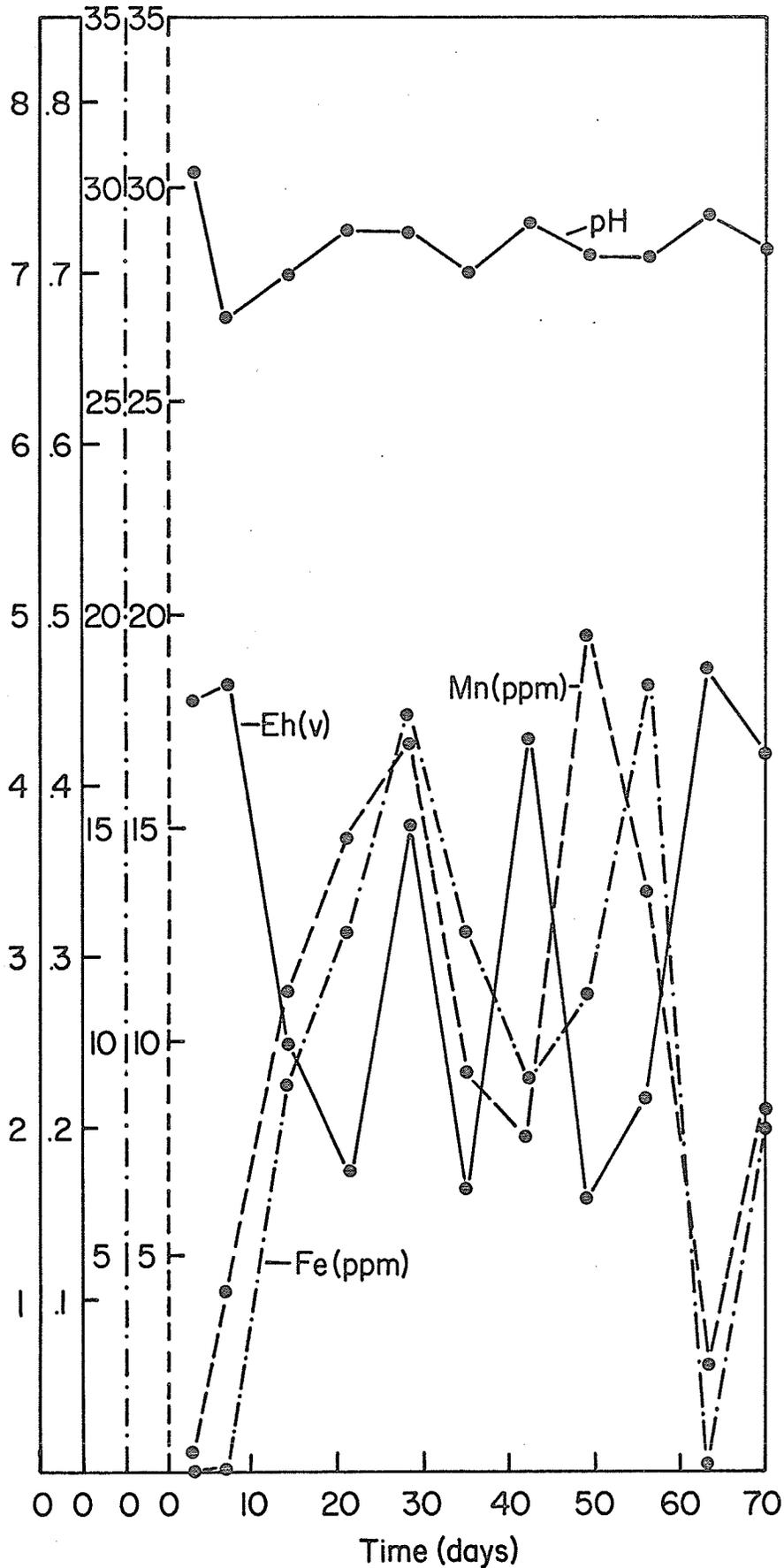


FIGURE 6. . Influence of Time of Saturation on pH, Eh and Concentration of Fe and Mn in the Newdale Soil.

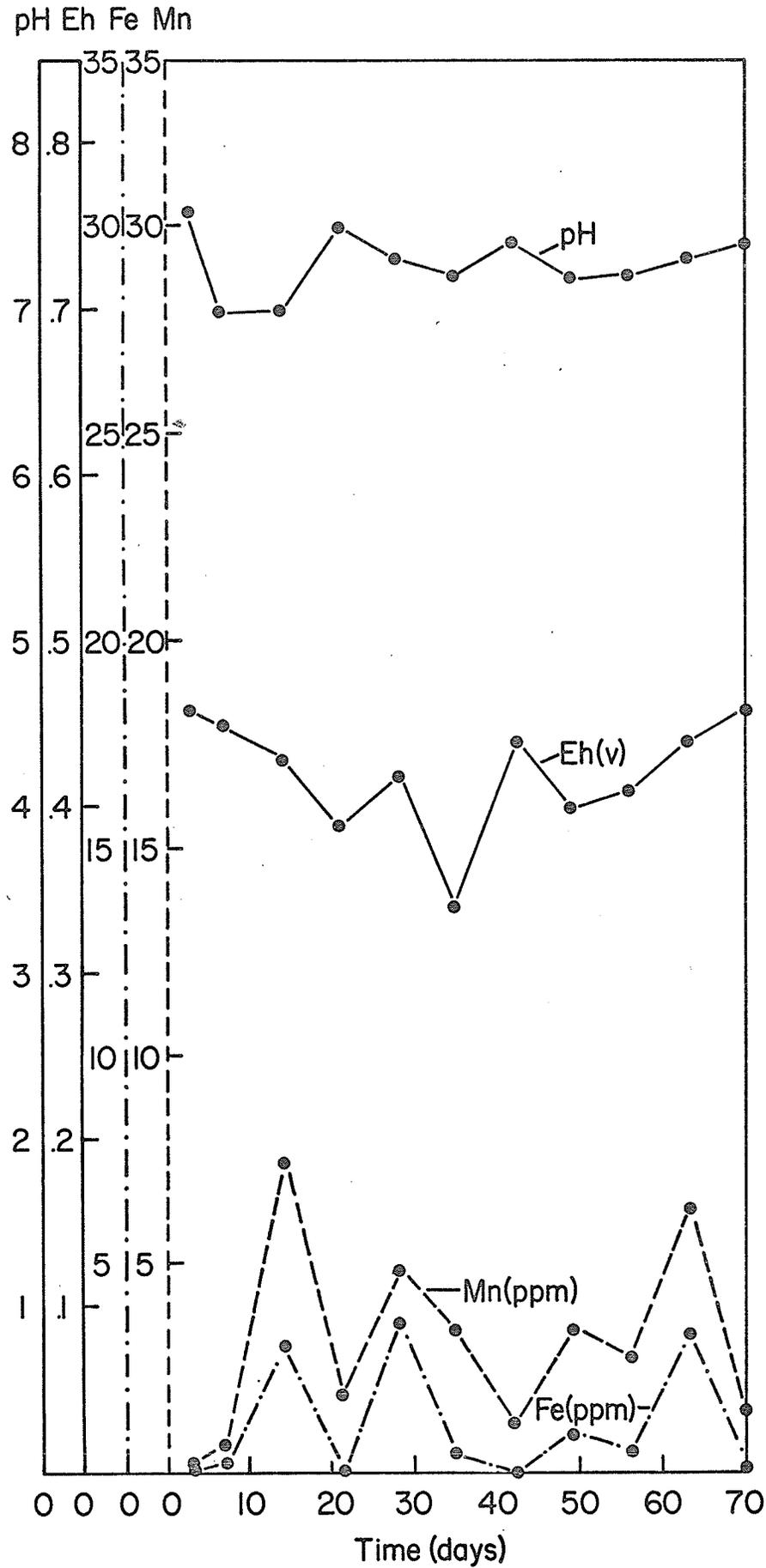


FIGURE 7. Influence of Time of Saturation on pH, Eh and Concentration of Fe and Mn in the Stockton Soil.

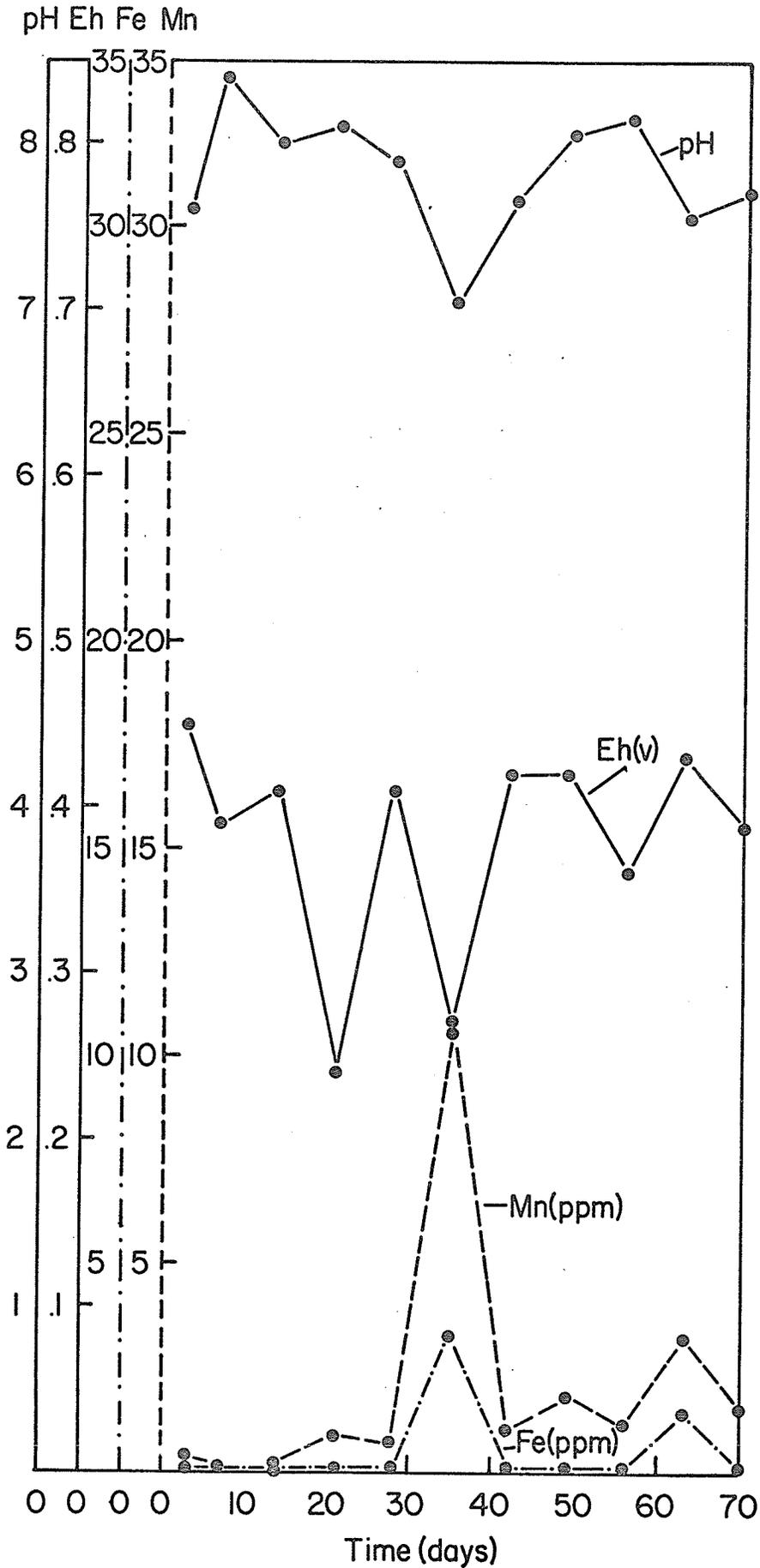


FIGURE 8. Influence of Time of Saturation on pH, Eh and Concentration of Fe and Mn in the Plum Ridge Soil.

time of incubation (Tables 3 to 8 and Figures 3 to 8). After saturation, there were initial pH decreases for the Red River, Tarno, Newdale and Stockton soils. The pH of the Lakeland and Plum Ridge soils increased immediately after saturation. The pH values of all soil solutions were about 7 or greater; the Plum Ridge soil was the only soil that attained a pH value of 8 or greater. With the exception of the Plum Ridge soil, the largest changes in pH for all the soils occurred within the first 21 days after saturation. The pH of the Red River soil remained nearly constant after 28 days of saturation. The pH of the Plum Ridge soil varied greatly, decreasing by more than one pH unit between the 21 and 35-day incubation periods. These large changes in the pH of the Plum Ridge soil may be due to the amounts of CO<sub>2</sub> present in the soil at the various sampling periods. The pH changes of the other four soils were intermediate between those of the Red River and Plum Ridge soils.

It has been reported that the pH of acid soils usually increases while that of calcareous and alkaline soils usually decreases on saturation or flooding (71,72,128, 132,136). Ponnamperuma et al. (132) state that the increase in pH of acid soils on flooding is related quantitatively to

the potential of the  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  redox system, and that the decrease in pH of calcareous soils is related to the partial pressure of  $\text{CO}_2$  through the  $\text{CaCO}_3 - \text{H}_2\text{O} - \text{CO}_2$  system. The reduction of  $\text{Fe}(\text{OH})_3$  to  $\text{Fe}^{2+}$  requires  $\text{H}^+$  ions and thus causes a pH increase in acid soils while the increased partial pressure of  $\text{CO}_2$  causes a decrease in pH in calcareous soils on flooding.

Thus, the variations in pH of the Tarno, Lakeland and Plum Ridge soils which are calcareous were probably due to accumulations of  $\text{CO}_2$  as a result of flooding and microbiological activities. The variations in pH of the non-calcareous soils were also probably influenced by the  $\text{CO}_2$  levels in the soils.

The Eh values for the various soils also varied with time of saturation. In general, the Eh values of the soil solutions did not show a continuous or uniform decline with time of saturation. Rather, there were periodic increases and decreases in Eh throughout the period of observation. The cyclic nature of these changes could be partly attributable to rapid changes in soil redox systems resulting from erratic microbiological activities. The Eh values for all soil solutions were positive throughout the 70-day observation period. This has been observed by other workers (9,72) who measured Eh in soil solution. These workers showed that Eh measured in soil solution extracts always remained more positive than Eh measured in situ for the same soils.

For all soils, the steepest decreases in Eh occurred between the 21st and 35th day after saturation. The Lakeland and Newdale soils were the most strongly reduced soils; the minimum Eh for the Lakeland soil was 0.130v (Table 5 and Figure 5) and that for the Newdale soil was 0.164v (Table 6 and Figure 6). These two soils had the lowest contents of  $\text{NO}_3 - \text{N}$  (Lakeland--2 ppm and Newdale--1 ppm). Both soils also had relatively large amounts of organic matter (5.70% for Lakeland and 6.7% for Newdale). These two factors, low  $\text{NO}_3 - \text{N}$  and high organic matter content have been shown to induce strong reduction in soils (128). The smallest decrease in Eh was found for the Tarno and Stockton soils. The decrease in Eh was intermediate for the Red River and Plum Ridge soils. In these four soils, the small decrease in Eh could be due to either initial high contents of  $\text{NO}_3 - \text{N}$  (Red River and Tarno) or of their relatively lower contents of organic matter (Stockton and Plum Ridge).

It has generally been reported that a pH increase must accompany an Eh decrease for the redox systems that operate in flooded soils since  $\text{H}^+$  ions are used up during reduction (128). This was generally true for most of the soils studied. However, there were instances where Eh and pH either increased or decreased simultaneously. The simultaneous increase or decrease of pH and Eh is more likely to occur in soils containing fresh organic matter. Microbial decomposition of fresh organic matter produces organic acids which decrease the pH while oxidation of

organic matter itself induces reducing conditions in the soil.

For all soils, release of Mn into the soil solution preceded that of Fe. This was because Mn is more readily reduced and rendered soluble than Fe (128). Also, the amount of Mn released into solution remained higher than that of Fe for most of the 70-day period of saturation. In most instances, the amounts of Fe and Mn in solution increased as Eh and/or pH decreased and decreased as Eh and/or pH increased. In some soils, increases in the concentrations of Fe and Mn did not occur immediately after a decrease in Eh and/or pH. This could be due to the combined effects of clay and organic matter which impede the release of Fe and Mn into solution following an Eh decrease (67). The delay in release of Fe or Mn on reduction was longer for soils with high clay and organic matter contents (Red River and Tarno soils) than for the other soils. These delays were absent or very short for the coarse-textured soils and the soils low in organic matter content (Stockton and Plum Ridge). It has been reported that the delay in release of Fe in calareous soils after reduction was due partly to the presence of Fe oxides in highly crystalline forms (159).

The changes in Fe and Mn concentrations with time followed the same trend for all soils. This is an indication that identical factors control the chemistry of both elements in the soil.

The two most strongly reduced soils, Lakeland and Newdale, released the highest amounts of Fe and Mn into the soil solution during the 70-day saturation period. The Newdale soil released about one and one-half times the amounts of Fe and Mn released by the Lakeland soil. In the first 28 days after saturation, the Lakeland soil was more strongly reduced than the Newdale soil, but the Newdale soil released about twice the amount of Fe and Mn as was released by the Lakeland soil. There are two possible reasons for this: (i) the Lakeland soil contained lower amounts of easily reducible Mn ( $Mn_2O_3$  and  $MnO_2$ ) and free Fe oxides ( $Fe_2O_3$ ) than did the Newdale soil. The lower content of easily reducible Mn may have allowed for a greater reduction to take place and at the same time limited the amount of Mn in solution. A low supply of active Fe ( $Fe_2O_3$ ) has been shown to be less favourable for Fe reduction (128). The Newdale soil had the highest content of free Fe oxides (0.83%  $Fe_2O_3$ ) of all soils, (ii) the Lakeland soil is calcareous while the Newdale soil is not and thus the higher amounts of  $HCO_3^-$  ion in the Lakeland soil could restrict Fe dissolution for a given change in Eh (61).

The Stockton and Plum Ridge soils released the lowest amounts of Fe into solution. These soils were not strongly reduced and contained low amounts of free Fe oxides

(0.24%  $\text{Fe}_2\text{O}_3$ ).

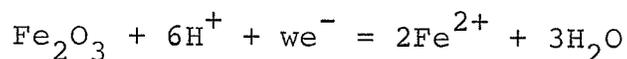
The amounts of Fe and Mn released into solution were very low when compared with those reported for flooded or saturated tropical soils (72,73,128,133). This is due to the higher amounts of free Fe oxides and easily reducible Mn found in tropical soils. Some tropical soils have  $\text{Fe}_2\text{O}_3$  contents ranging from 1 to 3% and easily reducible Mn contents of over 0.30% (133). The highest  $\text{Fe}_2\text{O}_3$  and active Mn contents for the six Manitoba soils were 0.83% and 0.02%, respectively. Temperatures are also generally higher in the tropics and this factor enhances the degree of reduction and the amounts of Fe and Mn released into solution under a given set of conditions. Nogina et al. (110) have reported that freezing temperatures decreased the solubility of Fe in some Russian soils as a result of a loss of part of the absorbed water and major changes in the structure of amorphous Fe. This finding could very well apply to Manitoba soils which are subjected to freezing temperatures for a considerable part of the year.

The Eh and pH values measured for the various soils were plotted on Eh - pH diagrams constructed for Fe (Figures 9 to 14) and Mn (Figures 15 to 20) in order to have an indication of the Fe and Mn compounds in equilibrium with the Fe and Mn in solution. The diagrams give an indication of the Fe and Mn redox systems thought to be operative in soils. A discussion of the principles involved in the

construction of Eh - pH diagrams is given in Appendix I.

$\text{Fe}_2\text{O}_3$  was probably the iron oxide involved in the Fe redox systems for all six soils (Figures 9 to 14).  $\text{Mn}_2\text{O}_3$  and  $\text{MnCO}_3$  were the Mn compounds involved in the Mn redox systems for most of the soils (Figures 15 to 20). The most strongly reduced soils, Lakeland and Newdale, had the most points falling within the stability area of  $\text{MnCO}_3$ .

Since  $\text{Fe}_2\text{O}_3$  was found to be the Fe oxide involved in the Fe redox system in the soils and since the Fe ions released into solution would theoretically be present mainly as  $\text{Fe}^{2+}$  at the observed pH values, the Fe redox system could be represented as follows:



$$\Delta G^\circ = -33.57 \text{ Kcal}; \quad E^\circ = 0.728 \text{ volt.}$$

In the above reaction, ferric iron in the form of  $\text{Fe}_2\text{O}_3$  is being reduced to ferrous ions which come into soil solution and are measured as total Fe in solution. The Nernst equation for the reaction is  $Eh = E^\circ - 0.059 \log(\text{Fe}^{2+}) - 0.177 \text{ pH}$ .

The Eh - pH diagrams indicate that the Fe oxide involved in the redox system in the soils should be  $\text{Fe}_2\text{O}_3$ . To further investigate the presence of this solid, the experimental data can be analysed in several ways. According to the Nernst equation,  $Eh = E^\circ - a \log(\text{Fe}^{2+}) - b\text{pH}$  where  $E^\circ$ ,  $a$  and  $b$  are constants which can be evaluated by making use

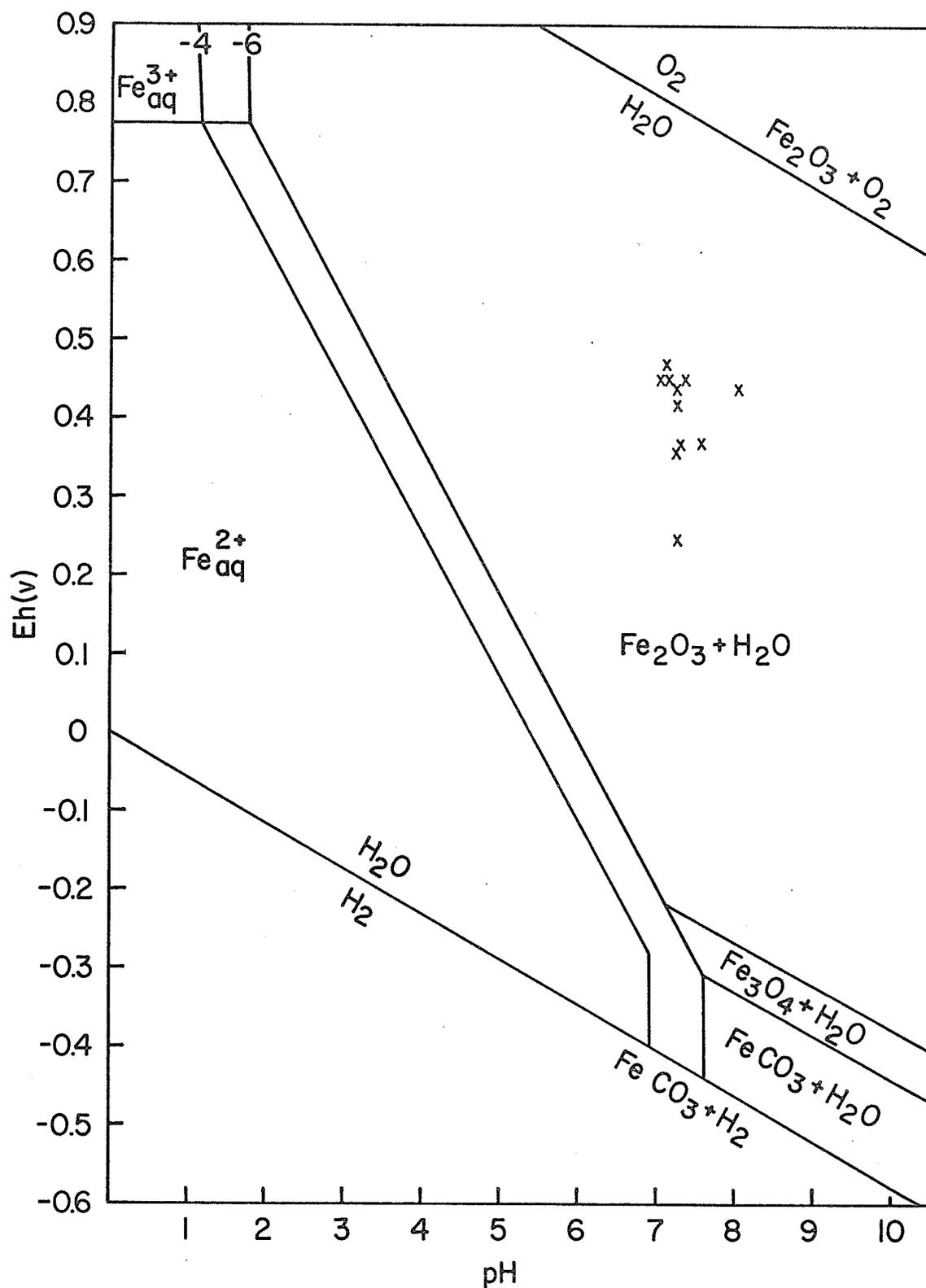


FIGURE 9. Eh-pH Values for the Red River Soil as Related to the Stability Fields of  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeCO}_3$  in Water with  $\text{pCO}_2 = 10^{-2.0}$  atmosphere at  $25^\circ\text{C}$  and 1 Atmosphere Total Pressure.

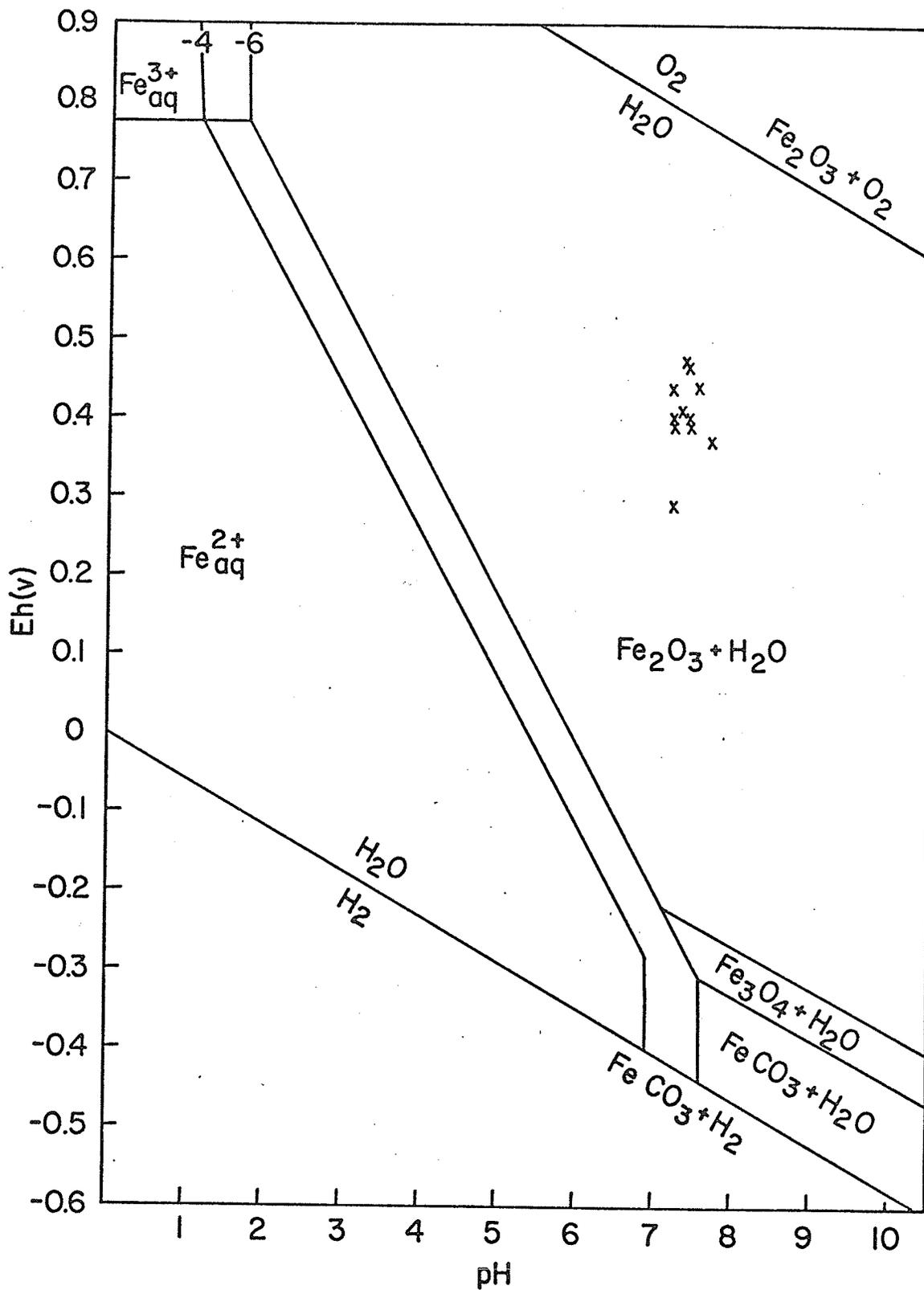


FIGURE 10. Eh-pH Values for the Tarno Soil as Related to the Stability Fields of  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeCO}_3$  in Water with  $\text{pCO}_2 = 10^{-2.0}$  Atmosphere at  $25^\circ\text{C}$  and 1 Atmosphere Total Pressure.

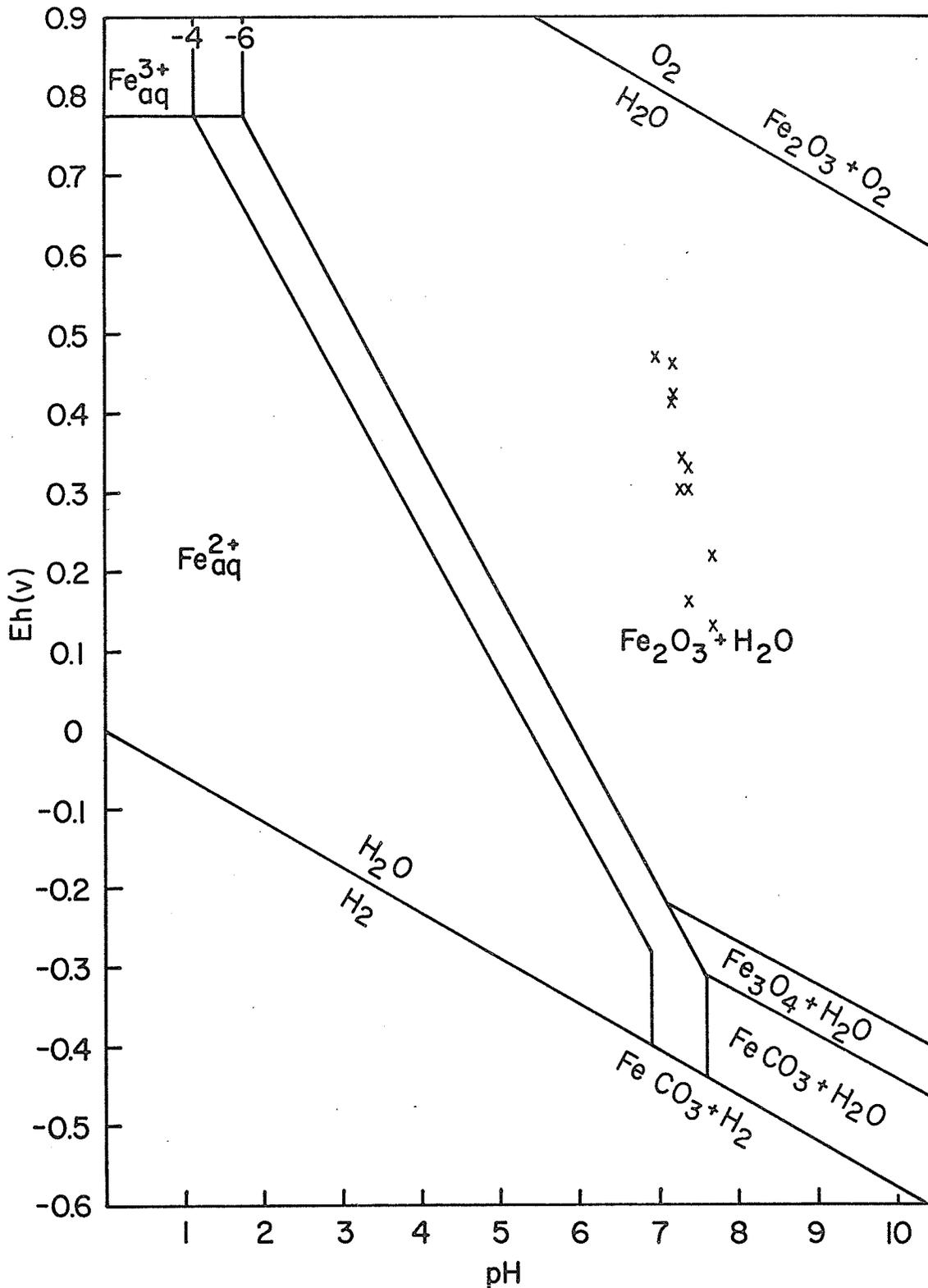


FIGURE 11. Eh-pH Values for the Lakeland Soil as Related to the Stability Fields of  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeCO}_3$  in Water with  $\text{pCO}_2 = 10^{-2.0}$  Atmosphere at  $25^\circ\text{C}$  and 1 Atmosphere Total Pressure

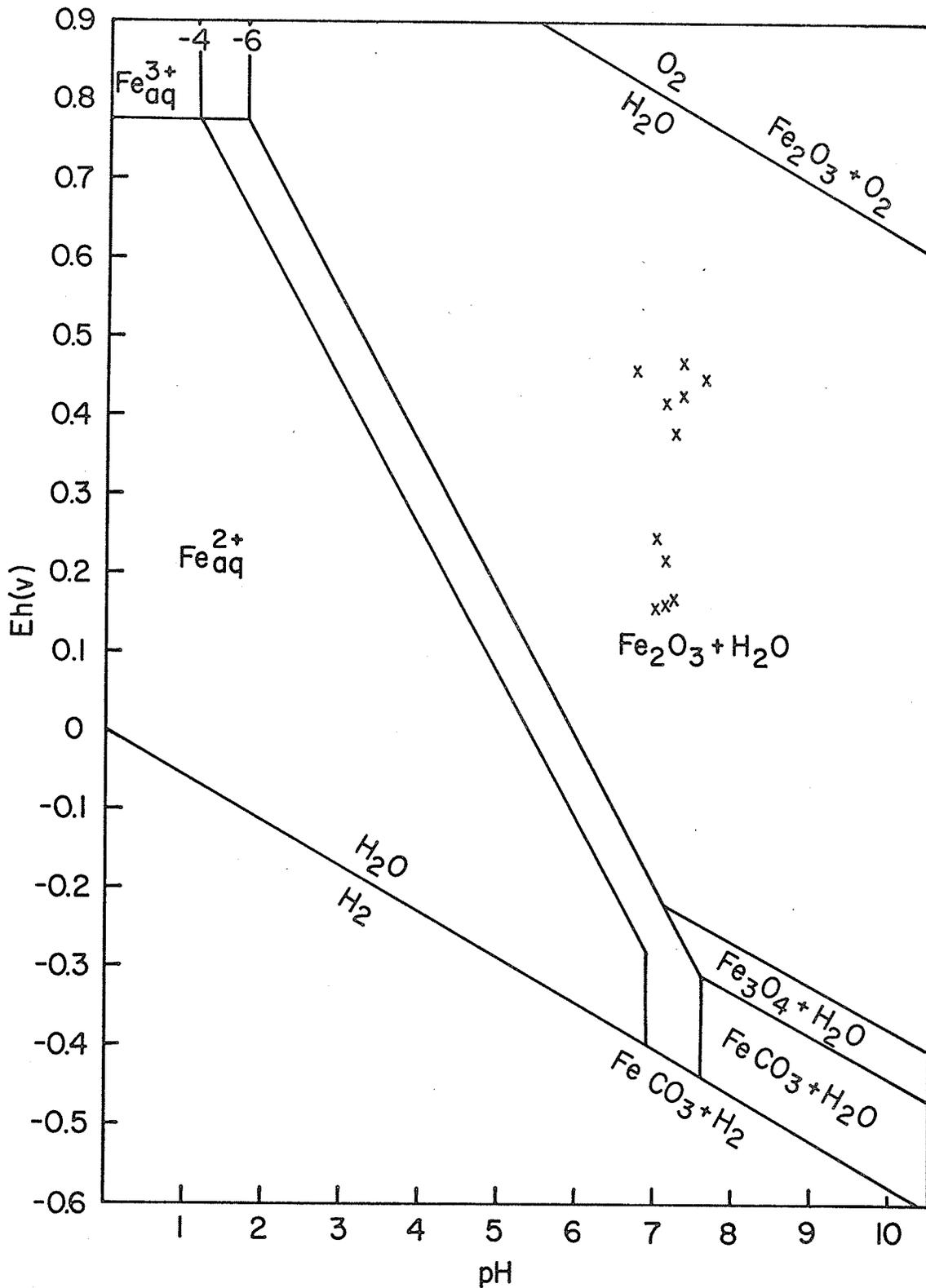


FIGURE 12. Eh-pH Values for the Newdale Soil as Related to the Stability Fields of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and FeCO<sub>3</sub> in Water with pCO<sub>2</sub>=10<sup>-2.0</sup> Atmosphere at 25° C and 1 Atmosphere Total Pressure.

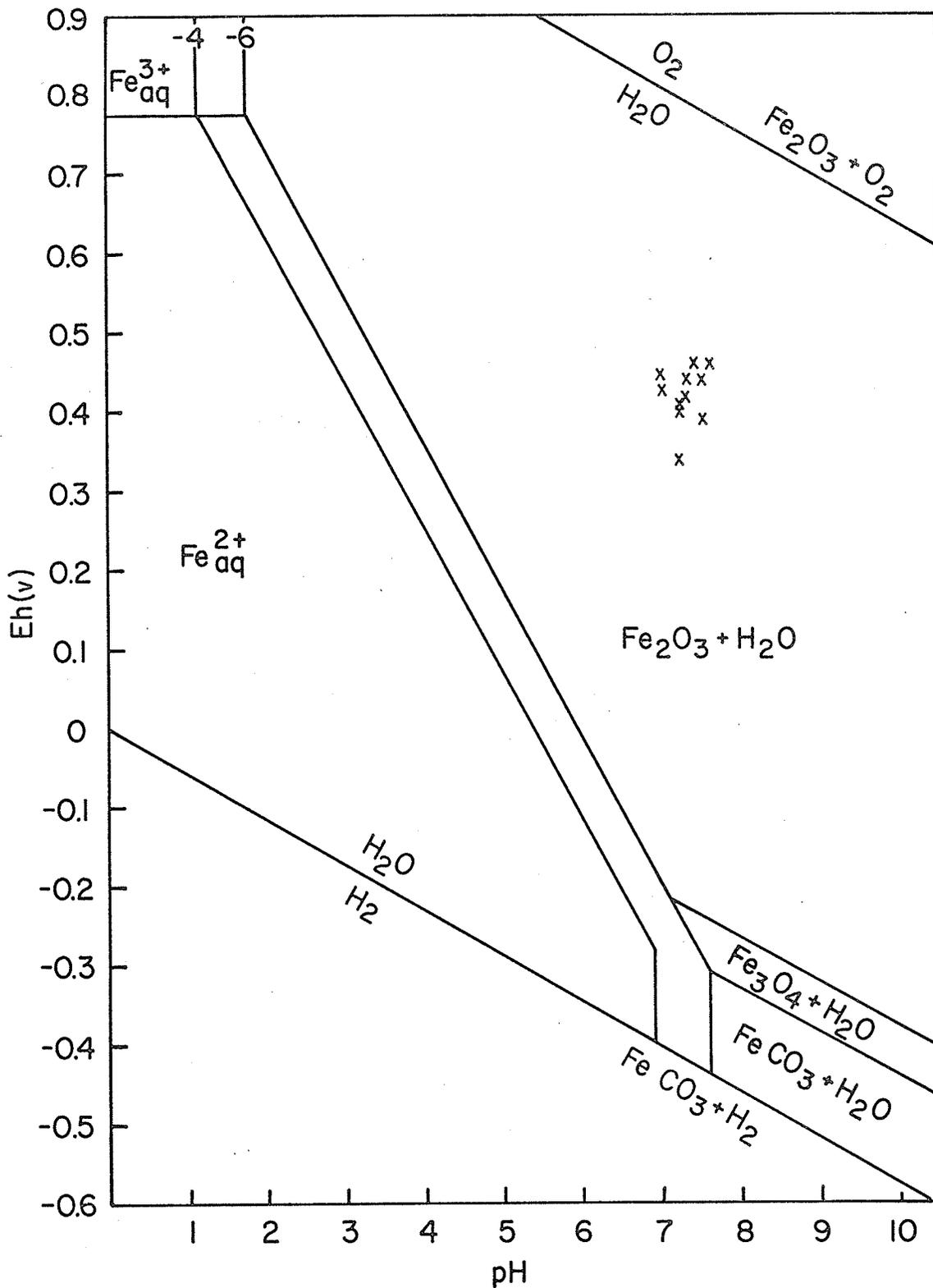


FIGURE 13. Eh-pH Values for the Stockton Soil as Related to the Stability Fields of  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeCO}_3$  in Water with  $\text{pCO}_2 = 10^{-2.0}$  Atmosphere at  $25^\circ\text{C}$  and 1 Atmosphere Total Pressure.

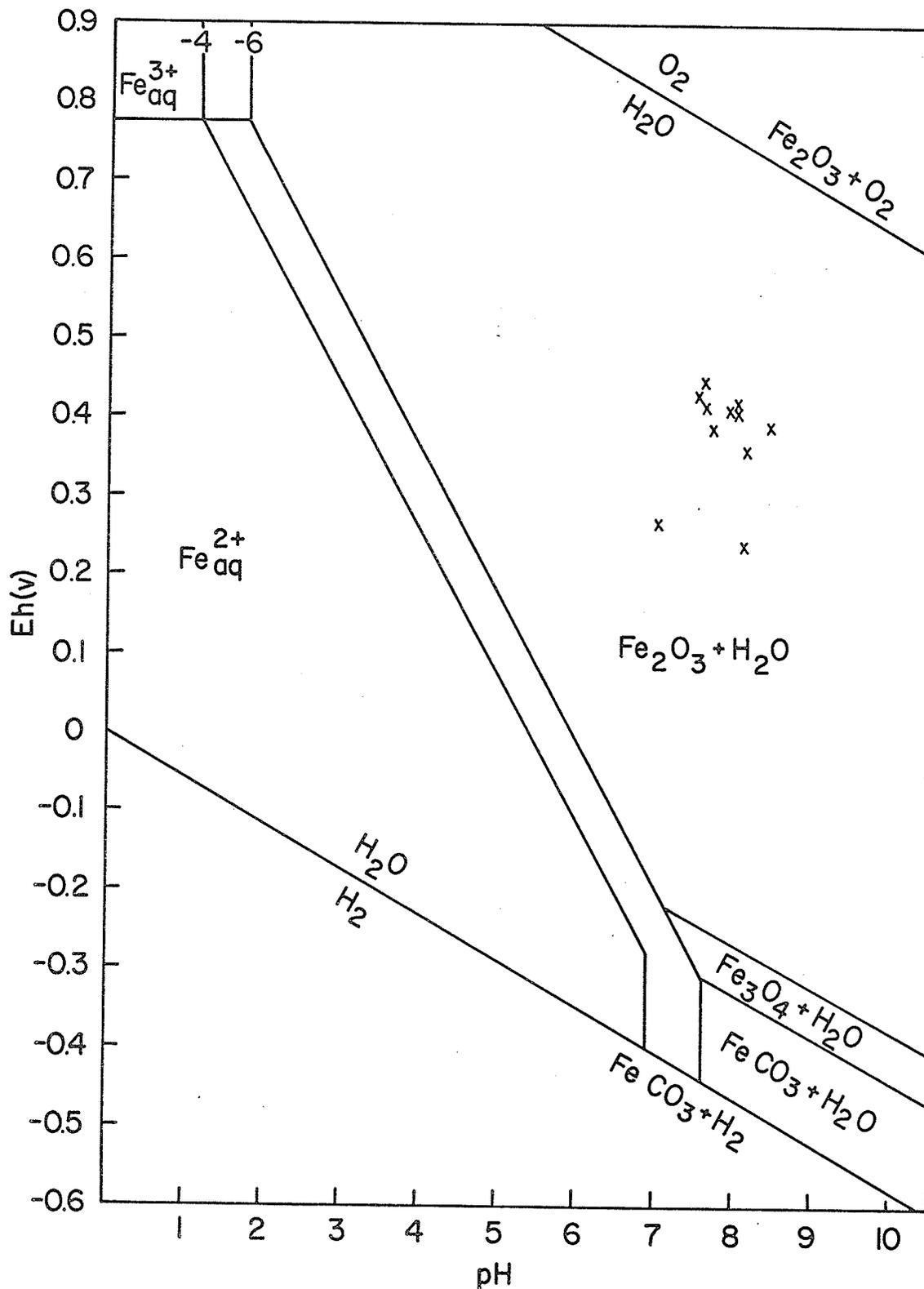


FIGURE 14. Eh-pH Values for the Plum Ridge Soil as Related to the Stability Fields of  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{FeCO}_3$  in Water with  $\text{pCO}_2 = 10^{-2.0}$  Atmosphere at  $25^\circ\text{C}$  and 1 Atmosphere Total Pressure.

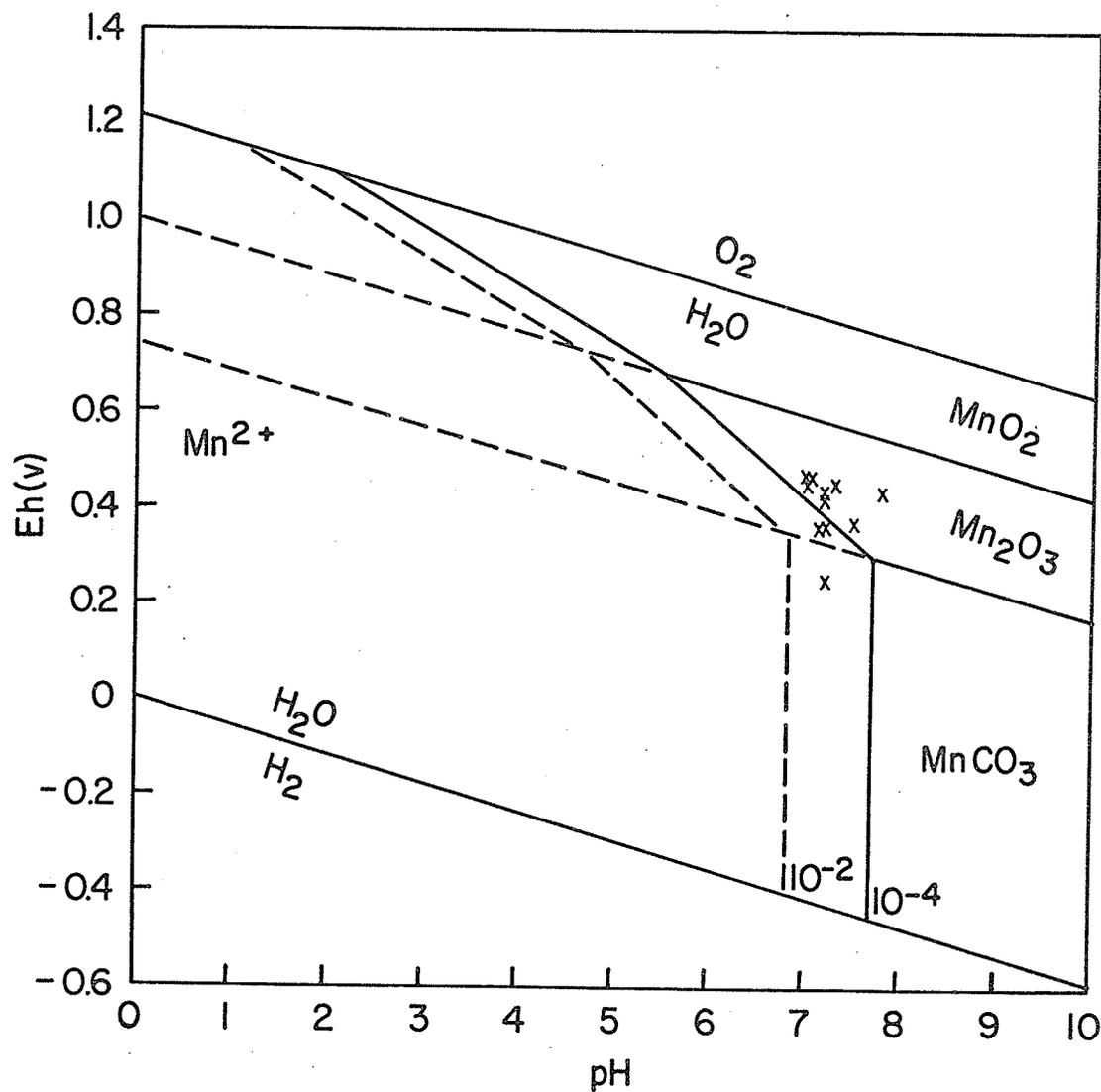


FIGURE 15. Eh-pH Values for the Red River Soil as Related to the Stability Fields of  $MnO_2$ ,  $Mn_2O_3$  and  $MnCO_3$  in Water with  $pCO_2=10^{-3.5}$  Atmosphere at  $25^\circ C$  and 1 Atmosphere Total Pressure.

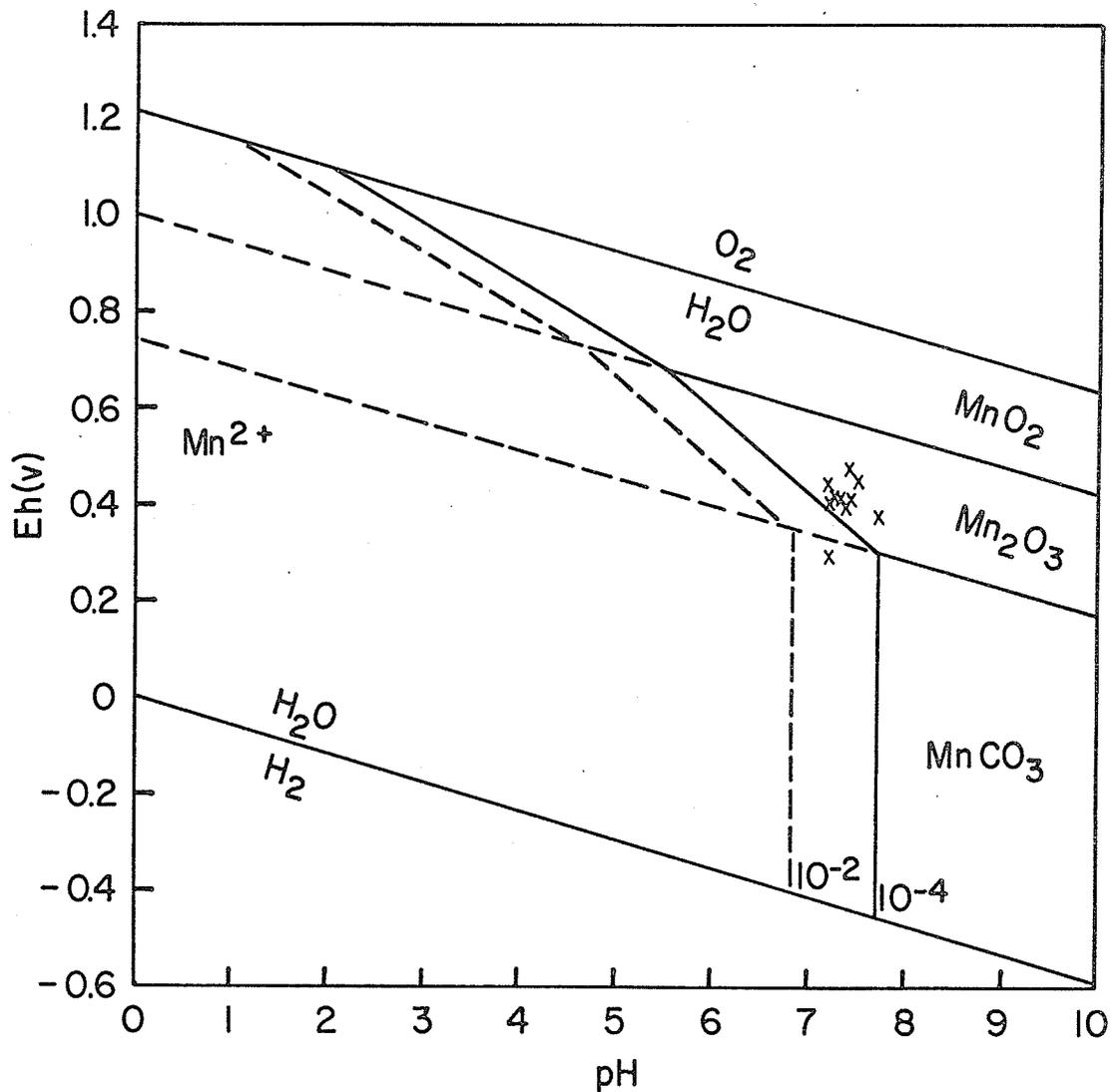


FIGURE 16. Eh-pH Values for the Tarno Soil as Related to the Stability Fields of  $MnO_2$ ,  $Mn_2O_3$  and  $MnCO_3$  in Water with  $pCO_2 = 10^{-3.5}$  Atmosphere at  $25^\circ C$  and 1 Atmosphere Total Pressure.

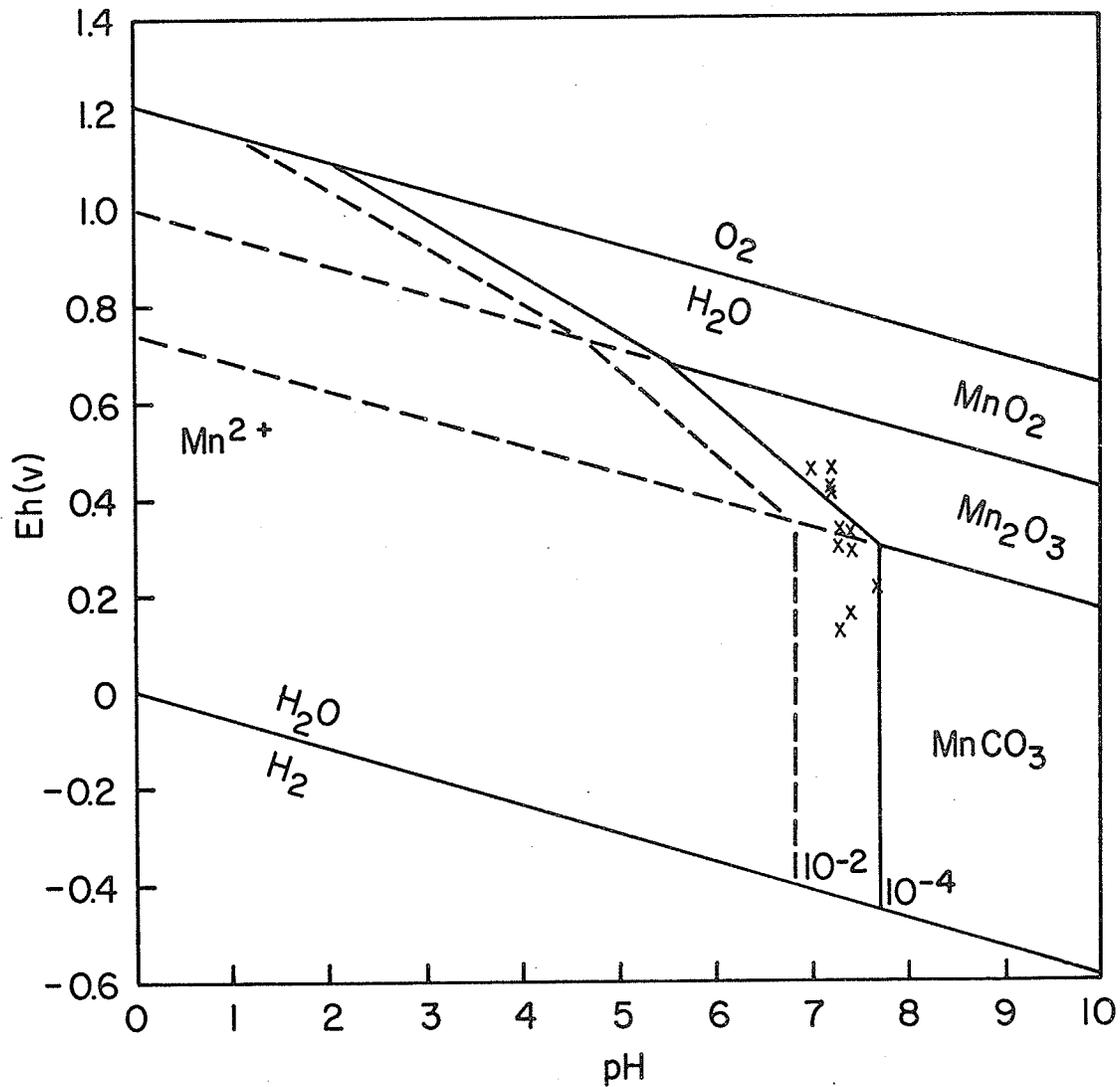


FIGURE 17. Eh-pH Values for the Lakeland Soil as Related to the Stability Fields of  $MnO_2$ ,  $Mn_2O_3$  and  $MnCO_3$  in Water with  $pCO_2 = 10^{-3.5}$  Atmosphere at  $25^\circ C$  and 1 Atmosphere Total Pressure.

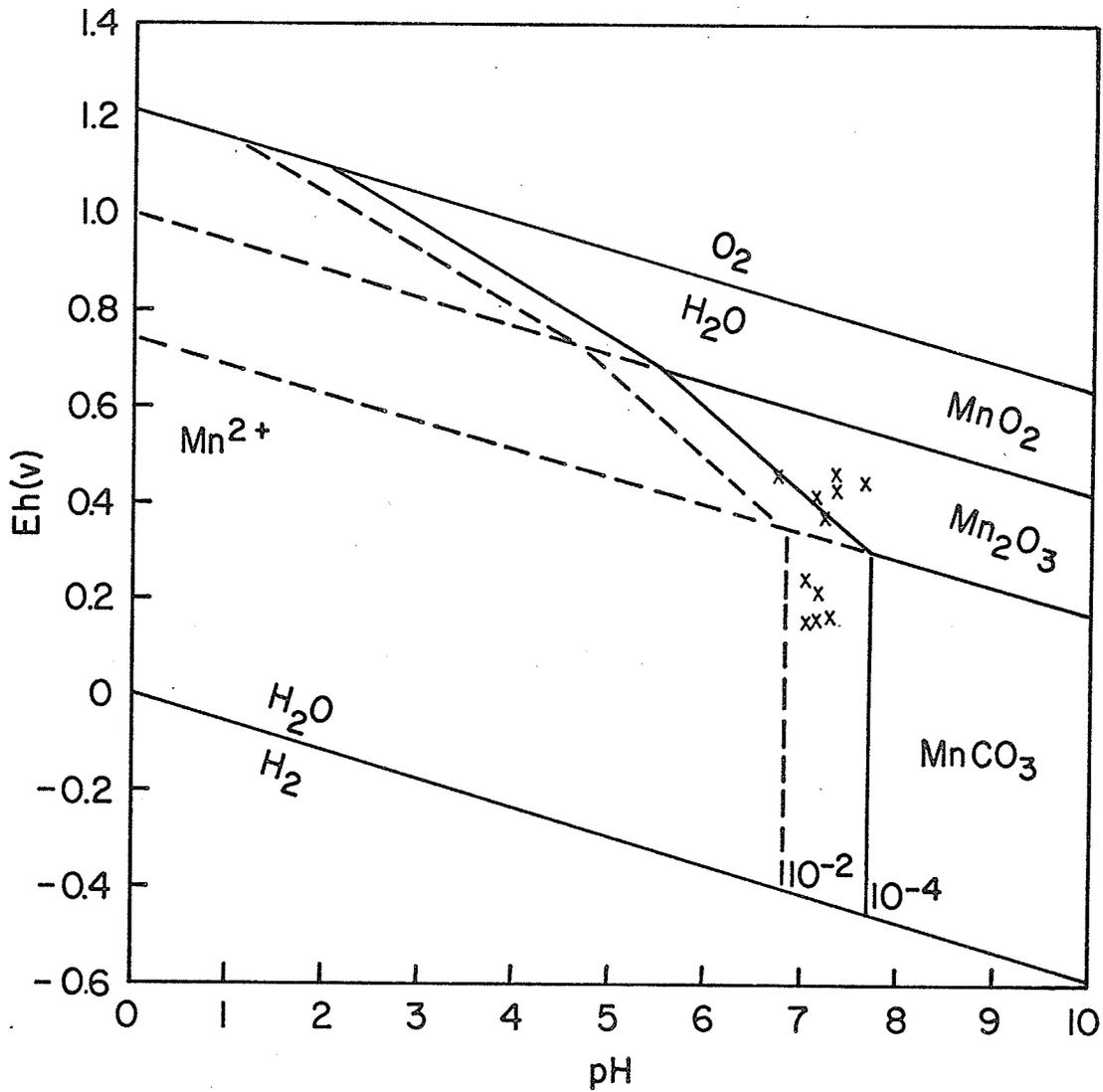


FIGURE 18. Eh-pH Values for the Newdale Soil as Related to the Stability Fields of  $MnO_2$ ,  $Mn_2O_3$  and  $MnCO_3$  in Water with  $pCO_2 = 10^{-3.5}$  Atmosphere at  $25^\circ C$  and 1 Atmosphere Total Pressure.

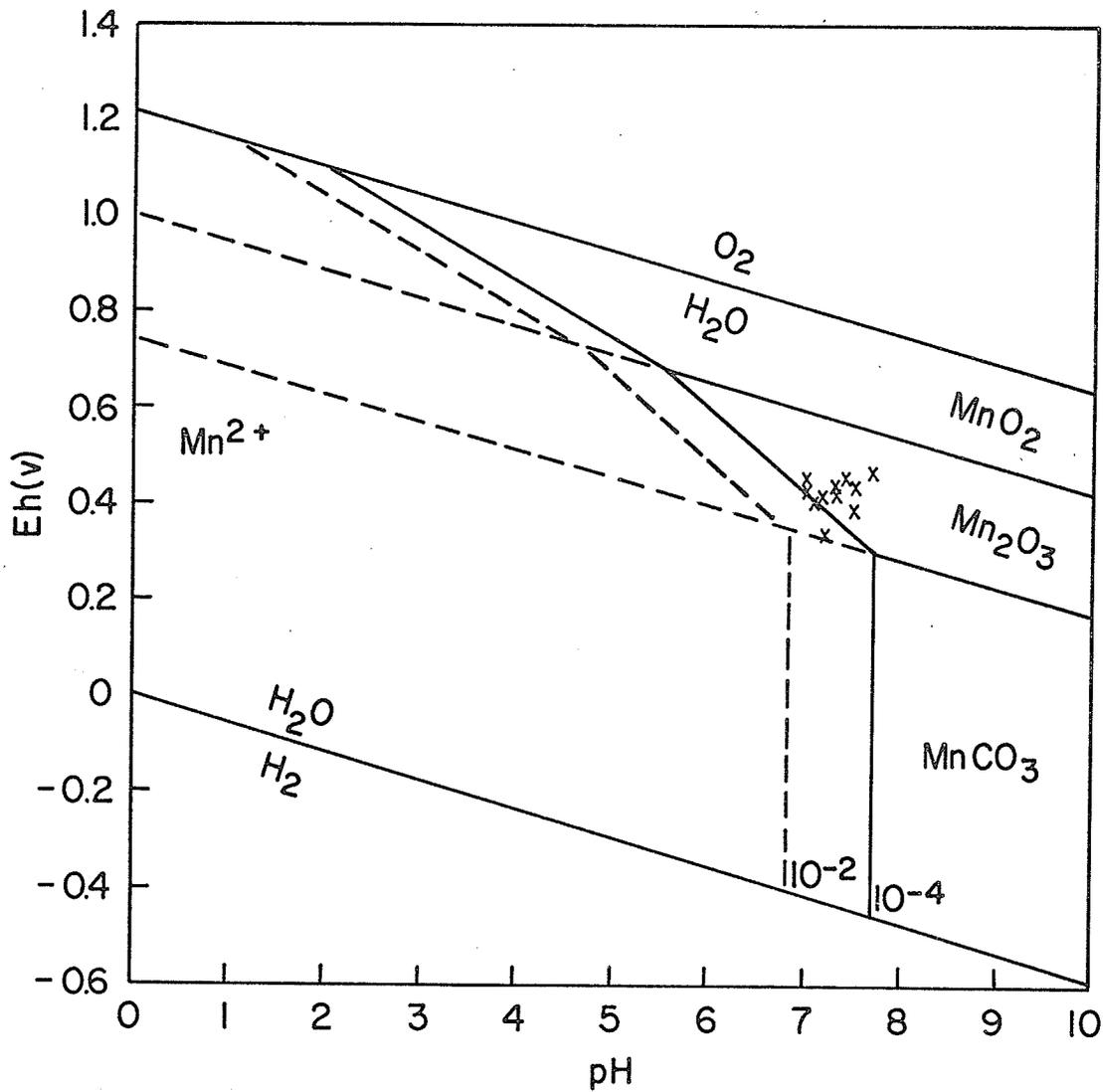


FIGURE 19. Eh-pH Values for the Stockton Soil as Related to the Stability Fields of  $MnO_2$ ,  $Mn_2O_3$  and  $MnCO_3$  in Water with  $pCO_2 = 10^{-3.5}$  Atmosphere at  $25^\circ C$  and 1 Atmosphere Total Pressure.

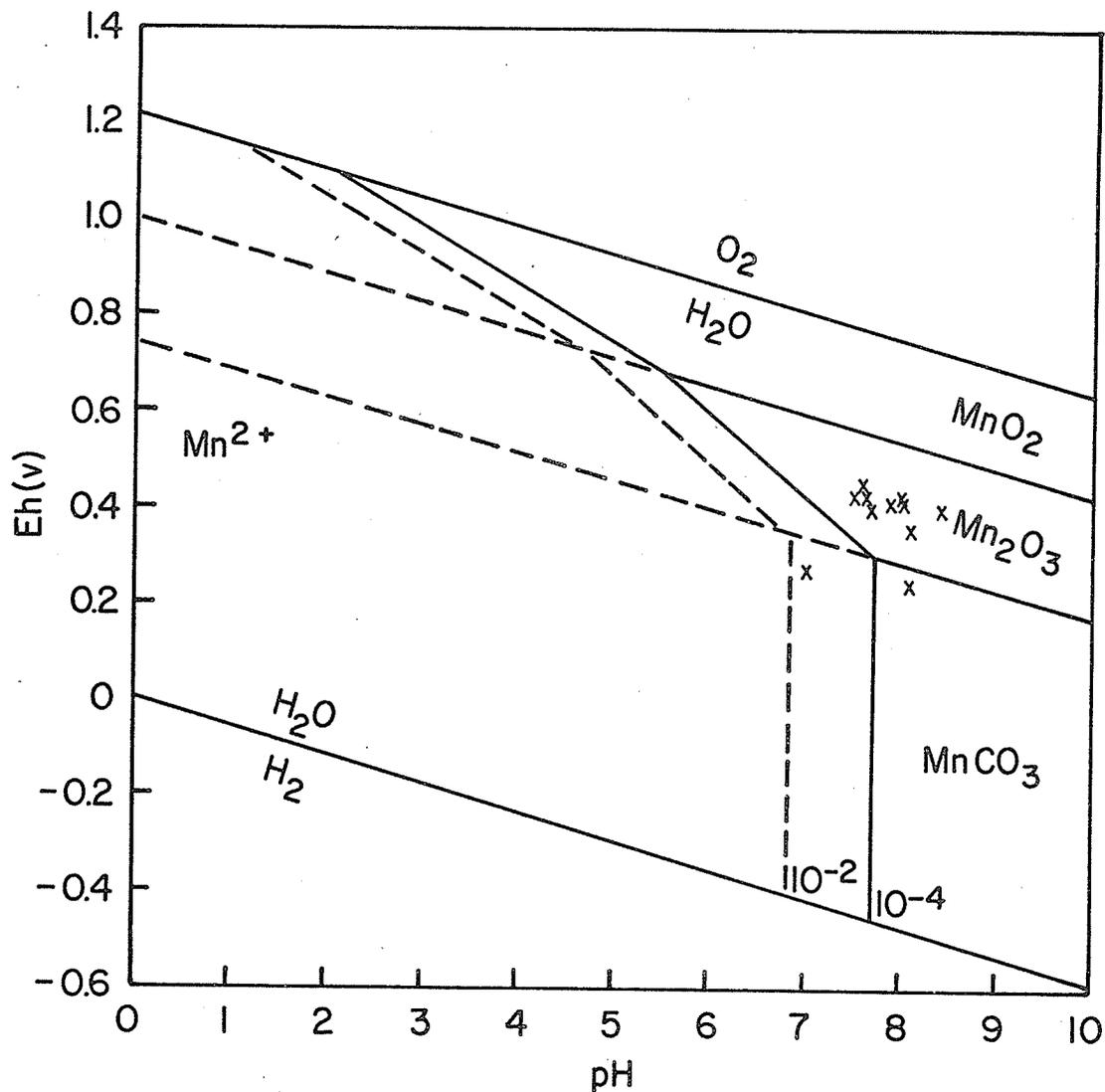


FIGURE 20. Eh-pH Values for the Plum Ridge Soil as Related to the Stability Fields of  $MnO_2$ ,  $Mn_2O_3$  and  $MnCO_3$  in Water with  $pCO_2 = 10^{-3.5}$  Atmosphere at  $25^\circ C$  and 1 Atmosphere Total Pressure.

of the experimentally measured values of Eh, [Fe] and pH.  $E^{\circ}$  and a or b can be evaluated from the following sets of equations.

(i)  $E^{\circ} = Eh + a \log(\text{Fe}^{2+}) + bpH$ : Calculate  $E^{\circ}$ .

(ii)  $Eh + bpH = E^{\circ} - a \log(\text{Fe}^{2+})$ : Calculate  $E^{\circ}$  and a.

(iii)  $Eh + a \log(\text{Fe}^{2+}) = E^{\circ} - bpH$ : Calculate  $E^{\circ}$  and b.

$E^{\circ} = 0.728$  volt,  $a = 0.059$  and  $b = 0.177$  for the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  redox system. A criterion for the presence of the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  redox system is the constancy and equality of the sum  $Eh + a \log(\text{Fe}^{2+}) + bpH$  to 0.728 irrespective of variations in measured Eh, pH and  $(\text{Fe}^{2+})$ . The second criterion for the presence of the system is the linear regression of  $(Eh + bpH)$  on  $\log(\text{Fe}^{2+})$ . If this redox system is present, the regression line has a slope or regression coefficient of  $-0.059$  ( $= -a$ ) and an intercept (constant) of  $0.728 = E^{\circ}$  (theoretical). The third criterion is the linear regression of  $Eh + a \log(\text{Fe}^{2+})$  on pH. If the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  redox system is operative in the soil, then the regression line has a slope of  $-0.177$  ( $= -b$ ) and an intercept (constant) of  $0.728 = E^{\circ}$  (theoretical).

The first and second criteria were applied using the experimental data. The third criterion was not used as pH did not vary markedly for most of the soils (Tables 3 to 8).

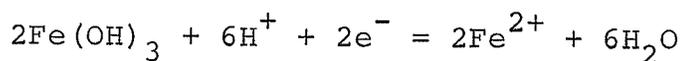
$E^{\circ}$  values were computed for each set of measured Eh,

pH and (Fe) by applying the relationship,  $E^\circ = \text{measured Eh} + 0.059 \log \text{measured (Fe)} + 0.177 \text{ measured pH}$  (Table 9). In these calculations, measured Fe concentration in ppm was assumed to be equal to the activity of Fe and converted to molarity by the relation (49):

$$\text{molarity} = \frac{\text{parts per million}}{\text{gram formula weight}} \times 10^{-3}.$$

The calculated  $E^\circ$  values were about double the theoretical  $E^\circ$  value for the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  redox system and there was thus no indication of the presence of this system, using the  $E^\circ$  value criterion.

Only two reports (9,133) were found in the literature citing calculated  $E^\circ$  values for redox systems from experimentally measured data. In one of these reports, Ponnampereuma et al. (133) postulated that  $\text{Fe}(\text{OH})_3$  was the metastable Fe compound present in the system and not  $\text{Fe}_2\text{O}_3$ , giving rise to the redox system



$$\Delta G^\circ = -24.4 \text{ Kcal}; \quad E^\circ = 1.06 \text{ volts.}$$

Ponnampereuma et al. (133) obtained calculated  $E^\circ$  values that were approximately the same as the theoretical  $E^\circ$  (= 1.06 volts). Breemen (9) failed to obtain calculated  $E^\circ$  values equal to the theoretical  $E^\circ$  for the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  system. Even if the  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  system is postulated for the six Manitoba soils, the calculated  $E^\circ$  values (Table 9) are still

TABLE 9

Calculated  $E^\circ$  Values for the Redox  
 System:  $\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$   
 (Theoretical  $E^\circ = 0.728$  volt)  
 $E^\circ = \text{Eh} + 0.059 \log(\text{Fe}^{2+}) + 0.177 \text{ pH}$

Number of Days after Saturation	Calculated $E^\circ$ in Volts for Each of the Soils					
	Red River	Tarno	Lakeland	Newdale	Stockton	Plum Ridge
3	-*	-	1.375	-	-	-
7	-	-	-	1.323	-	-
14	1.398	1.396	1.333	1.266	1.420	-
21	1.417	1.463	1.340	1.245	-	-
28	1.269	1.312	1.186	1.458	1.453	-
35	1.358	1.459	1.246	1.194	1.312	1.276
42	1.468	1.463	1.405	1.501	-	-
49	1.449	1.446	1.420	1.200	1.400	1.508
56	1.385	1.449	1.392	1.264	1.404	1.473
63	1.401	1.455	1.475	1.456	1.493	1.497
70	1.436	1.475	1.462	1.460	1.434	-
Mean $E^\circ$ (calc.) =	1.397	1.435	1.363	1.336	1.416	1.488

\*[Fe] in solution not detectable.

substantially different from the theoretical  $E^\circ$  values of 1.06 volts for the  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  system. Thus, neither the presence of the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  nor the  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  redox system was indicated for any of the six Manitoba soils by computation of  $E^\circ$  values.

The second criterion for the confirmation of the redox system present was applied to the experimental data (Table 10). The  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  and the  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  redox systems have the same theoretical slope of  $-0.059$  and intercepts of  $0.728 (= E^\circ)$  and  $1.06 (= E^\circ)$ , respectively.

The slope obtained for the Lakeland soil was equal to the theoretical value while those for the Red River and Tarno were close to the theoretical value of  $-0.059$  (Table 10). However, the intercepts obtained for all the soils were considerably different from the theoretical values for the  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  or the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  system.

The two criteria used above show that the  $E^\circ$  values determined using experimentally measured values of Eh, pH and  $[\text{Fe}]$  were different from the expected values for the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  or  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  redox system. One of the following factors probably account for the deviation of the observed  $E^\circ$  from the theoretical values: (i) the presence of a solid compound other than  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}(\text{OH})_3$ , (ii) the Fe measured in solution may not have been present as free ionic  $\text{Fe}^{2+}$ , (iii)  $E_{p_t}$  was not equal to Eh. The fact that the slopes obtained for some of the soils (Table 10) were close to the theoretical value would indicate that the Fe in solution may

TABLE 10

Regression of (Eh + 0.177 pH) on log (Fe)\*

Soil	Intercept (Constant)	Slope (Regression Coefficient=b)	Degrees of Freedom (n-2)	r <sup>2</sup>	r	
Red River	1.46	-0.045	7	0.134	-0.366	N.S.
Tarno	1.50	-0.043	7	0.200	-0.447	N.S.
Lakeland	1.36	-0.059	8	0.145	-0.381	N.S.
Newdale	1.19	-0.093	8	0.284	-0.533	N.S.
Stockton	1.59	-0.021	5	0.056	-0.236	N.S.
Plum Ridge	0.92	-0.162	2	0.724	-0.848	N.S.

N.S. Not Significant

$$*y = a + bx$$

where

$$y = Eh + 0.177 \text{ pH}$$

a = Intercept or constant

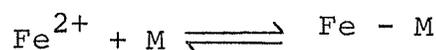
$$= 1.06 \text{ for } \text{Fe}(\text{OH})_3 - \text{Fe}^{2+} \text{ system}$$

$$= 0.728 \text{ for the } \text{Fe}_2\text{O}_3 - \text{Fe}^{2+} \text{ system}$$

b = -0.059 for both systems

$$x = \log(\text{Fe})$$

have been present as  $\text{Fe}^{2+}$ . There was, however, a displacement in the position of the lines relative to the theoretical line. The displacement of the regression lines was reflected by the higher values obtained for the intercepts. This displacement may be explained as follows: The  $\text{Fe}_{(\text{measured})}$  in solution may be present in free  $\text{Fe}^{2+}$  and as  $\text{Fe}^{2+}$  associated with soil constituent (M) which could be represented as follows:



and

$$\frac{(\text{Fe} - \text{M})}{(\text{Fe}^{2+}) (\text{M})} = K_{\text{assoc.}}$$

$$(\text{Fe}^{2+}) = \frac{(\text{Fe} - \text{M})}{K_{\text{assoc.}} (\text{M})}$$

If (M) is nearly constant, then  $\text{Fe}^{2+} \cong K' (\text{Fe} - \text{M})$ , where  $K'$  is an unknown constant.  $(\text{Fe})_{(\text{measured})}$  is assumed to be made up of two components:

$$\begin{aligned} (\text{Fe})_{(\text{measured})} &= (\text{Fe}^{2+}) + (\text{Fe} - \text{M}) \\ &\cong (1 + 1/K') (\text{Fe}^{2+}) \end{aligned}$$

and

$$\frac{(\text{Fe})_{\text{measured}}}{1 + 1/K'} = (\text{Fe}^{2+})$$

The Nernst equation for the reaction  $\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$  is  $(\text{Eh} + 0.177 \text{ pH}) = E^\circ - 0.059 \log(\text{Fe}^{2+})$ .

Substituting the relationship between  $(\text{Fe}^{2+})$  and  $(\text{Fe})_{(\text{measured})}$  (as described above) into the Nernst equation, leads to the expression:

$$\begin{aligned} (E_h + 0.177\text{pH}) &= E^\circ + 0.059 \log(1 + 1/K') - 0.059 \log(\text{Fe})_{\text{measured}} \\ &= E^{\circ'} - 0.059 \log(\text{Fe})_{\text{measured}}, \end{aligned}$$

where

$$E^{\circ'} = E^\circ + 0.059 \log(1 + 1/K').$$

$E^{\circ'}$ , thus represents the higher values of intercepts obtained which were different from the theoretical  $E^\circ$ . The slope of  $-0.059$  is, however, not affected. The unknown value of  $0.059 \log(1 + 1/K')$  represents the amount of displacement of the regression line from the theoretical  $E^\circ$  intercept.

Since the difference between  $E^{\circ'}$  and  $E^\circ = 0.059 \log(1 + 1/K')$ , it should be possible to evaluate  $K'$  and thus obtain the relative magnitude of  $K_{\text{assoc.}}$ , the association constant between Fe in solution and the soil component, M (e.g. organic matter). Considering the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  system, theoretical  $E^\circ = 0.728\text{v}$ . The average  $E^{\circ'}$  for all soils  $\cong 1.40$  volts (Tables 9 and 10). Therefore,  $E^{\circ'} - E^\circ = 1.40 - 0.728 = 0.672\text{v} = 0.059 \log(1 + 1/K')$  and  $\log(1 + 1/K') = \frac{0.672}{0.059} = 11.40$  and  $1 + 1/K' = 10^{11.40} \cong 1/K'$ .

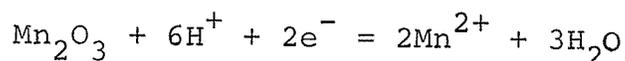
$$\text{Thus, } K' = 10^{-11.40} = \frac{1}{K_{\text{assoc.}}(M)}$$

$$\text{and } K_{\text{assoc.}}(M) = 10^{11.40}$$

$$\text{and } K_{\text{assoc.}} = \frac{10^{11.40}}{(M)}.$$

Thus, if the activity or concentration of M is known,  $K_{\text{assoc.}}$  could be evaluated. If (M) is, for example,  $10^{-10}$  molar,  $K_{\text{assoc.}} \cong 10^{21}$ .

$Mn_2O_3$  and  $MnCO_3$  were probably the Mn compounds involved in the Mn redox systems in the soils (Figures 15 to 20).  $Mn_2O_3$  is reduced to  $Mn^{2+}$  ions (in solution) as follows:

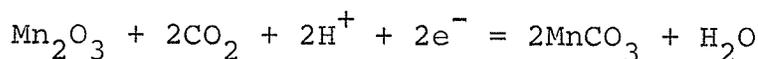


$$\Delta G^\circ = -66.57 \text{ Kcal}; \quad E^\circ = 1.443 \text{ volts.}$$

$$\text{and} \quad Eh = E^\circ - 0.059 \log(Mn^{2+}) - 0.177 \text{ pH.}$$

As was done for the Fe redox system,  $E^\circ$  values were calculated (Table 11) and regressions of  $(Eh + 0.177 \text{ pH})$  on  $\log(Mn^{2+})$  were determined (Table 12) to further investigate the presence of the  $Mn_2O_3 - Mn^{2+}$  redox system (Tables 11 and 12).

The calculated  $E^\circ$  values were close to the theoretical value of 1.443 (Table 11). However, the calculated values showed considerable variation with time of saturation, especially for the Lakeland and Newdale soils. These two soils were strongly reduced. Calculated  $E^\circ$  values, lower than the theoretical value of 1.443 volts, were mostly obtained in instances when the measured Eh was below about 0.400 volt (Tables 3 to 8 and 11). As the Eh - pH diagrams showed, there was a transition from the  $Mn_2O_3$  to the  $MnCO_3$  phase at Eh values below 0.400 volt. During the transition from the  $Mn_2O_3$  to the  $MnCO_3$  phase, the following equation (rather than the one for the  $Mn_2O_3 - Mn^{2+}$  system) will apply:



$$\Delta G^\circ = -44.47 \text{ Kcal}; \quad E^\circ = 0.96 \text{ volt}$$

TABLE 11

Calculated  $E^\circ$  Values for the Redox  
 System:  $Mn_2O_3 + 6H^+ + 2e^- = 2Mn^{2+} + 3H_2O$   
 (Theoretical  $E^\circ = 1.443$  volt)  
 $E^\circ = Eh + 0.059 \log(Mn^{2+}) + 0.177 pH$

Number of Days after Saturation	Calculated $E^\circ$ in Volts for Each of the Soils					
	Red River	Tarno	Lakeland	Newdale	Stockton	Plum Ridge
3	-*	1.437	1.393	1.448	1.504	1.496
7	1.439	1.499	1.487	1.413	1.402	1.544
14	1.427	1.455	1.355	1.273	1.444	1.508
21	1.456	1.498	1.357	1.250	1.468	1.390
28	1.285	1.326	1.197	1.457	1.472	1.528
35	1.353	1.443	1.234	1.187	1.359	1.306
42	1.471	1.468	1.410	1.498	1.484	1.502
49	1.441	1.441	1.418	1.215	1.436	1.562
56	1.389	1.450	1.392	1.258	1.447	1.532
63	1.473	1.525	1.471	1.515	1.499	1.519
70	1.454	1.482	1.469	1.463	1.504	1.485
Mean $E^\circ$ (calc.) =	1.418	1.456	1.380	1.362	1.456	1.488

\*[Mn] in solution not detectable.

TABLE 12

Regression of (Eh + 0.177 pH) on log(Mn) #

Soil	Intercept (Constant) =a	Slope (Regression Coefficient=b)	Degrees of Freedom = (n-2)	r <sup>2</sup>	r
Red River	1.45	-0.051	8	0.040	-0.200
Tarno	1.46	-0.056	9	0.231	-0.481
Lakeland	1.28	-0.083	9	0.174	-0.417
Newdale	0.66	-0.242	9	0.516	-0.718*
Stockton	1.37	-0.077	9	0.384	-0.619*
Plum Ridge	1.18	-0.124	9	0.499	-0.706*

\*Significant at the 5% level

$$y = a + bx$$

where

$$y = \text{Eh} + 0.177 \text{ pH}$$

a = Intercept or constant

= 1.443 for the  $\text{Mn}_2\text{O}_3 - \text{Mn}^{2+}$  system

b = -0.059

x = log(Mn)

and  $Eh = E^\circ + 0.059 \log pCO_2 - 0.059 \text{ pH}$ .

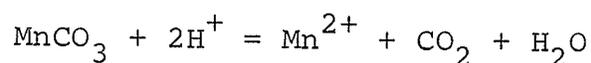
However, it is very difficult to separate the measured values into two groups for computing  $E^\circ$  values for the  $Mn_2O_3 - Mn^{2+}$  and the  $Mn_2O_3 - MnCO_3$  redox systems. Calculated  $E^\circ$  values higher than theoretical value may be due to factors such as the existence of Mn in solution in forms other than free  $Mn^{2+}$ .

Apart from those instances where  $MnCO_3$  must have formed as a result of strong reduction, the closeness of the calculated  $E^\circ$  values to the theoretical value for the  $Mn_2O_3 - Mn^{2+}$  system shows that the  $Mn_2O_3 - Mn^{2+}$  redox system operated in the soils and that the measured potentials were related to the potential of this system. This was in sharp contrast to the Fe system which did not appear to have any relationship with the measured Eh.

Apart from the Newdale and Plum Ridge soils, the slopes for the other four soils approximated the theoretical value for the  $Mn_2O_3 - Mn^{2+}$  system (Table 12). The deviations in slopes of the Newdale and Plum Ridge soils from the theoretical value may be due to the formation of  $MnCO_3$  during reduction. The intercept,  $E^\circ$ , for the Newdale soil deviated greatly from the theoretical value. Deviations of the intercepts for the Lakeland and Plum Ridge soils from the theoretical value were moderate. Strong reduction and/or the presence of carbonate in these three soils (Newdale, Lakeland and Plum Ridge) must have enhanced the formation of  $MnCO_3$ ; thus, the  $Mn_2O_3 - Mn^{2+}$  system, on which the theoretical calculations

were based, was not operative throughout the course of reduction. Generally, the data on Table 12 reasonably attest to the presence of the  $\text{Mn}_2\text{O}_3 - \text{Mn}^{2+}$  redox system in the soils for varying periods of time during reduction. Apart from the Newdale soil, the displacements in the positions of the intercepts for the Mn system were considerably less than those found for the Fe system. Also, the correlation coefficient ( $r$ ) between  $(\text{Eh} + 0.177 \text{ pH})$  and  $\log(\text{Mn}^{2+})$  was significant for the Newdale, Stockton and Plum Ridge soils.

The compound  $\text{MnCO}_3$  gives rise to  $\text{Mn}^{2+}$  ions as follows:



Log K (equilibrium constant) for the reaction is 8.10 and

$$\log (\text{Mn}^{2+}) + \log \text{pCO}_2 + 2\text{pH} = \log K = 8.10.$$

If experimentally measured  $\text{Mn}^{2+}$ ,  $\text{pCO}_2$  and pH are substituted into the above equation and found to be equal to 8.10 (= log K) the presence of solid phase  $\text{MnCO}_3$  in the system could be confirmed (131). This could not be done, however, since the  $\text{pCO}_2$  in the soil extracts was not measured.

If the redox systems operating in the soil or soil solutions at specific periods could be identified, it is possible to calculate the Fe or Mn concentrations in the soil solutions by substitution of the experimentally measured Eh and pH values into the Nernst equation. There are no reports in the literature that have compared experimentally

measured Fe and Mn with values predicted from measured Eh and pH. However, two reports (50,64) have indicated that appreciable discrepancies do exist between measured and calculated Fe and Mn concentrations. Hem and Cropper (64) have reported that Fe concentrations predicted by Eh and pH are generally much lower than measured amounts in solution as some of the Fe found in solution may consist of undissolved or complexed species. Geering et al. (50) predicted that the activities of  $Mn^{2+}$  in soil solutions are invariably several orders of magnitude higher than measured  $Mn^{2+}$  activities because of (i) incorrect prediction of the redox system, (ii) the uncertainty or inapplicability of Eh measurements and (iii) the localised chemical reactions of  $Mn^{2+}$  in soil, as affected by the presence of certain soil microbes and plant roots; the third reason may, however, not apply when Eh measurements are made in soil solutions.

Since Eh measurements are characteristically subject to error (135), activities or concentrations predicted by measured Eh are generally likely to be different from actual concentrations in solution. The exact identification of the operating redox system is also a very necessary prerequisite for correct predictions.

Despite the shortcomings listed above, experimentally measured Eh and pH were used to predict  $Fe^{2+}$  and  $Mn^{2+}$  concentrations by substituting the measured Eh and pH values into the Nernst equations for the respective Fe or Mn redox

systems.

For the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  system,

$$\text{Eh} = E^\circ - 0.059 \log(\text{Fe}^{2+}) - 0.177 \text{ pH}$$

and

$$\begin{aligned} \log(\text{Fe}^{2+}) &= \frac{E^\circ - \text{Eh} - 0.177 \text{ pH}}{0.059} \\ &= 16.95 (0.728 - \text{Eh} - 0.177 \text{ pH}) \end{aligned}$$

where  $E^\circ = 0.728$  volts.

For the  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  system,

$$\begin{aligned} \text{Eh} &= E^\circ - 0.049 \log(\text{Fe}^{2+}) - 0.177 \text{ pH} \\ &= 1.06 - 0.059 \log(\text{Fe}^{2+}) - 0.177 \text{ pH} \end{aligned}$$

and

$$\begin{aligned} \log(\text{Fe}^{2+}) &= \frac{1.06 - \text{Eh} - 0.177 \text{ pH}}{0.059} \\ &= 16.95 (1.06 - \text{Eh} - 0.177 \text{ pH}). \end{aligned}$$

The predicted values for the  $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  system and  $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  system are shown in Appendix IIA and Appendix IIB, respectively. For purposes of comparison, the  $[\text{Fe}]$  values measured in solution are given in Appendix IIC. The measured concentrations far exceed the calculated concentrations. The possible reasons for these discrepancies were investigated and reported in the next subsection. It was shown earlier that there was a shift in the position of the intercepts when the regression of  $(\text{Eh} + 0.177 \text{ pH})$  on  $\log(\text{Fe})$  was determined. The shift in the position of the intercept could further be explained by

the fact that the measured [Fe] which was used for the regression analysis was much higher than what would be predicted by the measured Eh and pH values.

Calculations of  $\text{Mn}^{2+}$  concentrations were based on the Nernst equation for the  $\text{Mn}_2\text{O}_3 - \text{Mn}^{2+}$  system as follows:

$$\begin{aligned} \text{Eh} &= E^{\circ} - 0.059 \log(\text{Mn}^{2+}) - 0.177 \text{ pH} \\ &= 1.443 - 0.059 \log(\text{Mn}^{2+}) - 0.177 \text{ pH} \end{aligned}$$

and

$$\begin{aligned} \log(\text{Mn}^{2+}) &= \frac{1.443 - \text{Eh} - 0.177 \text{ pH}}{0.059} \\ &= 16.95 (1.443 - \text{Eh} - 0.177 \text{ pH}). \end{aligned}$$

The calculated and measured Mn concentrations are shown in Appendices IIIA and IIIB, respectively. As compared with the Fe system, the calculated  $[\text{Mn}^{2+}]$  values approached much more closely the measured [Mn] values. There were a few instances in which the measured and calculated values were very nearly the same and several instances where the calculated values were within  $\pm 50\%$  of the measured values. The measured Eh thus reflected, to a certain degree, the concentration of Mn in solution. There were, however, several instances where large discrepancies between measured and calculated [Mn] were found. These occurred mostly in instances where the soil was strongly reduced and  $\text{MnCO}_3$  likely formed.

The equilibrium between  $\text{MnCO}_3$  and  $\text{Mn}^{2+}$  ions, as indicated earlier, is partly dependent on  $\text{pCO}_2$ . Calculations

of  $[\text{Mn}^{2+}]$  ions based on the  $\text{MnCO}_3 - \text{Mn}^{2+}$  system could not be made since the partial pressure of  $\text{CO}_2$  in the soil solutions was not measured.

In order to investigate the extent to which experimentally measured Eh and pH affected variations in measured [Fe] and [Mn], multiple regression analyses of the negative logarithms of Fe (pFe) and Mn (pMn) on Eh and pH were determined. The following models were used:

$$\text{pFe} = a_0 + a_1\text{Eh} + a_2\text{pH}$$

$$\text{pMn} = a_0 + a_1\text{Eh} + a_2\text{pH}$$

where  $a_0$  = a constant or intercept

$a_1$  = multiple regression coefficient for Eh

$a_2$  = multiple regression coefficient for pH.

The above models include both Eh and pH. Thus, there is a tacit assumption that the reactions in the soils involved oxidation and reduction because only such reactions could jointly depend on Eh and pH. Where there is no oxidation and/or reduction, the reaction will be independent of Eh and the above regression models would not apply. It is obvious from earlier discussions that not all the Mn systems found to be present in the soils involved oxidation and reduction since the  $\text{MnCO}_3$  system was also found to be operative in the soils. As discussed earlier, the Fe redox systems were ill-defined or unknown. Since the redox systems that operated in the soils could not be clearly identified, multiple regression analyses were conducted to determine the

variations in measured [Fe] and [Mn] that could be accounted for by variations in Eh and pH.

The theoretical regression equations for the above multiple regression models for the ideal systems involving only oxidation and reduction are as follows:

$$\text{Fe}_2\text{O}_3 - \text{Fe}^{2+} \text{ system: } p\text{Fe} = -12.34 + 16.95\text{Eh} + 3\text{pH}$$

$$\text{Fe}(\text{OH})_3 - \text{Fe}^{2+} \text{ system: } p\text{Fe} = -17.96 + 16.95\text{Eh} + 3\text{pH}$$

$$\text{Mn}_2\text{O}_3 - \text{Mn}^{2+} \text{ system: } p\text{Mn} = 24.45 + 16.95\text{Eh} + 3\text{pH}.$$

The regression equations and the squares of the correlation coefficient ( $R^2$ ) obtained for the different soils using the experimental data are given in Tables 13 and 14 for Fe and Mn, respectively. The regression equations deviated considerably from the theoretical equations. The experimental and theoretical values of  $a_0$ ,  $a_1$  and  $a_2$  differed markedly. These discrepancies were probably due to one or more of the following factors: (i) the regression models are equilibrium reaction equations and the Fe and Mn redox systems were either not in equilibrium or attained equilibrium at very slow rates; the delayed release of Fe and Mn following reduction, cited earlier, is a case in point; (ii) the redox systems on which the regression models were based were either absent or were not operative throughout the duration of saturation (e.g. the transition from  $\text{Mn}_2\text{O}_3$  to  $\text{MnCO}_3$ ); (iii) measured Fe and Mn were not present in solution as ionic  $\text{Fe}^{2+}$  or ionic  $\text{Mn}^{2+}$ , respectively.

The variations in Eh and pH accounted for about 20% to 95% of the variations in the concentration of Fe for the

TABLE 13

Multiple Regression Equations for Fe and Eh and pH  
 Model:  $p\text{Fe} = a_0 + a_1\text{Eh} + a_2\text{pH}$

Soil	Equation	$R^2$
Red River	$p\text{Fe} = -6.33 + 2.75\text{Eh} + 1.37\text{pH}$	0.207
Tarno	$p\text{Fe} = -6.18 + 4.04\text{Eh} + 1.23\text{pH}$	0.238
Lakeland	$p\text{Fe} = 13.11 + 1.48\text{Eh} - 1.29\text{pH}$	0.298
Newdale	$p\text{Fe} = 14.92 + 4.14\text{Eh} - 1.71\text{pH}$	0.561*
Stockton	$p\text{Fe} = -14.31 - 3.21\text{Eh} + 2.83\text{pH}$	0.349
Plum Ridge	$p\text{Fe} = -6.63 - 1.37\text{Eh} + 1.58\text{pH}$	0.949

\*R significant at the 5% level.

TABLE 14

Multiple Regression Equations for Mn and Eh and pH  
 Model:  $pMn = a_0 + a_1Eh + a_2pH$

Soil	Equation	R <sup>2</sup>
Red River	$pMn = 4.44 + 0.76Eh - 0.05pH$	0.048
Tarno	$pMn = -5.43 + 3.04Eh + 1.15pH$	0.255
Lakeland	$pMn = 13.91 + 1.01Eh - 1.40pH$	0.402
Newdale	$pMn = -1.26 + 1.88Eh + 0.63pH$	0.533*
Stockton	$pMn = -4.45 + 4.32Eh + 0.96pH$	0.382
Plum Ridge	$pMn = -4.57 + 2.16Eh + 1.08pH$	0.625*

\*R significant at the 5% level.

various soils (Table 13). The value of 95%, observed for the Plum Ridge soil, was obtained from only four sets of observations and thus not significant. Variations in Eh and pH accounted for about 5% to 62% of the variations in Mn concentration for the various soils (Table 14). The Red River and Tarno soils had the lowest  $R^2$  values. These two soils contain the highest amounts of clay and organic matter. The high amounts of organic matter and clay may have retarded the release of Fe and Mn into solution when the soil was reduced.  $R^2$  values and regression equations as calculated above were not found in the literature.

In order to investigate the effects of Eh or pH alone on the variations in Fe and Mn concentrations, simple regression analyses of pH on pFe or pMn and of Eh on pFe or pMn were determined. The simple regression equations and the corresponding simple correlation coefficients ( $r$ ) are shown in Tables 15 and 16 for Fe and Mn, respectively. The simple regression coefficients show the change in pFe or pMn for every unit change in Eh or pH of the soil solution. In four instances, the regression equations indicated that increases in pH resulted in decreases in pFe or pMn. These observations, however, were probably due to the pH remaining relatively constant or increasing while Eh decreased resulting in high concentrations of Fe or Mn in the soil solutions.

A limitation of simple regression analyses is that one factor (e.g. Eh) is regarded as fixed while the other

TABLE 15

Simple Regression Equations for Fe and Eh and pH

Model:  $p\text{Fe} = a_I + b_I \text{Eh}$

$p\text{Fe} = a_{II} + b_{II} \text{pH}$

Soil	Equation	r
Red River	$p\text{Fe} = 3.91 + 1.79 \text{Eh}$	0.219
	$p\text{Fe} = -2.97 + 1.05\text{pH}$	0.320
Tarno	$p\text{Fe} = 2.98 + 3.71\text{Eh}$	0.326
	$p\text{Fe} = -3.85 + 1.13\text{pH}$	0.336
Lakeland	$p\text{Fe} = 3.29 + 2.58\text{Eh}$	0.466
	$p\text{Fe} = 17.72 - 1.86\text{pH}$	-0.500
Newdale	$p\text{Fe} = 2.83 + 3.86\text{Eh}$	0.640*
	$p\text{Fe} = 13.65 - 1.35\text{pH}$	-0.305
Stockton	$p\text{Fe} = 4.71 + 0.18\text{Eh}$	0.013
	$p\text{Fe} = -12.91 + 2.45\text{pH}$	0.552
Plum Ridge	$p\text{Fe} = 3.09 + 5.22\text{Eh}$	0.503
	$p\text{Fe} = -6.22 + 1.46\text{pH}$	0.968

\*r significant at the 5% level.

TABLE 16

Simple Regression Equations for Mn and Eh and pH

Model:  $pMn = a_I + b_I Eh$

$pMn = a_{II} + b_{II}pH$

Soil	Equation	r
Red River	$pMn = 4.02 + 0.81Eh$	0.217
	$pMn = 5.27 - 0.17pH$	-0.109
Tarno	$pMn = 3.08 + 3.02 Eh$	0.317
	$pMn = -4.15 + 1.15pH$	0.391
Lakeland	$pMn = 3.28 + 2.21Eh$	0.516
	$pMn = 17.40 - 1.83pH$	-0.606*
Newdale	$pMn = 3.16 + 2.18Eh$	0.661*
	$pMn = -2.92 + 0.95pH$	0.486
Stockton	$pMn = 2.13 + 5.36Eh$	0.429
	$pMn = -3.61 + 1.09pH$	0.516
Plum Ridge	$pMn = 3.71 + 2.73Eh$	0.329
	$pMn = -4.03 + 1.12pH$	0.747*

\*r significant at the 5% level.

(e.g. pH) is varied or vice versa. However, in practice, this is not true as Eh and pH change simultaneously. The multiple regression analysis which involves the simultaneous variations of Eh and pH would therefore appear to be more meaningful in the interpretation of data of this nature.

The simple regression analysis involving pH and pMn may be useful for the  $\text{MnCO}_3 - \text{Mn}^{2+}$  system if  $\text{pCO}_2$  is constant; the latter system depends only on variations in  $\text{pCO}_2$  and pH.

Some of the simple correlation coefficients shown in Tables 15 and 16 were significant at the 5% level. In this study it was found that by considering both Eh and pH a greater percentage of the variations in the amounts of Fe and Mn in solution could be accounted for than by considering Eh or pH alone.

(b) The Nature of Fe and Mn in  
Extracted Soil Solutions

The results obtained in the previous experiment showed that the Fe redox system in the extracted soil solutions was ill-defined and could not be clearly identified. The values of  $E^{\circ}$  calculated from the experimentally determined Eh, pH and [Fe] values did not agree with values for known Fe redox systems. These calculations were based on the premise that the Fe measured in solution was present as  $\text{Fe}^{2+}$ . If this assumption was correct, the discrepancies between the theoretical and calculated values would probably not have been so pronounced. Some authors (64,133) who have

studied Fe redox systems in soil solutions have suggested that Fe in soil solutions may be complexed with organic matter. It was thus considered necessary to investigate more closely the forms in which Fe and Mn occurred in extracted soil solutions. An understanding of the forms in which Fe and Mn occur in soil solutions would aid in explaining the discrepancies between the observed and theoretical values discussed in the previous experiment.

One-thousand-gram samples of the soils used in the previous experiment were placed into 3.30-liter plastic pots (17.50 cm high and 16.00 cm I.D.) and kept at saturation moisture percentage for a period of six weeks. The soils were extracted at weekly intervals and the Eh and pH and Fe and Mn contents of the soil solutions measured as previously described. Portions of the soil extracts were saved for separation of complexed and uncomplexed Fe and Mn. (The Eh and pH data for this experiment are not presented. The pH values were similar to those reported earlier for each soil. However, the Eh values were higher than those reported for earlier studies.) The complexed and uncomplexed Fe and Mn were separated by passing 10 ml of the soil extract through a sodium-saturated cation exchange resin (Rexyn 101 (Na) Chromatographic Grade, supplied by the Fisher Scientific Company). Prior to use, the resin was packed to a height of about 10 cm in a glass column (40 cm high and 3.30 cm I.D.) and leached with one

liter of 5M HCl to remove traces of Fe. The method used was similar to that introduced by Samsahl (147) who found that 3M HCl was the lowest possible concentration of acid that kept the Fe in a negatively charged state in an anion exchange resin. Leaching with 5M HCl was found to remove all traces of Fe from the Na-saturated cation exchange resin. After the resin was leached with 5M HCl it was leached with de-ionised water until the pH of the effluent was neutral. The resin was then saturated with Na by leaching it several times with a 10% solution of  $\text{NaHCO}_3$ . On completion of saturation with  $\text{NaHCO}_3$ , the resin was leached with de-ionised water until the pH of the effluent was neutral. The resin was then stored and portions of it used to pack small columns for use with soil solutions.

Small resin columns, 2.5 cm in height were prepared in glass columns 8 cm high and 2 cm internal diameter. After packing, the excess water in the column was removed by suction.

A preliminary study was conducted using standard solutions of Fe and Mn to which known volumes of  $10^{-4}\text{M}$  EDTA (free acid) were added. The solutions were prepared from a 5 ppm Fe solution (SOLUTION A), a 5 ppm Mn solution (SOLUTION B) and  $10^{-4}\text{M}$  EDTA solution (SOLUTION C) as follows:

<u>Fe Samples</u>	<u>Total Volume</u>	<u>Final Fe Concentration</u>
(i) 50ml of Solution A	50ml	5 ppm
(ii) 40ml of A + 10ml of C	50ml	4 ppm
(iii) 35ml of A + 15ml of C	50ml	3.5 ppm
(iv) 25ml of A + 25ml of C	50ml	2.5 ppm

<u>Mn Samples</u>	<u>Total Volume</u>	<u>Final Mn Concentration</u>
(i) 50ml of Solution B	50ml	5 ppm
(ii) 40ml of B + 10ml of C	50ml	4 ppm
(iii) 35ml of B + 15ml of C	50ml	3.5 ppm
(iv) 25ml of B + 25ml of C	50ml	2.5 ppm

Ten ml portions of the above solutions were passed through the Na-saturated cation exchange resin columns and the effluents collected after discarding the first five drops. The Fe and Mn concentrations in the solutions were determined prior to and after passage through the resin. The Fe or Mn that was retained by the resin was considered to be not complexed with EDTA and the Fe or Mn which passed through the resin (in the effluent) was considered complexed with EDTA. Since the molarity of EDTA was known, it was possible to calculate the amounts of Fe or Mn that would be complexed by the EDTA.

The separation of Fe complexed with EDTA was quantitative while the separation of Mn was not (Tables 17 and 18). This difference can be explained as follows: The solutions had a pH of about 6.5, and since they were continuously

TABLE 17

Separation of Fe Complexed with  $10^{-4}$ M EDTA Solution

Sample	Fe in Sample (ppm)	Fe Complexed (ppm)		$\frac{x}{y}$
		Calculated (y)	By Resin Separation (x)	
(i) 50ml of A	5.00	Nil	Nil	-
(ii) 40ml of A + 10ml of C	4.00	1.12	1.15	~ 1
(iii) 35ml of A + 15ml of C	3.50	1.68	1.60	~ 1
(iv) 25ml of A + 25ml of C	2.50	2.80	2.50	*

A = solution of 5 ppm Fe

C = solution of  $10^{-4}$ M EDTA

\*Fe in solution (2.50 ppm) < 2.80 ppm (=y) and thus all Fe in solution was complexed.

TABLE 18  
 Separation of Mn Complexed with  $10^{-4}$ M EDTA Solution

Sample	Mn in Sample (ppm)	Mn Complexed (ppm)		$\frac{x}{y}$
		Calculated (y)	By Resin Separation (x)	
(i) 50ml of B	5.00	Nil	Nil	-
(ii) 40ml of B + 10ml of C	4.00	1.10	0.65	0.59
(iii) 35ml of B + 15ml of C	3.50	1.65	1.17	0.71
(iv) 25ml of B + 25ml of C	2.50	2.75	1.95	0.71

B = solution of 5 ppm Mn.

C = solution of  $10^{-4}$ M EDTA.

exposed to air, most of the Fe in solution would be  $\text{Fe}^{3+}$ . The Mn in solution would be present as  $\text{Mn}^{2+}$  since  $\text{Mn}^{2+}$  does not normally exist in solution (75,92,149). The stability constants ( $\log K$ ) of  $\text{Fe}^{\text{III}} - \text{EDTA}$  and  $\text{Mn}^{\text{II}} - \text{EDTA}$  are 25.10 and 13.40, respectively (96). The stability constant for  $\text{Fe}^{\text{II}} - \text{EDTA}$  is 14.45. The resin gets associated with some of the Fe or Mn that passes through it. If the association constant between the metal ion and EDTA is much greater than that between the metal ion and resin, the EDTA-metal chelate could pass through the resin (short column) quickly without breaking down. If the resin-metal association constant is equal to or greater than the EDTA-metal association constant, the EDTA-metal chelate would break down on passing through the resin and separation will not be quantitative. It is thus likely that the  $\text{Fe}^{\text{III}} - \text{EDTA}$  association constant (= 25.10) was much greater than that of resin-Fe while that of  $\text{Mn}^{\text{II}} - \text{EDTA}$  (= 13.40) was equal to or less than that for resin-Mn and hence broke down on passing through the resin. The results, however, show that complexes as stable or more stable than those formed between Fe and EDTA can be quantitatively separated by using a Na-saturated cation exchange resin.

The results obtained when 10 ml samples of extracted soil solutions were passed through the Na-saturated resin columns are shown in Tables 19 to 24. Fe or Mn present in the effluent was considered to be in a complexed form. The differences between the  $[\text{Fe}]$  or  $[\text{Mn}]$  in the influent and

TABLE 19

Separation of Complexed and Uncomplexed Fe and Mn by a  
Na-Saturated Cation Exchange Resin--Red River Soil

Number of Days after Saturation	Fe in Influent (ppm)	Fe in Effluent (ppm)	Mn in Influent (ppm)	Mn in Effluent (ppm)	% Fe Complexed	% Mn Complexed
7	0.15	0.15	0.80	0.00	100	0
14	0.42	0.42	1.00	0.00	100	0
21	0.30	0.20	0.70	0.00	66	0
28	0.40	0.40	1.00	0.00	100	0
35	0.80	0.60	1.10	0.00	75	0
42	1.10	0.80	2.50	0.00	73	0

TABLE 20

Separation of Complexed and Uncomplexed Fe and Mn by a  
Na-Saturated Cation Exchange Resin--Tarno Soil

Number of Days after Saturation	Fe in Influent (ppm)	Fe in Effluent (ppm)	Mn in Influent (ppm)	Mn in Effluent (ppm)	% Fe Complexed	% Mn Complexed
7	0.15	0.15	1.20	0.00	100	0
14	0.20	0.20	1.75	0.00	100	0
21	0.25	0.20	1.00	0.00	80	0
28	0.50	0.50	1.70	0.00	100	0
35	0.90	0.70	1.60	0.00	77	0
42	1.10	1.00	1.20	0.00	91	0

TABLE 21

Separation of Complexed and Uncomplexed Fe and Mn by a  
Na-Saturated Cation Exchange Resin--Lakeland Soil

Number of Days after Saturation	Fe in Influent (ppm)	Fe in Effluent (ppm)	Mn in Influent (ppm)	Mn in Effluent (ppm)	% Fe Complexed	% Mn Complexed
7	0.10	0.10	1.00	0.00	100	0
14	0.50	0.50	2.70	0.00	100	0
21	0.40	0.35	2.10	0.00	87	0
28	0.80	0.80	3.60	0.00	100	0
35	1.40	1.30	2.40	0.00	93	0
42	2.10	2.10	4.60	0.00	100	0

TABLE 22

Separation of Complexed and Uncomplexed Fe and Mn by a  
Na-Saturated Cation Exchange Resin--Newdale Soil

Number of Days after Saturation	Fe in Influent (ppm)	Fe in Effluent (ppm)	Mn in Influent (ppm)	Mn in Effluent (ppm)	% Fe Complexed	% Mn Complexed
7	0.10	0.10	2.45	0.00	100	0
14	3.10	3.10	7.40	0.00	100	0
21	1.30	1.10	4.20	0.00	85	0
28	1.50	1.30	9.80	0.00	86	0
35	5.70	5.40	8.40	0.00	95	0
42	5.20	5.20	6.20	0.00	100	0

TABLE 23

Separation of Complexed and Uncomplexed Fe and Mn by a  
Na-Saturated Cation Exchange Resin--Stockton Soil

Number of Days after Saturation	Fe in Influent (ppm)	Fe in Effluent (ppm)	Mn in Influent (ppm)	Mn in Effluent (ppm)	% Fe Complexed	% Mn Complexed
7	0.10	0.10	0.54	0.00	100	0
14	0.60	0.60	3.25	0.00	100	0
21	1.30	1.10	4.20	0.00	85	0
28	0.10	0.10	1.30	0.00	100	0
35	1.30	1.20	3.30	0.00	92	0
42	0.40	0.30	1.40	0.00	75	0

TABLE 24

Separation of Complexed and Uncomplexed Fe and Mn by a  
Na-Saturated Cation Exchange Resin--Plum Ridge Soil

Number of Days after Saturation	Fe in Influent (ppm)	Fe in Effluent (ppm)	Mn in Influent (ppm)	Mn in Effluent (ppm)	% Fe Complexed	% Mn Complexed
7	0.10	0.10	0.51	0.00	100	0
14	0.20	0.20	0.90	0.00	100	0
21	0.10	0.10	1.10	0.00	100	0
28	0.10	0.10	0.50	0.00	100	0
35	0.10	0.10	0.65	0.00	100	0
42	0.10	0.10	0.70	0.00	100	0

effluent (i.e. the amounts retained on the resin) were taken to be amounts of Fe or Mn not complexed. It was found that all the Mn in the soil solution was uncomplexed while 75% to 100% of Fe was complexed in the various soils (Tables 19 to 24). It is possible that some of the Mn in the extracts was complexed, but the complex was destroyed when passed through the resin. Mn - EDTA dissociated when passed through the resin. Therefore, it is highly likely that if a complex existed, it may have been destroyed when passed through the resin. In soils, Fe and Mn are most likely complexed with organic matter (67).

Since the complexed Fe passed through the cation exchange resin column without being retained on the resin, the Fe complexes were neutral or negatively charged. The charge on metal-organic matter complexes in soil solutions have not been widely reported. Hem (62), however, stated that Fe-organic matter complexes could be cationic, neutral or anionic. In order to determine the charge on the Fe complexes isolated, another set of soil extracts was passed through a chloride-saturated anion exchange resin (Rexyn 201 (Cl) Chromatographic Grade supplied by the Fisher Scientific Company). These resin columns were prepared as described for the cation exchange resin studies. The anion exchange resin was leached only with de-ionised water before use. It contained no traces of Fe and leaching with 5M HCl was not required. Separate portions of soil extracts were simultaneously passed through a cation and anion exchange.

resins. Almost all of the Fe in solution was complexed (Table 25). Approximately 27% to 47% of the Mn was held by the Cl-saturated resin (Table 26). All the Mn was retained by the Na-saturated resin. Thus, most of the Fe in the soil extracts of the six soils was complexed while the Mn in the extracts was either not complexed or only weakly complexed. The Mn-organic matter complexes probably broke down when passed through the cation exchange resin indicating that complexes between Mn and soil constituents are not very stable.

The complexes were negatively charged since they were retained by the anion exchange resin but not by the cation-exchange resin. The effluents from the anion resin columns were colourless indicating that all the organic matter in solution had been retained on the resin along with the complexed metal ions. On the other hand, the effluents from the cation exchange resins were coloured with dissolved organic matter indicating that the organic matter was not retained on the resin.

The poor Eh - pH relationships obtained for Fe in the previous experiment was probably due to the complexation of Fe in the soil extracts by organic matter. Thus the amounts of Fe in solution will be considerably higher than would be predicted by the measured Eh and pH, when Fe-organic matter complexes are formed (64,96). The association of Fe with organic matter also accounts for the shift in the position of the intercepts when the regressions of

TABLE 25

Separation of Complexed and Uncomplexed Fe  
by a Cation or Anion Exchange Resin

Soil	Fe in Influent (ppm)	Fe (ppm) in Effluent from		% Fe Complexed	
		Anion Resin	Cation Resin	Anion Resin	Cation Resin
Red River	0.15	0.00	0.10	100	66
Tarno	0.15	0.00	0.15	100	100
Lakeland	0.10	0.00	0.10	100	100
Newdale	0.10	0.00	0.10	100	100
Stockton	0.10	0.00	0.10	100	100
Plum Ridge	0.10	0.00	0.10	100	100

TABLE 26

Separation of Complexed and Uncomplexed Mn  
by a Cation or Anion Exchange Resin

Soil	Mn in Influent (ppm)	Mn (ppm) in Effluent from		% Mn Complexed	
		Anion Resin	Cation Resin	Anion Resin	Cation Resin
Red River	4.40	3.20	0.00	27	0
Tarno	2.80	2.00	0.00	29	0
Lakeland	1.60	1.00	0.00	37	0
Newdale	3.00	1.60	0.00	47	0
Stockton	8.00	5.70	0.00	29	0
Plum Ridge	11.00	8.20	0.00	25	0

( $Eh + 0.177 \text{ pH}$ ) on  $\log(\text{Fe}^{2+})$  were determined. In these regressions, the observed slopes were very nearly the same as the theoretical but the intercepts were all greater than the theoretical value. This indicates that there is a constant or fixed source of Fe-complexing organic matter irrespective of the concentration of Fe in the soil solution. Mn was found to exist mainly as  $\text{Mn}^{2+}$  and/or as weakly complexed forms. Hence the better Eh - pH relationships obtained for Mn.

Earlier workers (5,9) who related measured Eh to Fe or Mn in soil solution concluded that the Fe oxides in the soil were ill-defined (9) or that Eh measured by the platinum electrode was a mixed potential not related to the Nernstian distribution of oxidised and reduced species (5). They did not consider the possibility of the Fe or Mn being complexed with soil organic matter. The extensive complexing of the Fe with organic matter therefore explains some of the difficulties encountered in relating measured Eh to Fe in soil solutions, especially for soils having high contents of organic matter.

Ponnamperuma et al. (133) reported good relationships between Eh and Fe in solution. They worked with tropical soils in the Philippines. The Eh - pH

relationships obtained for Mn for these same tropical soils, however, were generally poor (131); the poor relationships were attributed to the formation of non-stoichiometric Mn oxides.

Geering et al. (50) reported that 84 to 99% of the Mn in the soil solutions of a number of surface U.S.A. soils was complexed. They did not specify the nature of the complexes formed. They based their calculations on the fact that the quantity of metal bound to a known weight of resin at equilibrium is proportional to the concentration of free ions in solution (96). This assumption may not be valid in soil solutions especially where the complexing agent in the soil solution competes with the resin for the free ions in solution. Also, equilibrium may not be easily attained in a soil solution containing large amounts of organic matter.

If the Mn in the six Manitoba soil extracts had been complexed to as great a degree as for Fe, there probably would not have been as large a difference in the Eh - pH relationships noted for Fe and Mn.

The complexing capacities of the various soil solutions were compared by passing 10 ml portions of extracted soil solutions (after saturation for 10 days) through a Na-saturated cation exchange resin to which a known concentration of Fe had been added. Four grams of resin

were used in the columns. One ml of 1000 ppm Fe standard solution was added to the resin, allowed to pass through the resin in about five minutes and excess water removed by suction. Ten ml of soil extract was then passed through the resin to determine the amount of Fe removed from the resin by the soil extracts. The Fe eluted was obtained from the difference in the concentrations of Fe in the effluent and influent. Ten ml of  $10^{-4}$ M EDTA (free acid) or de-ionised water were also used to elute the Fe from the resin in order to compare their complexing capacities with those of the soil solutions. All determinations were made in duplicate.

All the soil extracts eluted more Fe from the resin than did  $10^{-4}$ M EDTA and de-ionised water indicating that the soil solutions had a higher capacity to complex Fe than  $10^{-4}$ M EDTA (Table 27). This observation may have some significance in plant nutrition where micronutrients are added to soil in the form of EDTA chelates (at  $10^{-4}$ M to  $10^{-5}$ M concentrations). If the soil solution has a greater capacity than EDTA to complex a micronutrient element, microelements added in the form of EDTA chelate could be removed from the EDTA chelate by the soil solution. This may adversely affect the efficacy of chelated micronutrients as correctives for micronutrient deficiencies in soils.

The soil solutions differed considerably in their Fe complexing capacities. Thus, the organic matter contents of the soil solutions were determined to see if the organic

TABLE 27

Fe (ppm) Eluted from Cation Exchange  
Resin Columns by Soil Solutions,  
 $10^{-4}$ M EDTA (Free Acid) Solution and Water

Leaching Solution	Fe (ppm) Eluted from Resin Column
(i) Red River Soil Solution	2.10
(ii) Tarno Soil Solution	3.60
(iii) Lakeland Soil Solution	1.80
(iv) Newdale Soil Solution	1.35
(v) Stockton Soil Solution	1.45
(vi) Plum Ridge Soil Solution	1.20
(vii) $10^{-4}$ M EDTA Solution	1.10
(viii) De-Ionised Water	0.45

matter dissolved in solution was related to the amount of Fe eluted from the resins. Fifty ml of extract from each soil was added to a weighed 150 ml beaker, evaporated on a hot plate, dried at 105° C, cooled and reweighed to obtain the weight of residue. The organic matter content of the residue was determined by chromic acid oxidation; the excess chromic acid was determined by titration with ferrous sulfate solution (75).

The organic matter contents for the soil solutions (expressed on a soil solution basis) are shown in Table 28. Organic matter contents in the original samples of the six soils along with the Fe eluted from resin by the solution of each soil are also included.

The organic matter contents of the various soil solutions were approximately the same and not related to the organic matter in the soil (Table 28). The amount of Fe eluted by the soil extracts appeared to be more closely related to the organic matter contents of the soils than to the organic matter contents of the soil extracts. The Red River and Tarno soils which had the highest amounts of organic matter eluted the highest amounts of Fe from the resins. The Plum Ridge soil which had the lowest organic matter content eluted the lowest amount of Fe. It is very likely that the complexing capacity of a given soil solution may depend more on the specific type of organic matter present in solution rather than on the amount of organic matter present.

TABLE 28  
Organic Matter Contents of Soil Solutions

Soil	% Organic Matter in Soil Solution	% Organic Matter in Original Soil	Fe (ppm) Eluted from Resin Column (from Table 27)
Red River	0.19	10.00	2.10
Tarno	0.24	7.00	3.60
Lakeland	0.23	5.70	1.80
Newdale	0.19	6.70	1.35
Stockton	0.23	4.40	1.45
Plum Ridge	0.26	4.30	1.20

In an attempt to determine the oxidation state of the Fe in the Fe-organic matter complex, the following calculations, involving the stability constants of  $\text{Fe}^{\text{II}} - \text{EDTA}$  and  $\text{Fe}^{\text{III}} - \text{EDTA}$  were made: As shown earlier, most of the soil solutions had a greater capacity to complex Fe than did  $10^{-4}\text{M}$  EDTA. The stability constant for  $\text{Fe}^{\text{III}} - \text{EDTA}$  and  $\text{Fe}^{\text{II}} - \text{EDTA}$  are 25.10 (= Log  $K_3$ ) and 14.45 (= Log  $K_2$ ), respectively (96). These are the log equilibrium formation constants for 1:1 chelates. If EDTA is represented by Ch, the following equations could be written:

$$K_3 = 10^{25.10} = \frac{(\text{Fe}^{\text{III}} - \text{Ch}_x)}{(\text{Fe}^{\text{III}}) (\text{Ch})^x} \quad \dots (i)$$

$$K_2 = 10^{14.45} = \frac{(\text{Fe}^{\text{II}} - \text{Ch}_x)}{(\text{Fe}^{\text{II}}) (\text{Ch})^x} \quad \dots (ii)$$

Taking the ratio,

$$\frac{K_3}{K_2} = \frac{10^{25.10}}{10^{14.45}} = 10^{10.65} = \frac{(\text{Fe}^{\text{II}}) (\text{Fe}^{\text{III}} - \text{Ch}_x)}{(\text{Fe}^{\text{III}}) (\text{Fe}^{\text{II}} - \text{Ch}_x)} \quad \dots (iii)$$

Therefore,

$$\frac{(\text{Fe}^{\text{III}} - \text{Ch}_x)}{(\text{Fe}^{\text{II}} - \text{Ch}_x)} = 10^{10.65} \frac{(\text{Fe}^{\text{III}})}{(\text{Fe}^{\text{II}})} \quad \dots (iv)$$

Equation (iv) represents the ratio of  $\text{Fe}^{\text{III}} - \text{EDTA}$  and  $\text{Fe}^{\text{II}} - \text{EDTA}$  in a solution where  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  exist. In order to determine which form of the chelate is predominant at the experimentally observed Eh, the Nernst equation for the  $\text{Fe}^{\text{III}} - \text{Fe}^{\text{II}}$  system (49),

$$\frac{(\text{Fe}^{\text{III}})}{(\text{Fe}^{\text{II}})} = 10^{\frac{(\text{Eh}-0.77)}{0.059}},$$

is substituted into equation (iv).

Thus,

$$\frac{(\text{Fe}^{\text{III}} - \text{Ch}_x)}{(\text{Fe}^{\text{II}} - \text{Ch}_x)} = (10^{10.65}) (10^{\frac{(\text{Eh}-0.77)}{0.059}}) \quad \dots (v)$$

In a system where

$$\frac{(\text{Fe}^{\text{III}} - \text{Ch}_x)}{(\text{Fe}^{\text{II}} - \text{Ch}_x)} = 1,$$

$$(10^{10.65}) (10^{\frac{(\text{Eh}-0.177)}{0.059}}) = 1 \quad \dots (vi)$$

and

$$(10.65) + \left(\frac{\text{Eh} - 0.77}{0.059}\right) = \log 1 = 0.$$

Therefore

$$\frac{\text{Eh} - 0.77}{0.059} = -10.65$$

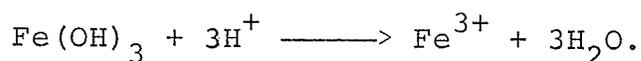
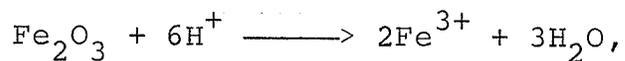
and

$$\text{Eh} = (-10.65 \times 0.059) + .77 = 0.142 \text{ volt.}$$

If a system is more oxidised than  $\text{Eh} = 0.142$  volt,  $(\text{Fe}^{\text{III}} - \text{Ch}_x)$  is predominant while a more reduced system favours the formation of  $(\text{Fe}^{\text{II}} - \text{Ch}_x)$ .

The experimentally observed Eh values for the soil solutions were generally higher (more oxidised) than 0.142 volt (Tables 3 to 8). Therefore, if the stability constants of soil organic matter and  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  are of the orders similar to those of EDTA, then, it could be inferred that most of the Fe-organic matter complex was  $\text{Fe}^{\text{III}}$ -organic matter

rather than Fe<sup>II</sup>-organic matter. Fe<sup>3+</sup> ions could come into soil solution by dissolution as follows:



An equilibrium exists between the Fe-organic matter complex and Fe<sup>2+</sup> and Fe<sup>3+</sup> in solution with most of the Fe in soil solution being present as an organic matter Fe. The equilibrium between the very small amounts of Fe<sup>3+</sup> and Fe<sup>2+</sup> in solution could still give the theoretical Nernstian slope of -0.059 but the presence of the Fe-organic matter complex displaces the intercept (= theoretical E°). However, further work is needed to confirm the above hypothesis.

## 2. GREENHOUSE STUDIES

### a. Influence of Soil Water Regimes on the Fe and Mn Status of Flax and Oat Plants

Flax plants grown on a number of Manitoba soils have been observed to become chlorotic when grown on wet or waterlogged soils. On the other hand, cereal crops such as oats, grown adjacent to the chlorotic flax plants have been observed to develop normally. LaCroix and Lenz (84) studied chlorosis of PI soybeans in Manitoba; one of their observations was that yearly variations in the extent of chlorosis appeared to be due to yearly variations in temperature and moisture conditions.

There have been claims and counter claims that chlorotic plants contain less Fe than normal (non-chlorotic) plants of the same species (44,76,115,154). An imbalance between Fe and Mn in the plant has also been implicated as one of the causes of chlorosis (15). Elgala and Maier (44) grew soybean plants (variety Lee) at two moisture levels, 75% and 120% of moisture equivalent, and observed that the plants grown at the higher moisture level became chlorotic while those grown under the low moisture level were green in appearance. They found that the chlorotic and non-chlorotic plants contained the same amounts of total Fe while the chlorotic plants contained less water-soluble Fe and "active Fe" (extracted with 1N HCl). Elgala and Maier (44), however, did not wash the plants with 0.1N HCl before

analysis. The plants were dipped in 0.0001N HCl and rinsed in de-ionized water. This washing procedure may not have removed all the surface contaminants, resulting in higher than normal values for total Fe.

There are no reports on the total Fe content of chlorotic flax plants in Manitoba. This experiment was therefore conducted to investigate if chlorotic and non-chlorotic flax plants grown on a number of Manitoba soils differed in their Fe and Mn contents. Oat plants were included in the experiment for purposes of comparison.

The plants were grown in 4.40-liter glazed porcelain pots containing 2000 g. of soil. Two water regimes (100% of field capacity and 150% of field capacity) were established in the soils one week after emergence of the seedlings. The total weight of pot plus the weight of soil plus water was marked on each pot. The pots were weighed daily and the appropriate amount of de-ionised water added to bring them to the correct weight. Approximate allowances were made for the weights of plants growing in the pots.

Ten flax plants and six oat plants were grown in each pot. Each water treatment was replicated six times for each soil and for both crops. Flax plants were grown on all the six soils while oat plants were grown on only five soils (the Plum Ridge soil was not used for oats).

The plants were observed visually as they developed. In four of the soils, Red River, Tarno, Lakeland and Plum Ridge, the flax plants grown at 150% of field capacity became

chlorotic about one week after the establishment of the water regimes. Initially, the chlorosis was a yellowing of the interveinal portions of the youngest leaves. As the severity of chlorosis increased, some of the leaves became entirely yellow and almost white in colour. Necrotic spots also developed in some leaves. The severity of chlorosis of flax plants grown in the soils decreased in the order: Lakeland, Red River, Tarno and Plum Ridge. There were also noticeable differences in vegetative growth of normal and chlorotic flax plants; the normal plants exhibited marked superiority in growth. Some of the chlorotic plants started to recover after three weeks of growth. This recovery progressed with time but was least obvious in the plants grown on the Lakeland soil. Despite the recoveries, marked differences in vegetative growth of normal and chlorotic flax plants still persisted. The flax plants grown on the Lakeland soil at 100% of field capacity became chlorotic after five weeks of growth. Flax plants grown at both water regimes in the Stockton and Newdale soils developed normally and did not become chlorotic.

The oat plants on all soils at both water regimes developed normally and showed no visible deficiency symptoms.

Twenty-eight days after the establishment of the water regimes, three replicates of each crop were harvested. The remaining three replicates were harvested 14 days after the first harvest.

Yields of the chlorotic flax plants grown on the Red River, Tarno, Lakeland and Plum Ridge soils at the higher water regimes were significantly lower than those of plants grown at the lower water regime (Table 29). These differences persisted at both harvests. In the Stockton and Newdale soils, water treatment did not significantly influence yields at the first harvest. However, at the second harvest, the yields of flax obtained with the higher water regime in both the Newdale and Stockton soils were significantly higher than at the lower water regimes. The flax yields varied with soil type, the highest yields being obtained on the Stockton soil.

Yields of oats also varied with soil type (Table 30). Oat yields on the Red River and Tarno soils decreased with increases in soil water content at both harvests. Oat yields on the Lakeland, Newdale and Stockton soils increased with increases in soil water content at both harvests. The Red River and Tarno soils are both clays. Thus, the oxygen supply to the oat roots may have been reduced at the higher water contents in these two soils and decreased oat yields.

Flax plants grown at the higher moisture level and which developed chlorosis, contained significantly less Fe than the non-chlorotic plants grown at the lower moisture levels in the Red River, Tarno and Lakeland soils (Table 31). These differences persisted at both harvests. The Fe content of the chlorotic plants grown on the Plum Ridge soil

TABLE 29  
 Yields of Flax Grown under Two Soil  
 Water Regimes (g./pot)  
 (Means of Three Replicates)

Harvests Water Regimes*	First				Second			
	W <sub>1</sub>		W <sub>2</sub>		W <sub>1</sub>		W <sub>2</sub>	
<u>Soils:</u>								
Red River	3.20	A a	0.90	DE b	8.20	A x	3.20	D y
Tarno	1.35	B a	1.10	C b	3.50	D x	3.20	D y
Lakeland	1.10	D a	0.85	E b	2.40	F x	1.55	E y
Newdale	1.40	B a	1.45	B a	3.20	E y	3.50	C x
Stockton	3.25	A a	3.20	A a	7.80	B y	8.20	A x
Plum Ridge	1.25	C a	0.95	D b	4.80	C x	4.20	B y

Duncan's Multiple Range Test. Means of Treatments followed by the same letter are not significantly different. Lower case letters are for comparisons within each soil and within each harvest. Upper case letters are for comparisons among soils within each treatment.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 150% of Field Capacity

TABLE 30

Yields of Oats Grown Under Two Soil  
Water Regimes (g./pot)  
(Means of Three Replicates)

Harvests Water Regimes*	First		Second	
	W <sub>1</sub>	W <sub>2</sub>	W <sub>1</sub>	W <sub>2</sub>
<u>Soils:</u>				
Red River	6.00 A a	3.20 D b	15.00 A x	12.30 C y
Tarno	5.55 A a	4.20 C b	12.50 B x	11.30 D y
Lakeland	3.90 D b	4.10 C a	9.00 E y	10.50 E x
Newdale	3.60 E b	4.80 B a	9.50 D y	13.00 B x
Stockton	5.10 C b	5.30 A a	11.10 C y	13.90 A x

Duncan's Multiple Range Test. Means of Treatments followed by the same letter are not significantly different. Lower case letters are for comparisons within each soil and within each harvest. Upper case letters are for comparisons among soils within each treatment.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 150% of Field Capacity

TABLE 31  
 Fe Content of Flax Grown Under Two  
 Soil Water Regimes (ppm)  
 (Means of Three Replicates)

Harvests Water Regimes*	First		Second	
	W <sub>1</sub>	W <sub>2</sub>	W <sub>1</sub>	W <sub>2</sub>
<u>Soils:</u>				
Red River	70 C a	53 BC b	51 AB b	42 BC c
Tarno	66 C a	47 C bc	54 AB b	42 BC c
Lakeland	89 A a	59 B b	55 A b	47 BC c
Newdale	65 C a	58 B a	58 A a	58 A a
Stockton	81 B a	81 A a	57 A b	50 B b
Plum Ridge	65 C a	58 B a	46 B b	41 C b

Duncan's Multiple Range Test. Means of Treatments followed by the same letter are not significantly different. Lower case letters are for comparisons among treatments within each soil. Upper case letters are for comparisons among soils within each treatment.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 150% of Field Capacity

was lower than that of the normal plants but the differences were not statistically significant. The Fe content of flax grown on the Stockton and Newdale soils was not significantly influenced by soil moisture levels.

There was considerable variation among soils in the Fe contents of normal and chlorotic flax plants. Therefore, a value for Fe sufficiency in flax plants could not be established. Wallace (168) cited values of 60 and 24 ppm Fe (on a dry matter basis) as levels for healthy and deficient mature flax plants, respectively. The levels of Fe in the chlorotic plants in this study, however, were much greater than the level of 24 ppm suggested by Wallace (168).

With the exception of the Newdale soil in which the Fe content of oats increased with increasing soil moisture, the Fe content of oats was not significantly influenced by the soil water regimes at the first harvest (Table 32). The Fe content of oats did not vary with moisture level in the Lakeland and Stockton soils but decreased with increasing soil moisture in the Red River, Tarno and Newdale soils at the second harvest. Cheng et al. (32) recently reported that oats grown on a Tilly soil in Quebec increased in Fe content as a result of increased soil moisture. Wallace (168) suggested a value of 100 ppm (on a dry matter basis) as the level for Fe in the tops of healthy young oat plants. The oat plants grown on the five Manitoba soils, however, showed no visible signs of Fe deficiency even though they

TABLE 32

Fe Content of Oats Grown Under Two  
Soil Water Regimes (ppm)  
(Means of Three Replicates)

Harvests Water Regimes*	First		Second	
	W <sub>1</sub>	W <sub>2</sub>	W <sub>1</sub>	W <sub>2</sub>
<u>Soils:</u>				
Red River	66 A a	64 A a	48 A b	44 A c
Tarno	55 B a	56 C a	38 C b	30 C c
Lakeland	49 C a	48 D a	39 C b	37 B b
Newdale	54 B b	60 B a	43 B c	38 B d
Stockton	66 A a	65 A a	38 C b	41 AB b

Duncan's Multiple Range Test. Means of Treatments followed by the same letter are not significantly different. Lower case letters are for comparisons among treatments within each soil. Upper case letters are for comparisons among soils within each treatment.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 150% of Field Capacity

all contained less than 70 ppm Fe. The Fe content of oats was generally lower than that of flax.

Except for the Lakeland and Stockton soils, the Mn content of flax increased with increased soil water content at the first harvest (Table 33). The flax grown on the calcareous soils contained higher amounts of Mn than did the flax grown on the non-calcareous soils. The Mn content of flax increased with increased soil water content for all soils except the Lakeland and Tarno soils at the second harvest. The Mn levels in the flax plants were generally much higher than the Fe levels. The laboratory studies, previously reported, showed that higher amounts of Mn than Fe were released into solution when these soils were saturated with water. However, the ratio of Fe and Mn in flax tops was different from the ratio of Fe and Mn that was released into soil solution on saturation. The flax plants absorbed Mn in preference to Fe, especially at the higher moisture levels. Flax plants grown on the Lakeland and Plum Ridge soils accumulated high amounts of Mn even at the lower moisture levels (Table 33).

The Mn content of oat plants generally increased with increasing moisture level at both harvests (Table 34). A similar finding for oats has been recently reported (32). Wallace (168) cited a value of 66 ppm Mn (on a dry matter basis) as the level of Mn in the tops of healthy oat plants. However, the oat plants which had less than this level of

TABLE 33

Mn Content of Flax Grown Under Two  
Soil Water Regimes (ppm)  
(Means of Three Replicates)

Harvests Water Regimes*	First		Second	
	W <sub>1</sub>	W <sub>2</sub>	W <sub>1</sub>	W <sub>2</sub>
<u>Soils:</u>				
Red River	121 E c	214 D a	87 D d	153 C b
Tarno	199 C b	259 C a	143 B c	144 D c
Lakeland	299 A a	299 B a	246 A b	245 A b
Newdale	110 F c	214 D a	91 D d	125 E b
Stockton	139 D a	141 E a	99 C b	73 F c
Plum Ridge	243 B b	343 A a	143 B d	231 B c

Duncan's Multiple Range Test. Means of Treatments followed by the same letter are not significantly different. Lower case letters are for comparisons among treatments within each soil. Upper case letters are for comparisons among soils within each treatment.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 150% of Field Capacity

TABLE 34

Mn Content of Oats Grown Under Two  
Soil Water Regimes (ppm)  
(Means of Three Replicates)

Harvests Water Regimes*	First				Second			
	W <sub>1</sub>		W <sub>2</sub>		W <sub>1</sub>		W <sub>2</sub>	
<u>Soils:</u>								
Red River	38	D c	61	B a	33	C d	56	C b
Tarno	34	D b	61	B a	29	C c	65	AB a
Lakeland	48	C c	64	B a	34	C d	51	D b
Newdale	68	A b	82	A a	50	B c	69	A b
Stockton	54	B b	64	B a	64	A a	63	B a

Duncan's Multiple Range Test. Means of Treatments followed by the same letter are not significantly different. Lower case letters are for comparisons among treatments within each soil. Upper case letters are for comparisons among soils within each treatment.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 150% of Field Capacity

Mn in this experiment did not show any obvious signs of Mn deficiency. Mn contents of oats were considerably lower than those of flax plants.

The Mn:Fe ratios in the tops of the flax and oat plants were computed and are shown on Tables 35 and 36. Mn:Fe ratios in flax tops significantly increased with increased moisture content in all soils, with the exception of the Stockton soil at the first harvest (Table 35). All the chlorotic flax plants had Mn:Fe ratios of four or greater. The Mn:Fe ratios of the flax plants were not influenced by soil water contents in the Lakeland, Newdale, and Stockton soils at the second harvest. During the growth period between the first and second harvests, flax plants grown at the lower water content in the Lakeland soil had become chlorotic and the Mn:Fe ratio in the plants increased from 3.40 to 4.50. There were decreases in the Mn:Fe ratios of chlorotic flax plants on the Red River, Tarno and Plum Ridge soils between harvests but the decrease was only significant in the Tarno soil. These plants showed slight to marked recoveries from chlorosis. The Mn:Fe ratio of flax plants grown at the higher moisture regime in the Lakeland soil remained at five at both harvests (Table 35); these plants did not show any recovery from chlorosis. Thus, chlorotic flax plants had very high Mn:Fe ratios as compared with the non-chlorotic plants and thus the chlorosis in flax probably resulted from the large amounts of Mn

TABLE 35

Mn:Fe Ratios of Tops of Flax Grown  
Under Two Soil Water Regimes  
(Means of Three Replicates)

Harvests Water Regimes*	First				Second			
	W <sub>1</sub>		W <sub>2</sub>		W <sub>1</sub>		W <sub>2</sub>	
<u>Soils:</u>								
Red River	1.70	C b	4.00	C a	1.70	D b	3.60	C a
Tarno	3.00	B c	5.50	AB a	2.60	C c	3.50	C b
Lakeland	3.40	AB b	5.00	B a	4.50	A a	5.00	B a
Newdale	1.70	C b	3.70	C a	1.60	D b	2.00	D b
Stockton	1.70	C a	1.80	D a	1.75	D a	1.50	D a
Plum Ridge	3.70	A b	6.00	A a	3.20	B b	5.60	A a

Duncan's Multiple Range Test. Means of Treatments followed by the same letter are not significantly different. Lower case letters are for comparisons among treatments within each soil. Upper case letters are for comparisons among soils within each treatment.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 150% of Field Capacity

TABLE 36

Mn:Fe Ratios of Tops of Oats Grown  
Under Two Soil Water Regimes  
(Means of Three Replicates)

Harvests Water Regimes*	First				Second			
	W <sub>1</sub>		W <sub>2</sub>		W <sub>1</sub>		W <sub>2</sub>	
<u>Soils:</u>								
Red River	0.57	D c	0.95	B b	0.69	D c	1.26	D a
Tarno	0.62	D c	1.08	B b	0.75	CD c	2.13	A a
Lakeland	0.98	B b	1.31	A a	0.87	C b	1.35	D a
Newdale	1.26	A bc	1.36	A b	1.14	B c	1.83	B a
Stockton	0.82	C c	0.97	B b	1.65	A a	1.54	C a

Duncan's Multiple Range Test. Means of Treatments followed by the same letter are not significantly different. Lower case letters are for comparisons among treatments within each soil. Upper case letters are for comparisons among soils within each treatment.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 150% of Field Capacity

utilised by the plants. The oat plants had much lower Mn:Fe ratios as compared with those of the flax plants (Table 36).

The data presented above clearly show that increases in soil moisture generally resulted in increases in the Mn content of flax and oat plants. Except for the Stockton and Newdale soils in which flax plants did not become chlorotic as a result of soil moisture increase, increased soil moisture decreased the Fe content of flax plants. The Fe content of oats was not influenced by soil moisture level at the first harvest but decreased slightly with increased soil moisture content at the second harvest. Thus, increases in soil moisture did not result in increases in the Fe contents of flax and oats. Since Fe and Mn are released into solution as soil moisture increases and reduction takes place, as was shown in the laboratory studies, it would be expected that plant uptake of both elements would increase with increased soil moisture content above field capacity. However, only Mn uptake increased with increased soil moisture content.

Simple regression analyses of flax and oat yields on Fe, Mn and Mn:Fe ratios in plant tops were conducted (Tables 37 and 38). Mn and Mn:Fe ratios in flax tops were negatively correlated with flax yields at both harvests. The Fe content of flax was positively correlated with flax yields only at the first harvest (Table 37). It appears therefore that Mn was present in amounts toxic to the flax plants and thus depressed yields. The toxic effects were more pronounced at the first than at the second harvest. This toxicity was

TABLE 37

Regressions of Flax Yields on Fe,  
Mn and Mn:Fe Ratios in Plant Tops  
#Model:  $Y = a + bx$

Harvests	Independent Variable (x)	Regression Equation	$r^2$	r
First	Fe (ppm)	$Y = -1.22 + 0.044x$	0.33	+0.57*
	Mn (ppm)	$Y = 3.60 - 0.01x$	0.54	-0.73**
	Mn:Fe Ratio	$Y = 3.31 - 0.48x$	0.59	-0.76**
Second	Fe (ppm)	$Y = 2.02 + 0.049x$	0.02	+0.14N.S.
	Mn (ppm)	$Y = 8.35 - 0.03x$	0.48	-0.69*
	Mn:Fe Ratio	$Y = 7.63 - 1.02x$	0.41	-0.64*

\* Significant at the 5% level.

\*\* Significant at the 1% level.

N.S. Not significant.

#Y represents yield (dependent variable).

x represents Fe, Mn or Mn/Fe ratio (independent variables).

TABLE 38

Regressions of Oat Yields on Fe,  
Mn and Mn:Fe Ratios in Plant Tops  
#Model:  $Y = a + bx$

Harvests	Independent Variable(x)	Regression Equation	$r^2$	r	
First	Fe (ppm)	$Y = 0.96 + 0.06x$	0.21	+0.46	N.S.
	Mn (ppm)	$Y = 6.28 - 0.03x$	0.22	-0.47	N.S.
	Mn:Fe Ratio	$Y = 6.62 - 2.06x$	0.37	-0.61	N.S.
Second	Fe (ppm)	$Y = 6.17 + 0.14x$	0.13	+0.36	N.S.
	Mn (ppm)	$Y = 11.52 + 0.006x$	0.002	+0.04	N.S.
	Mn:Fe Ratio	$Y = 12.05 - 0.18x$	0.002	-0.04	N.S.

N.S. Not significant

#Y represents yield (dependent variable)

x represents Fe, Mn or Mn/Fe ratio (independent variables).

probably responsible for the chlorotic condition of some of the flax plants. Other workers have also shown that Mn toxicity caused reduced yields in various crops (54,102,117,118,119,120).

Mn contents and Mn:Fe ratios were negatively correlated with oat yields at the first harvest but the correlation coefficients were not significant (Table 38). The Fe content of the plant was positively correlated with oat yields at both harvests but these correlations were also not significant. Correlations of Mn content and Mn:Fe ratio with oat yields at the second harvest were not significant. There is thus some indication of a slight Mn toxicity in oats.

After each harvest, soil samples were taken with a copper cylinder from each pot and the samples from the three replicates for each water treatment composited and air-dried. After drying, the soils were crushed, thoroughly mixed and duplicate samples taken for extraction of "available" Fe and Mn with DTPA-TEA (diethylenetriamine pentaacetic acid--triethanolamine) (91) and neutral normal  $\text{NH}_4\text{OAc}$  solution containing 0.2% hydroquinone (75), respectively. Ten grams of soil were extracted with 20 ml of DTPA-TEA for two hours (91). Five grams of soil were extracted with 50 ml of  $\text{NH}_4\text{OAc}$ -quinol extractant for 30 minutes (137). The concentrations of Fe and Mn extracted are shown in Appendix IV.

The correlations between the concentrations of Fe and Mn extracted with these reagents and the uptake of Fe and Mn by flax and oats were determined. Uptake of Fe or Mn was computed by multiplying the yield by the concentrations of Fe or Mn in the plant. The correlation coefficients (r) and the corresponding regression equations obtained are shown in Table 39. Fe extracted with DTPA-TEA was positively correlated with Fe uptake by flax at both harvests (Table 39). Mn extracted by  $\text{NH}_4\text{OAc}$ -quinol was not related to the amounts of Mn utilised by flax or oats.

b. A Study of the Fe and Mn Status of Flax and Oat Plants Grown under Three Water Regimes in the Lakeland and Stockton Soils

It was shown in the previous experiment that flax and oat plants usually absorbed more Mn and less Fe as soil moisture content increased. However, the laboratory experiments showed that both Fe and Mn concentrations in soil solution increased with soil water content and reduction. Thus, the absorption or translocation of Fe was reduced by the conditions resulting from the high soil water contents. It is possible, since Fe in soil solution would increase with increased soil water content, that the Fe was not being translocated from the roots to the tops of the plants. An experiment was thus initiated in which the Fe content of both the plant tops and roots was measured after being grown under different soil water regimes.

Two soils (Lakeland and Stockton), were selected

TABLE 39

Correlations between DTPA-TEA Extractable Fe, Quinol Extractable Mn and Fe and Mn Uptake by Flax and Oats

Crop	Variables Correlated	Regression Equation	$r^2$	r	
Flax	(1st Harvest)	DTPA Fe vs. Fe Uptake	$Y = 0.03 + 0.005x$	0.52	0.72**
		Quinol Mn vs. Mn Uptake	$Y = 0.29 + 0.00x$	0.004	0.06 N.S.
	(2nd Harvest)	DTPA Fe vs. Fe Uptake	$Y = 0.10 + 0.006x$	0.33	0.58*
		Quinol Mn vs. Mn Uptake	$Y = 0.66 - 0.00x$	0.06	0.24 N.S.
Oats	(1st Harvest)	DTPA Fe vs. Fe Uptake	$Y = 0.20 + 0.003x$	0.30	0.55 N.S.
		Quinol Mn vs. Mn Uptake	$Y = 0.19 + 0.00x$	0.16	0.40 N.S.
	(2nd Harvest)	DTPA Fe vs. Fe Uptake	$Y = 0.45 + 0.00x$	0.01	0.10 N.S.
		Quinol Mn vs. Mn Uptake	$Y = 0.39 + 0.001x$	0.23	0.48 N.S.

\*\* Significant at the 1% level.

\* Significant at the 5% level.

N.S. Not significant.

and oats and flax grown. The Lakeland and Stockton soils were selected as chlorosis in flax was most severe on the Lakeland soil while plants grown on the Stockton soil were non-chlorotic and gave the highest yields. These two soils thus represented the two extreme conditions.

Three water regimes, 100, 120 and 150% of field capacity were selected. Each treatment was replicated four times. Each pot contained 2000 g. of soil and six oat or flax plants. The water regimes were established as described for the previous experiment.

As was noted for the previous experiment, flax plants grown at 150% of field capacity moisture content in the Lakeland soil became chlorotic one week after the establishment of the water regimes. Flax plants grown at 100% and 120% of field capacity in the Lakeland soil and at the three water regimes in the Stockton soil were not chlorotic. The oat plants did not show any visible deficiency symptoms.

Twenty-eight days after the establishment of the water regimes, the tops of the flax and oat plants were harvested. After the harvest of the tops, the roots were recovered by carefully removing the soil from the pots onto a fibre-glass screen of 2 mm mesh. The roots within the soil mass were washed free of soil with water.

Flax yields on the Lakeland soil were lowest when grown at 150% of field capacity and highest when grown at

120% of field capacity (Table 40). The same trend was observed for yields of flax obtained on the Stockton soil. Soil water content did not influence root growth in the Lakeland soil. Root yields decreased with increased soil water content in the Stockton soil.

Yields of oat tops at the three water regimes in the Lakeland soil were not significantly different but yields of oat roots increased with increasing soil moisture content (Table 41). Yields of oat tops at the three water regimes in the Stockton soil did not show any specific trends. Yields of oat roots in the Stockton soil declined with increasing soil moisture content.

The flax and oat tops and the flax roots were analysed for Fe and Mn. Since the flax root yields were very low, the yields from the four replicates within each treatment were composited prior to analysis. Before analysis, the roots were thoroughly washed in 0.1N HCl and rinsed several times with de-ionised water. The Fe content in the tops of flax plants grown on the Lakeland soil declined with increasing soil moisture content (Table 42). The chlorotic plants, grown at 150% of field capacity, had the lowest Fe contents. The Mn contents of flax tops grown at 100% and 150% of field capacity in the Lakeland soil were not significantly different. However, the Mn content of the flax plants grown at 120% of field capacity in the Lakeland soil were higher than those of plants grown at 100% and 150% of

TABLE 40

Yields of Tops and Roots of Flax Grown  
under Three Soil Water Regimes in the  
Lakeland and Stockton Soils (g./pot)  
(Means of Four Replicates)

Soils	Water Regimes*	Yields (Grams)	
		Tops	Roots
Lakeland	W <sub>1</sub>	0.50 b	0.08 a
	W <sub>2</sub>	0.60 a	0.08 a
	W <sub>3</sub>	0.40 c	0.08 a
Stockton	W <sub>1</sub>	1.60 c	0.36 a
	W <sub>2</sub>	1.80 a	0.24 b
	W <sub>3</sub>	1.73 b	0.21 b

Duncan's Multiple Range Test. Means of Treatments (within each soil) followed by the same letter are not significantly different.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 120% of Field Capacity

W<sub>3</sub> = 150% of Field Capacity

TABLE 41

Yields of Tops and Roots of Oats Grown  
under Three Soil Water Regimes in the  
Lakeland and Stockton Soils (g./pot)  
(Means of Four Replicates)

Soils	Water Regimes*	Yields (Grams)	
		Tops	Roots
Lakeland	W <sub>1</sub>	3.45 a	0.44 b
	W <sub>2</sub>	3.40 a	0.98 a
	W <sub>3</sub>	3.40 a	0.84 a
Stockton	W <sub>1</sub>	3.95 ab	1.55 a
	W <sub>2</sub>	3.90 b	0.95 b
	W <sub>3</sub>	4.00 a	0.63 c

Duncan's Multiple Range Test. Means of Treatments (within each soil) followed by the same letter are not significantly different.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 120% of Field Capacity

W<sub>3</sub> = 150% of Field Capacity

TABLE 42

Fe and Mn Contents of Tops and Roots of Flax  
Grown under Three Soil Water Regimes  
in Lakeland and Stockton Soils (ppm)  
(Means of Four Replicates)

Soils	Water Regimes*	Fe (ppm)		Mn (ppm)	
		Tops	Roots#	Tops	Roots#
Lakeland	W <sub>1</sub>	87 a	3,120	309 b	25
	W <sub>2</sub>	75 b	2,500	360 a	27
	W <sub>3</sub>	63 c	3,585	315 b	31
Stockton	W <sub>1</sub>	85 a	2,910	144 b	28
	W <sub>2</sub>	79 b	3,010	138 b	27
	W <sub>3</sub>	85 a	2,500	151 a	20

Duncan's Multiple Range Test. Means of Treatments (within each soil) followed by the same letter are not significantly different.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 120% of Field Capacity

W<sub>3</sub> = 150% of Field Capacity

# Composites of four replicates analysed.

field capacity moisture content. The Fe content of flax tops grown on the Stockton soil was significantly lower for plants grown at 120% of field capacity than for plants grown at the other moisture regimes. This may be due to biological dilution since the yields of plants at 120% of field capacity were the highest. The Mn content of flax tops grown on the Stockton soil was significantly increased at 150% of field capacity.

The Fe contents of flax roots were exceedingly high when compared with those of tops. The Mn contents of roots were low when compared with those of tops. Thus, it would appear that Fe accumulated in the roots of flax plants while Mn did not. The movement of Fe from the roots to the tops of the plants appears, therefore, to be restricted after it has entered the roots. The Fe content of the roots showed similar trends in both soils. In both soils, the flax plants that contained the lowest amounts of Fe in the tops contained the highest amounts of Fe in the roots. Thus, it is possible that, in instances where the Fe content of tops was decreased by higher soil moisture contents, more Fe was retained in the roots. A particular moisture level for a given soil may thus induce conditions that favour the retention of Fe in the roots. The Mn levels in the flax roots decreased with increased soil water content for the Stockton soil, but increased with increased soil water content for the Lakeland soil. The fact that the Mn levels

in the roots were very low is an indication that almost all the Mn that entered the roots was translocated to the tops, resulting in relatively high Mn concentrations in the tops. Gupta et al. (54) reported that carrots grown on an acid sphagnum peat soil contained 7,100 to 9,600 ppm of Mn in tops and 133 to 236 ppm of Mn in the roots.

Fe content of oat tops grown on the Lakeland soil increased when soil water content was increased from 100% to 120% of field capacity (Table 43). The Fe content of oats grown on the Stockton soil decreased with increasing soil moisture content. In both soils, Mn content of oat tops increased with increasing soil moisture content. Also, as was noted for the previous experiment, the Fe and Mn contents of oat tops were lower than those of flax tops.

c. A Study of Soil Aeration Effects  
on the Fe and Mn Contents of  
Flax Plants

One of the effects of increasing soil moisture content is a decrease in the oxygen level in the soil. As moisture level increases, the soil pores are gradually filled with water and the amount of air in the soil is decreased (53). In the previous two experiments, it was observed that increased soil moisture levels decreased the Fe content of flax tops. It was also found that the Fe content of flax roots was extremely high in all instances and appeared not to be greatly influenced by soil water content. Since decreases in soil aeration can decrease

TABLE 43

Fe and Mn Contents of Tops of Oats Grown  
under Three Soil Water Regimes in  
the Lakeland and Stockton Soils (ppm)  
(Means of Four Replicates)

Soils	Water Regimes*	Fe (ppm)	Mn (ppm)
Lakeland	W <sub>1</sub>	46 b	55 c
	W <sub>2</sub>	55 a	61 b
	W <sub>3</sub>	55 a	66 a
Stockton	W <sub>1</sub>	73 a	52 c
	W <sub>2</sub>	60 b	60 b
	W <sub>3</sub>	57 c	65 a

Duncan's Multiple Range Test. Means of Treatments (within each soil) followed by the same letter are not significantly different.

\* W<sub>1</sub> = 100% of Field Capacity

W<sub>2</sub> = 120% of Field Capacity

W<sub>3</sub> = 150% of Field Capacity

nutrient uptake (53,158,173), an experiment was initiated to investigate the influence of soil oxygen levels on the absorption and translocation of Fe and Mn by flax plants.

Flax plants were grown on the Lakeland and Stockton soils subjected to varying degrees of aeration. The aeration levels were as follows for each soil:

Treatment I: Soil at 100% of field capacity with air passed into it.

Treatment II: Soil at 150% of field capacity with air passed into it.

Treatment III: Soil at 100% of field capacity with 99.995% N<sub>2</sub> gas passed into it.

Treatment IV: Soil at 150% of field capacity with 99.995% N<sub>2</sub> gas passed into it.

Treatment V: Soil at 100% of field capacity (check).

Treatment VI: Soil at 150% of field capacity (check).

Each treatment was replicated four times and six flax plants were grown per pot. One thousand and five hundred grams of soil were placed into 4.4-liter plastic pots constructed to allow for the circulation of air or N<sub>2</sub> gas through the soils (Figure 21). The construction of the pots was similar to that used by Campbell et al. (28). The water regimes (100% and 150% of field capacity) were established one week after the emergence of the flax seedlings. The circulations of air and N<sub>2</sub> gas were initiated one day after the water

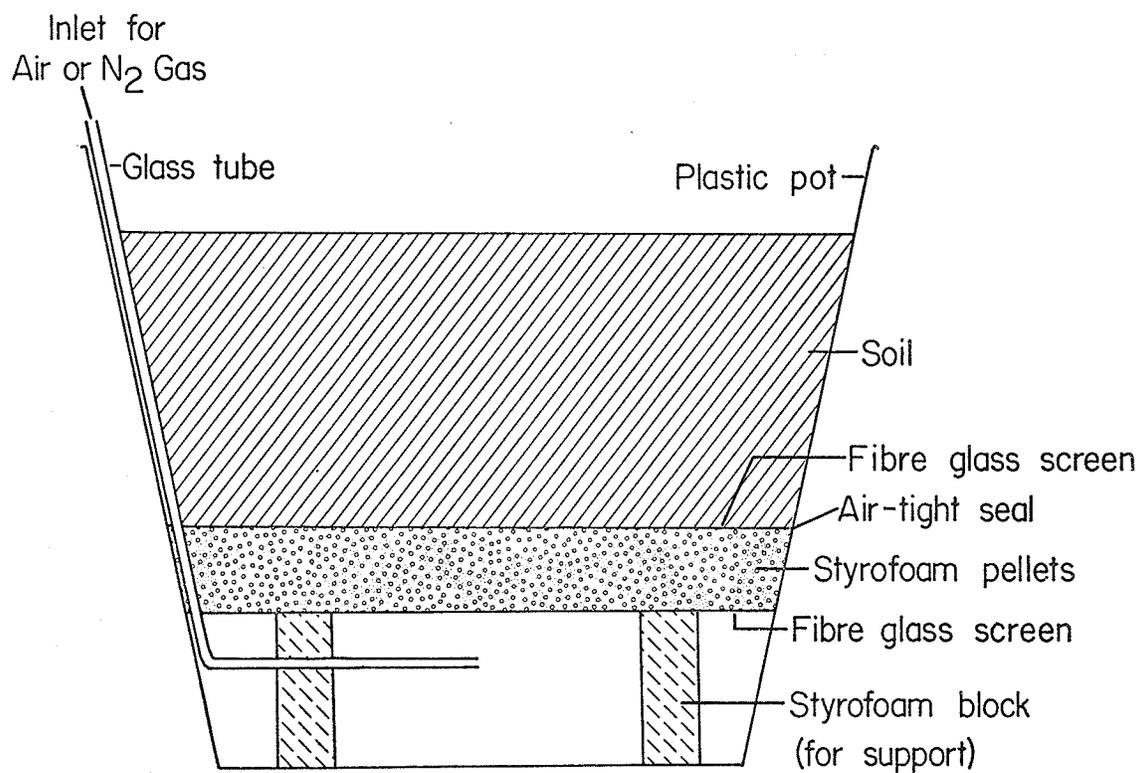


FIGURE 21. Soil Aeration Unit.

regimes were established. Air and  $N_2$  gas were circulated at a rate of approximately 200 cc per minute. Except during weighing and watering of the pots, the air or  $N_2$  gas was supplied continuously until the flax was harvested. One day after the air and  $N_2$  gas supplies were initiated, the oxygen diffusion rate (ODR) in each pot was measured by means of platinum microelectrodes (87,158). This technique is commonly used for characterising soil aeration (87,158). These measurements were conducted every two days for the duration of the experiment. The platinum electrodes were constructed of 22-gauge platinum wire. Five platinum electrodes were placed into each pot in all measurements and inserted at a soil depth of approximately 4.5 cm (one-half the total depth of soil). A voltage of 0.65 volt was applied to the electrodes and readings (microamperes) taken after allowing four minutes for steady state conditions (158). The ODR varied only slightly with time. The ODR values obtained for each treatment were averaged and are shown on Table 44. The oxygen diffusion rates (ODR) in the soils were greatly decreased by increases in soil water content or the circulation of  $N_2$  gas. The decreases were greater in the fine-textured Lakeland soil than in the coarse-textured Stockton soil. However, the absolute ODR values for the Lakeland soil in Treatments I and V (Table 44) were higher than the corresponding values for the Stockton soil. This may have been due to surface cracking

TABLE 44

Oxygen Diffusion Rates (ODR) in Lakeland and Stockton  
Soils with Different Levels of Aeration

Soils and ODR	Aeration Treatments					
	I	II	III	IV	V	VI
	100% H <sub>2</sub> O + Air	150% H <sub>2</sub> O + Air	100% H <sub>2</sub> O + N <sub>2</sub> Gas	150% H <sub>2</sub> O + N <sub>2</sub> Gas	100% H <sub>2</sub> O (Check)	150% H <sub>2</sub> O (Check)
<u>Lakeland:</u> ODR x 10 <sup>8</sup> (g. cm <sup>-2</sup> min <sup>-1</sup> )	81	20	6	2.5	75	12
<u>Stockton:</u> ODR x 10 <sup>8</sup> (g. cm <sup>-2</sup> min <sup>-1</sup> )	64	41	7.5	5.0	52	39

of the Lakeland soil when at field capacity moisture level. Also, as was shown later, there was more root growth in the Stockton soil than in the Lakeland soil and the higher demand for  $O_2$  by the roots may have decreased  $O_2$  levels in the Stockton soil.

Flax plants grown on the Lakeland soil at 150% of field capacity with air,  $N_2$  gas and no circulation (Treatments II, IV and VI) became chlorotic a few days after the water regimes were established. The flax plants fully recovered from chlorosis about 15 days after the establishment of the water regimes when air was supplied (Treatment II). Plants grown on the Lakeland soil at 150% moisture content and with  $N_2$  gas or no gas supplied were chlorotic for the duration of the experiment. Plants grown on the Lakeland soil at 100% of field capacity moisture content plus  $N_2$  gas were not chlorotic. The plants grown on the Stockton soil were not chlorotic.

Twenty-eight days after the water regimes were established, the flax tops were harvested and the roots recovered from the soil as described in the previous experiment. The yields of tops and roots on both soils were lowest for plants grown on soils subjected to  $N_2$  gas circulation (Table 45). The yield of flax tops on the Lakeland soil was greatest when grown at 150% of field capacity moisture content with air passed into the soil. In previous experiments, yields of flax tops were lowest when grown at 150% of field capacity.

TABLE 45

Yields of Tops and Roots of Flax Grown under Different Levels of  
Soil Aeration in the Lakeland and Stockton Soils (g./pot)  
(Means of Four Replicates)

Soils	Plant Part	Aeration Treatments					
		I 100% H <sub>2</sub> O + Air	II 150% H <sub>2</sub> O + Air	III 100% H <sub>2</sub> O + N <sub>2</sub> Gas	IV 150% H <sub>2</sub> O + N <sub>2</sub> Gas	V 100% H <sub>2</sub> O (Check)	VI 150% H <sub>2</sub> O (Check)
Lakeland:	Tops (Grams)	0.44 c	0.63 a	0.30 d	0.35 d	0.49 bc	0.54 b
	Roots (Grams)	0.14 a	0.13 a	0.09 a	0.07 a	0.14 a	0.13 a
Stockton:	Tops (Grams)	1.89 d	2.54 b	1.23 f	1.53 e	2.10 c	2.71 a
	Roots (Grams)	0.65 c	1.07 a	0.37 d	0.40 d	0.68 c	0.96 b

Duncan's Multiple Range Test. Means of Treatments (within each soil) followed by the same letter are not significantly different.

The circulation of air through the soil therefore had a favourable effect on flax yields at 150% of field capacity. The favourable effect of air circulation was also manifested by the recovery of the plants from chlorosis. The circulation of air probably increased  $O_2$  supply to the roots and thus promoted growth. Yields of flax tops on the Stockton soil were highest at 150% soil moisture content with and without air supplied and lowest where  $N_2$  gas was supplied (Table 45).

The weights of roots obtained from the Lakeland soil were very low, the smallest amounts being found in the soils supplied with  $N_2$  gas. These differences, however, were not statistically significant. Root weights paralleled flax top weights on the Stockton soil.

The Fe and Mn contents of the flax tops and roots were determined (Table 46). Root samples from the four replicates of each treatment were composited prior to analysis. Flax roots from the Stockton soil were not analysed as separation of roots from soil contaminants could not be achieved. The Fe content of flax tops grown on the Lakeland soil at 100% of field capacity was greater than that of flax grown at 150% of field capacity. This was not found for the Stockton soil. The Fe content of the plants was not related to the ODR measured in the soils. The flax plants on the Lakeland soil which remained chlorotic throughout the experiment contained the lowest amounts of Fe.

TABLE 46

Fe and Mn Contents of Tops and Roots of Flax Grown under Different Levels of  
Soil Aeration in Lakeland and Stockton Soils  
(Means of Four Replicates)

Soils	Aeration Treatments					
	I	II	III	IV	V	VI
	100% H <sub>2</sub> O + Air	150% H <sub>2</sub> O + Air	100% H <sub>2</sub> O + N <sub>2</sub> Gas	150% H <sub>2</sub> O + N <sub>2</sub> Gas	100% H <sub>2</sub> O (Check)	150% H <sub>2</sub> O (Check)
Lakeland:						
Fe (ppm) in Tops	84 a	68 b	85 a	60 c	69 b	50 d
Fe (ppm) in Roots <sup>#</sup>	3,650	3,300	4,250	2,800	3,550	3,640
Mn (ppm) in Tops	302 c	353 a	144 d	127 e	324 b	325 b
Mn (ppm) in Roots <sup>#</sup>	23	24	28	24	22	24
Stockton:						
Fe (ppm) in Tops	74 bc	71 c	74 bc	75 b	79 a	77 a
Fe (ppm) in Roots	--	--	--	--	--	--
Mn (ppm) in Tops	144 a	118 d	131 c	142 a	136 b	128 c
Mn (ppm) in Roots	--	--	--	--	--	--

Duncan's Multiple Range Test. Means of Treatments (within each soil) followed by the same letter are not significantly different.

<sup>#</sup> Composites of Four Replicates were analysed.

Circulation of  $N_2$  gas greatly decreased the Mn content of flax tops grown on the Lakeland soil. It is possible that the  $N_2$  gas removed  $CO_2$  from the soil (71,72), caused an increase in pH and thus decreased Mn in soil solution (108). This decrease in Mn content with the application of  $N_2$  gas was not observed for the Stockton soil which is non-calcareous and slightly acid. In this soil, a much greater increase in pH would be required before the solubility of Mn would be noticeably decreased.

As noted in the previous experiment, the Fe contents of roots in the Lakeland soil were very high when compared with the Fe content of the tops. The Mn content of roots was similar for all treatments; the Mn content of roots was also similar to those obtained for the Lakeland soil in the previous experiment.

The relationships between ODR values and yields, Fe and Mn content of tops, and Fe and Mn uptake were tested by means of correlation analysis (Table 47). None of the factors tested was significantly correlated with ODR. The correlation between ODR and Mn uptake was negative.

As shown above, Fe content of flax tops grown on the Lakeland soil decreased in all cases when the moisture level was increased from 100% to 150% of field capacity, irrespective of air or  $N_2$  gas supply. Soil aeration (as measured by ODR) was not significantly correlated with the Fe content of flax tops. Therefore, soil aeration or lack of oxygen supply was not the factor limiting the uptake or translocation

TABLE 47  
 Correlation of ODR<sup>#</sup> with Yields, Fe and Mn  
 in Tops, and Fe and Mn Uptake of Flax Plants  
 Grown on the Lakeland and Stockton Soils

Factors Correlated	Df (n-2)	Square of Correlation Coefficient (r <sup>2</sup> )	Correlation Coefficient (r)
(i) ODR vs. Yield	10	0.04	0.20 N.S.
(ii) ODR vs. Fe in Tops	10	0.13	0.36 N.S.
(iii) ODR vs. Mn in Tops	10	0.08	0.28 N.S.
(iv) ODR vs. Fe Uptake	10	0.05	0.22 N.S.
(v) ODR vs. Mn Uptake	10	0.15	-0.38 N.S.

# Oxygen Diffusion Rate

N.S. Not significant.

of Fe.

Carbonate ( $\text{CO}_3^{=}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) ions in soils have often been implicated as possible factors causing chlorosis. Thus, an experiment was conducted to measure the amounts of  $\text{CO}_3^{=}$  and/or  $\text{HCO}_3^-$  in the soil at the various moisture and aeration levels. The aeration treatments and soils used were the same as above except that no flax plants were grown in the pots. Fourteen days after initiation of the water and aeration treatments, wet soil samples were taken from each pot and the  $\text{CO}_3^{=}$  and  $\text{HCO}_3^-$  content of the soil determined. A 20-gram sample was shaken with 100 ml of distilled water for one hour, filtered, and the concentrations of  $\text{CO}_3^{=}$  and  $\text{HCO}_3^-$  in the filtrate determined by titration with 0.01N  $\text{H}_2\text{SO}_4$  using phenolphthalein and methyl orange as indicators (4). The distilled water used for extraction was boiled for 15 minutes (to render it  $\text{CO}_3^{=}$  free) and cooled prior to use. Blank titrations were made using 5 ml of the distilled water used for extraction. Separate 20-gram sub-samples of soil were taken for determination of pH, using a 1:1 soil to water ratio. Carbonate was not detected in any of the samples. The mean values for the  $\text{HCO}_3^-$  concentrations and pH values measured are shown on Table 48. Bicarbonate content increased slightly as moisture level was increased from 100% to 150% of field capacity. The extracts from the calcareous Lakeland soil contained considerably more  $\text{HCO}_3^-$  than extracts from the

TABLE 48

Bicarbonate Ion Concentrations and pH of Lakeland and  
Stockton Soils under Different Levels of Aeration

Soils	Aeration Treatments					
	I	II	III	IV	V	VI
	100% H <sub>2</sub> O + Air	150% H <sub>2</sub> O + Air	100% H <sub>2</sub> O + N <sub>2</sub> Gas	150% H <sub>2</sub> O + N <sub>2</sub> Gas	100% H <sub>2</sub> O	150% H <sub>2</sub> O
<u>Lakeland:</u>						
HCO <sub>3</sub> <sup>-</sup> (meq./liter)	0.85	1.12	0.90	1.00	0.90	1.03
pH (1:1 Soil-Water Ratio)	8.35	8.30	8.60	8.35	8.30	8.25
<u>Stockton:</u>						
HCO <sub>3</sub> <sup>-</sup> (meq./liter)	0.13	0.20	0.11	0.18	0.13	0.18
pH (1:1 Soil-Water Ratio)	6.35	6.50	6.65	6.40	6.30	6.45

non-calcareous Stockton soil. Soil pH was greatest when  $N_2$  gas was circulated through the soils at 100% of field capacity. This was probably due to removal of  $CO_2$  from the soils by the  $N_2$  gas. There were no marked increases in pH of soils at 150% of field capacity with  $N_2$  gas supplied. Air-filled soil porosity would be less at 150% of field capacity and thus removal of  $CO_2$  by the  $N_2$  gas would be less.

The relationships between  $HCO_3^-$  concentrations and yields, Fe and Mn in tops, and Fe and Mn uptake of flax plants were determined by means of correlation analysis (Table 49). The data for each soil were treated separately since the two soils differed widely in  $HCO_3^-$  concentration. In both soils, soil  $HCO_3^-$  concentration was negatively correlated with the Fe content of tops; a higher r value was obtained for the Lakeland than for the Stockton soil. Although these correlation coefficients were not significant, they indicate that the concentrations of  $HCO_3^-$  found in the soil, particularly in the Lakeland soil, may be inhibiting translocation of Fe within the plant. None of the other correlation coefficients was significant. Yields were positively correlated with  $HCO_3^-$  concentration for both soils. Unlike the Lakeland soil, the concentration of  $HCO_3^-$  in the Stockton soil was negatively correlated with Mn in tops.

Since the  $HCO_3^-$  ion was extracted from the soils with distilled water, it is likely that the  $HCO_3^-$  concentrations in the soils prior to removal from the pots were

TABLE 49

Correlation of Bicarbonate Ion Concentration with Yields,  
Fe and Mn in Tops, Fe and Mn Uptake of Flax Plants  
Grown on the Lakeland and Stockton Soils

Soil	Factors Correlated	Df (n-2)	Square of Correlation Coefficient ( $r^2$ )	Correlation Coefficient (r)
Lakeland	(i) $\text{HCO}_3^-$ vs. Yield	4	0.40	0.63 N.S.
	(ii) $\text{HCO}_3^-$ vs. Fe in Tops	4	0.43	-0.65 N.S.
	(iii) $\text{HCO}_3^-$ vs. Mn in Tops	4	0.06	0.24 N.S.
	(iv) $\text{HCO}_3^-$ vs. Fe Uptake	4	0.03	0.17 N.S.
	(v) $\text{HCO}_3^-$ vs. Mn Uptake	4	0.005	0.07 N.S.
Stockton	(i) $\text{HCO}_3^-$ vs. Yield	4	0.40	0.63 N.S.
	(ii) $\text{HCO}_3^-$ vs. Fe in Tops	4	0.05	-0.22 N.S.
	(iii) $\text{HCO}_3^-$ vs. Mn in Tops	4	0.24	-0.48 N.S.
	(iv) $\text{HCO}_3^-$ vs. Fe Uptake	4	0.32	0.56 N.S.
	(v) $\text{HCO}_3^-$ vs. Mn Uptake	4	0.28	0.53 N.S.

N.S.: Not significant.

different from those measured. A technique for measuring the  $\text{HCO}_3^-$  concentrations of undisturbed soils, however, was not available. Although the measurements of  $\text{HCO}_3^-$  concentrations may have been in error, it appears that the  $\text{HCO}_3^-$  ion retarded Fe translocation. This is evident when comparisons of Fe content in flax tops and  $\text{HCO}_3^-$  concentrations within each aeration treatment are made. The process or processes by which  $\text{HCO}_3^-$  limits Fe translocation are unknown. Further work on the influence of  $\text{HCO}_3^-$  on Fe translocation would be necessary to understand more fully the behaviour of Fe in plants subjected to high soil moisture contents.

## CHAPTER V

### SUMMARY AND CONCLUSIONS

Studies were conducted to investigate (i) changes in Eh, pH and concentrations of Fe and Mn in three calcareous and three non-calcareous Manitoba soils continuously saturated with water for ten weeks and (ii) the utilisation of Fe and Mn by flax and oat plants when grown under varying soil moisture regimes.

The Eh and pH trends and the amounts of Fe and Mn released into soil solution varied markedly with soil type. In general, the concentrations of Fe and Mn in solution increased as Eh and/or pH decreased. Increase in Mn concentration preceded that of Fe after the initiation of saturation and Mn remained at a higher concentration than Fe for the entire duration of saturation. The Red River and Tarno soils which contain large amounts of clay and organic matter showed noticeable delays in the release of Fe and Mn into solution following soil reduction. These delays in the release of Fe and Mn, following reduction, were either negligible or absent in the soils that were coarse-textured and contained small amounts of organic matter. The Lakeland and Newdale soils which contained the lowest amounts of  $\text{NO}_3\text{-N}$  and relatively high amounts of organic matter were the most strongly reduced of the six soils

studied; these two soils also released the largest amounts of Fe and Mn into soil solution.

Eh - pH diagrams showed that  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{MnCO}_3$  were the Fe and Mn compounds in equilibrium with Fe and Mn ions in the soil solutions.  $E^\circ$  values, calculated from experimentally measured Eh, pH and  $\log(\text{Fe})$  or  $\log(\text{Mn})$ , failed to indicate the presence of the  $\text{Fe}_2\text{O}_3\text{-Fe}^{2+}$  redox system. The presence of the  $\text{Mn}_2\text{O}_3\text{-Mn}^{2+}$  redox system, however, was indicated by the calculated  $E^\circ$  values. Concentrations of Fe, calculated from experimentally measured Eh and pH, were several fold lower than the concentrations of Fe measured in soil solution. The concentrations of Mn, similarly calculated, came to within  $\pm 50\%$  of measured concentrations in about 33% of the instances.

Simple and multiple regression analyses showed that measurements of both Eh and pH accounted for more of the variation in the concentrations of Fe and Mn in soil solution than did Eh or pH alone. The poorest correlations between Fe and Mn in solution and pH and Eh were obtained for the Red River and Tarno soils which showed noticeable delays in the release of Fe and Mn following soil reduction.

The data indicated that almost all the Fe in soil solution was complexed with organic matter. Mn was either not complexed or only weakly complexed. The metal-organic matter complexes were negatively charged. The soil solutions had a greater affinity for Fe than did  $10^{-4}\text{M}$  EDTA.

Calculations based on the assumption that the relative stability constants of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  with soil organic matter are the same as those with EDTA, indicated that the Fe in the Fe-organic matter complexes was probably  $\text{Fe}^{\text{III}}$ . The very high degree of complexing of Fe in soil solution was most probably responsible for the failure to obtain the theoretical  $E^\circ$  values for the  $\text{Fe}_2\text{O}_3\text{-Fe}^{2+}$  redox system from the experimental data.

Flax plants grown at 150% of field capacity moisture content in the Red River, Tarno, Lakeland and Plum Ridge soils developed varying degrees of chlorosis with resultant decreases in yields. The oat plants developed normally on all soils under all water levels; yields of oats decreased with increasing soil moisture content in the Red River and Tarno soils but increased with increasing soil moisture content in the Lakeland, Newdale and Stockton soils.

The chlorotic flax plants contained less Fe and more Mn than did the non-chlorotic plants. The ratio of Mn to Fe in chlorotic flax plants was four or greater; the non-chlorotic plants had lower Mn:Fe ratios. Yields of flax, measured after 35 days of growth, decreased with increase in the Mn content and Mn:Fe ratio of the plants. The  $r^2$  values for the relationships of yield and Mn content and yield and Mn:Fe ratio were 0.54 and 0.59 respectively. The yields of flax increased with increases in the Fe content of the plants ( $r^2 = 0.33$ ). Contents of Fe and Mn and Mn:Fe

ratio in oat tops were lower than those for flax. Mn content of oats increased with increasing soil moisture content but was not present in toxic amounts.

Iron contents of flax roots were exceedingly high when compared with those of tops while Mn contents of roots were low as compared with those of tops. Thus, irrespective of soil moisture content, large amounts of Fe and only slight amounts of Mn accumulated in the roots. The translocation of Fe from the roots to the tops of flax plants appeared to be retarded at higher moisture levels in soils producing chlorotic plants. Soil aeration experiments showed that the absorption or translocation of Fe by flax plants was unrelated to oxygen supply in the soil. Bicarbonate contents in the Lakeland and Stockton soils were measured; the bicarbonate ion concentrations were negatively correlated with Fe in the tops of flax grown on these two soils. These correlation coefficients, however, were not statistically significant.

It is suggested that the complexing of Fe possibly as  $\text{Fe}^{\text{III}}$  by organic matter in soil solution and the accumulation of bicarbonate in saturated soils may be partly responsible for the decreased utilisation of Fe by flax plants under increased soil moisture conditions.

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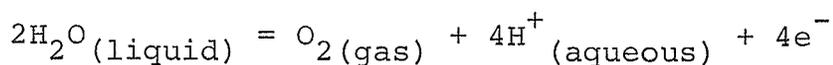
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APPENDIXES

## APPENDIX I

### CONSTRUCTION OF EH-PH DIAGRAMS

The construction of Eh-pH diagrams has been discussed in detail by Garrels and Christ (49). The diagrams are constructed with Eh as the ordinate and pH as the abscissa. Reactions not involving oxidation or reduction will be Eh-independent while reactions involving oxidation or reduction are Eh-dependent and may be pH-dependent as well. All the mineral and ionic relationships for each diagram are within the upper and lower stability limits of water since the systems being considered are aqueous ones. The upper limit of water stability is the equilibrium between water and oxygen at one atmosphere pressure and is defined by the equation:



From the relationship,  $Eh = E^\circ + \frac{RT}{nF} \ln \frac{(\text{oxidised state})}{(\text{reduced state})}$ , the Nernst equation for the above reaction is  $Eh = E^\circ + \frac{0.059}{4} \log \frac{p\text{O}_2 (\text{H}^+)^4}{(\text{H}_2\text{O})^2}$  where  $p\text{O}_2$  = partial pressure of  $\text{O}_2$ .

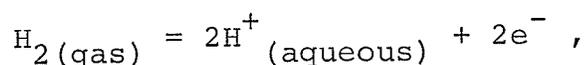
Under the conditions chosen,  $p\text{O}_2$  is unity, as is the activity of pure liquid water. Thus,

$$Eh = E^\circ + \frac{0.059}{4} \log (\text{H}^+)^4.$$

Substituting  $-\text{pH}$  for  $(\text{H}^+)$  gives  $Eh = E^\circ - 0.059 \text{ pH}$ .

Therefore, the equilibrium between water and oxygen at a partial pressure of one atmosphere is a straight line in an Eh-pH plot, with a slope of -0.059 and an intercept of  $E^\circ$ .  $E^\circ$  for the above reaction, calculated from the free energy change, has a value of 1.23 volts.

The lower limit of water stability is derived from the following relationships:



$$\text{Eh} = E^\circ + \frac{0.059}{2} \log \frac{(\text{H}^+)^2}{p_{\text{H}_2}} \quad \text{and}$$

$$\text{Eh} = E^\circ - \frac{0.059}{2} \log p_{\text{H}_2} - 0.059 \text{ pH}$$

where  $p_{\text{H}_2}$  = the partial pressure of  $\text{H}_2$ .

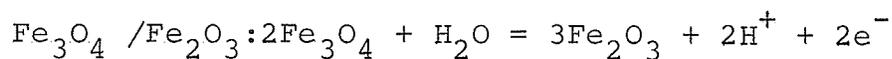
If  $p_{\text{H}_2}$  = unity, the equation becomes  $\text{Eh} = E^\circ - 0.059 \text{ pH}$ .

$E^\circ$  for the reaction has a value of zero. Thus, the equilibrium between  $\text{H}_2$  and water is a line with a slope of -0.059 and an intercept of 0 volt.

The Eh-pH diagram for Fe shows the stability areas for hematite ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and siderite ( $\text{FeCO}_3$ ) at 25° C and one atmosphere total pressure, with a partial pressure of  $\text{CO}_2$  ( $p_{\text{CO}_2}$ ) =  $10^{-2.0}$  atmosphere. The stability fields of the various ions are labelled with the dominant ionic species present and contour lines of the log of the activity of dissolved species at  $10^{-4}$  and  $10^{-6}$  M. The boundary of the iron oxides was drawn at a total activity of ions equal to  $10^{-6}$  M.

The solid/solid and solid/ionic boundaries for Fe

were constructed as follows:



$$\Delta G^\circ = + 10.2 \text{ Kcal}; \quad E^\circ = 0.221 \text{ volt.}$$

$$\text{Eh} = 0.221 + \frac{0.059}{2} \log \frac{(\text{Fe}_2\text{O}_3)^3 (\text{H}^+)^2}{(\text{Fe}_3\text{O}_4) (\text{H}_2\text{O})}$$

$$\text{Eh} = 0.221 + \frac{0.059}{2} \log (\text{H}^+)^2$$

$$\text{Eh} = 0.221 - 0.059 \text{ pH}$$

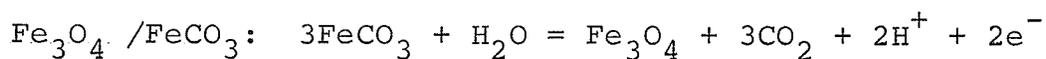
Thus, the boundary line between hematite and magnetite has a slope of -0.059 and an intercept of 0.221 volt on the Eh axis.



$$\Delta G^\circ = -33.57 \text{ Kcal}; \quad E^\circ = 0.728 \text{ volt.}$$

$$\text{Eh} = E^\circ - 0.059 \log \text{Fe}^{2+} - 0.177 \text{ pH}$$

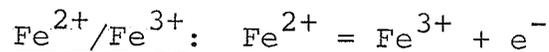
If  $(\text{Fe}^{2+}) = 1$ ,  $\text{Eh} = E^\circ - 0.177 \text{ pH}$  and the intercept is  $= E^\circ$ .



$$\Delta G^\circ = 14.69 \text{ Kcal}; \quad E^\circ = 0.319 \text{ volt}$$

$$\text{Eh} = 0.319 + 0.0885 \log \text{pCO}_2 - 0.059 \text{ pH}$$

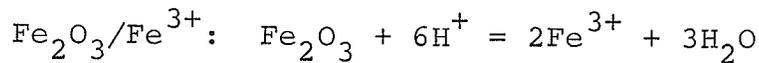
The slope of the boundary line is -0.059 and the intercept varies with the partial pressure of  $\text{CO}_2$ . For the diagrams shown in Figures 9 to 14, a  $\text{pCO}_2$  of  $10^{-2.0}$  atmosphere was used and the intercept  $= 0.319 + (0.0885)(-2) = 0.14$  volt.



$$\Delta G^{\circ} = 17.78 \text{ Kcal}; \quad E^{\circ} = 0.771 \text{ volt.}$$

$$E_h = E^{\circ} + 0.059 \log \frac{(\text{Fe}^{3+})}{(\text{Fe}^{2+})}.$$

Since  $(\text{Fe}^{2+}) = (\text{Fe}^{3+})$ ,  $0.059 \log \frac{(\text{Fe}^{3+})}{(\text{Fe}^{2+})} = 0$  and  $E_h = E^{\circ} = 0.771$  volt. This reaction is only  $E_h$  dependent and so the boundary between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  is a horizontal line parallel to the pH axis.



$\Delta G^{\circ} = + 2.0$  Kcal. Oxidation or reduction is not involved in the reaction. The equilibrium constant is

$$\log K = \frac{\Delta G^{\circ}}{-1.364} = \frac{2.0}{-1.364} = -1.45$$

Since the activities of  $\text{Fe}_2\text{O}_3$  and  $\text{H}_2\text{O}$  are unity,  $\log \frac{(\text{Fe}^{3+})}{(\text{H}^{+})^6} = -1.45$ .

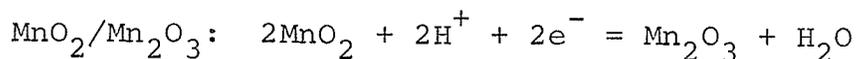
Rearranging the equation and substituting  $-\text{pH}$  for  $\log (\text{H}^{+})$ ,

$$2 \log (\text{Fe}^{3+}) = -1.45 - 6 \text{ pH}$$

$$\log (\text{Fe}^{3+}) = -0.72 - 3 \text{ pH.}$$

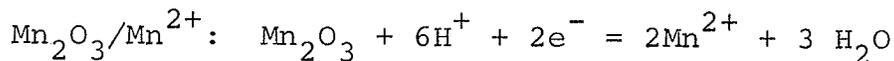
Thus, the log of the activity of ferric ion is a linear function of pH. If the pH is stipulated,  $(\text{Fe}^{3+})$  is fixed, and vice versa. Because  $E_h$  is not involved, the boundary between  $\text{Fe}^{3+}$  and  $\text{Fe}_2\text{O}_3$  lies parallel to the  $E_h$  axis.

The Eh-pH diagram for Mn was developed using the same principles as for the Fe diagram. The stable Mn compounds shown are  $\text{MnO}_2$  (pyrolusite),  $\text{Mn}_2\text{O}_3$  (manganic oxide) and  $\text{MnCO}_3$  (rhodochrosite). The mineral and ionic boundaries are defined as follows:



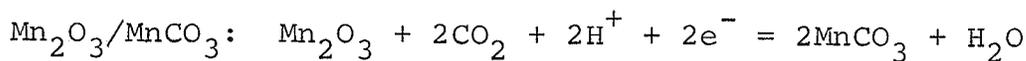
$$\Delta G^\circ = 46.19 \text{ Kcal}; \quad E^\circ = 1.004 \text{ volts}$$

and  $Eh = E^\circ - 0.059 \text{ pH}.$



$$\Delta G^\circ = -66.57 \text{ Kcal}; \quad E^\circ = 1.443 \text{ volts.}$$

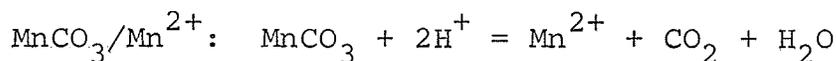
$$Eh = E^\circ - 0.059 \log (\text{Mn}^{2+}) - 0.177 \text{ pH}.$$



$$\Delta G^\circ = -44.47 \text{ Kcal}; \quad E^\circ = 0.96 \text{ volt.}$$

$$Eh = E^\circ + 0.059 \log p\text{CO}_2 - 0.059 \text{ pH}.$$

Thus, the boundary between  $\text{Mn}_2\text{O}_3$  and  $\text{MnCO}_3$  has a slope of -0.059. The intercept, and hence the stability area of  $\text{MnCO}_3$  on the phase diagram depends on  $p\text{CO}_2$ . In Figures 15 to 20, a  $p\text{CO}_2$  of  $10^{-3.5}$  atmosphere was used and the intercept =  $0.96 + (0.059) (-3.5) = 0.75$  volt on the Eh axis.

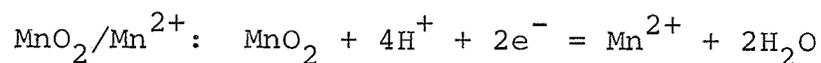


$$\Delta G^\circ = -11.05 \text{ Kcal}; \quad \log K = 8.10$$

$$K = 10^{8.10}$$

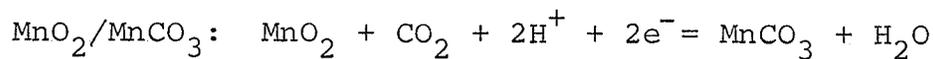
$$\log (\text{Mn}^{2+}) = \log K - \log p\text{CO}_2 - 2\text{pH}$$

This reaction is independent of Eh and dependent only on pH and  $p\text{CO}_2$ . The boundary line between  $\text{MnCO}_3$  and  $\text{Mn}^{2+}$  is thus parallel to the Eh axis.  $(\text{Mn}^{2+})$  will depend on pH and  $p\text{CO}_2$ . If  $p\text{CO}_2$  or  $(\text{Mn}^{2+})$  increases, the  $\text{MnCO}_3/\text{Mn}^{2+}$  boundary moves to the left.



$$\Delta G^\circ = -56.68 \text{ Kcal}; \quad E^\circ = 1.23 \text{ volts}$$

$$\text{Eh} = E^\circ - 0.0295 \log (\text{Mn}^{2+}) - 0.118 \text{ pH.}$$



$$\Delta G^\circ = -45.29 \text{ Kcal}; \quad E^\circ = 0.98 \text{ volt}$$

$$\text{Eh} = E^\circ + 0.0295 \log p\text{CO}_2 - 0.059 \text{ pH}$$

$\text{Mn}^{3+}$  does not exist in solution and so it does not appear on the Eh-pH phase diagram for Mn.

APPENDIX IIA

Calculated Values of  $(\text{Fe}^{2+})$  Based on the  
 $\text{Fe}_2\text{O}_3 - \text{Fe}^{2+}$  System ( $E^\circ = 0.728$  volt)  
 $\text{Log} (\text{Fe}^{2+}) = 16.95 (E^\circ - E_h - 0.177 \text{ pH})$

Number of Days after Saturation	Calculated $(\text{Fe}^{2+})$ for Each of the Soils (Molarity)					
	Red River	Tarno	Lakeland	Newdale	Stockton	Plum Ridge
3	$8.91 \times 10^{-20}$	$2.14 \times 10^{-18}$	$1.95 \times 10^{-17}$	$8.91 \times 10^{-19}$	$2.88 \times 10^{-19}$	$7.58 \times 10^{-19}$
7	$1.62 \times 10^{-17}$	$2.45 \times 10^{-18}$	$8.91 \times 10^{-18}$	$1.86 \times 10^{-16}$	$4.78 \times 10^{-17}$	$2.75 \times 10^{-20}$
14	$6.31 \times 10^{-17}$	$2.18 \times 10^{-17}$	$2.29 \times 10^{-15}$	$1.23 \times 10^{-13}$	$1.05 \times 10^{-16}$	$2.18 \times 10^{-19}$
21	$2.29 \times 10^{-17}$	$6.31 \times 10^{-18}$	$3.38 \times 10^{-15}$	$3.89 \times 10^{-13}$	$1.00 \times 10^{-17}$	$8.91 \times 10^{-17}$
28	$2.18 \times 10^{-14}$	$5.75 \times 10^{-15}$	$2.18 \times 10^{-12}$	$1.38 \times 10^{-16}$	$2.29 \times 10^{-17}$	$3.46 \times 10^{-19}$
35	$4.78 \times 10^{-16}$	$2.75 \times 10^{-17}$	$3.63 \times 10^{-13}$	$2.04 \times 10^{-11}$	$1.17 \times 10^{-15}$	$3.10 \times 10^{-14}$
42	$1.86 \times 10^{-17}$	$3.24 \times 10^{-17}$	$4.26 \times 10^{-16}$	$1.28 \times 10^{-17}$	$3.38 \times 10^{-18}$	$1.41 \times 10^{-18}$
49	$5.75 \times 10^{-17}$	$9.33 \times 10^{-17}$	$3.80 \times 10^{-16}$	$2.04 \times 10^{-16}$	$6.61 \times 10^{-17}$	$1.07 \times 10^{-19}$
56	$5.01 \times 10^{-16}$	$5.25 \times 10^{-17}$	$1.12 \times 10^{-15}$	$2.69 \times 10^{-13}$	$3.24 \times 10^{-17}$	$5.62 \times 10^{-19}$
63	$7.08 \times 10^{-18}$	$1.74 \times 10^{-18}$	$3.80 \times 10^{-17}$	$2.08 \times 10^{-18}$	$1.00 \times 10^{-17}$	$2.29 \times 10^{-18}$
70	$3.23 \times 10^{-17}$	$1.62 \times 10^{-17}$	$3.89 \times 10^{-17}$	$5.62 \times 10^{-17}$	$1.95 \times 10^{-18}$	$4.07 \times 10^{-18}$

## APPENDIX IIB

Calculated Values of  $(\text{Fe}^{2+})$  Based on the  
 $\text{Fe}(\text{OH})_3 - \text{Fe}^{2+}$  System ( $E^\circ = 1.06$  volt)  
 $\text{Log} (\text{Fe}^{32+}) = 16.95(E^\circ - E_h - 0.177 \text{ pH})$

Number of Days after Saturation	Calculated $(\text{Fe}^{2+})$ for Each of the Soils (Molarity)					
	Red River	Tarno	Lakeland	Newdale	Stockton	Plum Ridge
3	$3.80 \times 10^{-14}$	$8.91 \times 10^{-13}$	$8.32 \times 10^{-12}$	$3.80 \times 10^{-13}$	$1.23 \times 10^{-13}$	$3.24 \times 10^{-13}$
7	$6.76 \times 10^{-12}$	$1.05 \times 10^{-12}$	$3.80 \times 10^{-12}$	$7.94 \times 10^{-11}$	$2.04 \times 10^{-11}$	$1.17 \times 10^{-14}$
14	$2.69 \times 10^{-11}$	$9.33 \times 10^{-12}$	$9.55 \times 10^{-10}$	$5.25 \times 10^{-8}$	$4.46 \times 10^{-11}$	$9.33 \times 10^{-14}$
21	$9.55 \times 10^{-12}$	$2.69 \times 10^{-12}$	$1.41 \times 10^{-9}$	$1.66 \times 10^{-7}$	$4.26 \times 10^{-12}$	$3.80 \times 10^{-11}$
28	$9.33 \times 10^{-9}$	$2.45 \times 10^{-9}$	$9.33 \times 10^{-7}$	$5.75 \times 10^{-11}$	$9.55 \times 10^{-12}$	$1.48 \times 10^{-13}$
35	$2.04 \times 10^{-10}$	$1.17 \times 10^{-11}$	$1.55 \times 10^{-7}$	$1.23 \times 10^{-6}$	$5.01 \times 10^{-10}$	$1.38 \times 10^{-8}$
42	$7.94 \times 10^{-12}$	$1.38 \times 10^{-11}$	$1.77 \times 10^{-10}$	$5.37 \times 10^{-12}$	$1.41 \times 10^{-12}$	$6.03 \times 10^{-13}$
49	$2.45 \times 10^{-11}$	$3.89 \times 10^{-11}$	$1.62 \times 10^{-10}$	$8.51 \times 10^{-7}$	$2.75 \times 10^{-11}$	$4.57 \times 10^{-14}$
56	$2.14 \times 10^{-10}$	$2.18 \times 10^{-11}$	$4.78 \times 10^{-10}$	$1.12 \times 10^{-7}$	$1.38 \times 10^{-11}$	$2.34 \times 10^{-13}$
63	$3.02 \times 10^{-12}$	$7.24 \times 10^{-11}$	$1.62 \times 10^{-11}$	$8.91 \times 10^{-13}$	$4.26 \times 10^{-12}$	$1.00 \times 10^{-12}$
70	$1.38 \times 10^{-11}$	$6.76 \times 10^{-12}$	$1.66 \times 10^{-11}$	$2.34 \times 10^{-11}$	$8.32 \times 10^{-13}$	$1.74 \times 10^{-12}$

APPENDIX IIC  
Measured Values of  $[\text{Fe}^{2+}]$  in Soil Solutions

Number of Days after Saturation	Measured $[\text{Fe}^{2+}]$ for Each of the Soils (Molarity $\times 1 \times 10^{-5}$ )					
	Red River	Tarno	Lakeland	Newdale	Stockton	Plum Ridge
3	0.00	0.00	0.17	0.00	0.00	0.00
7	0.00	0.00	0.00	0.22	0.00	0.00
14	1.41	0.45	6.31	15.80	5.62	0.00
21	1.07	1.77	7.76	22.40	0.00	0.00
28	3.16	4.46	12.60	31.60	4.36	0.00
35	2.24	6.76	21.80	22.40	0.89	5.88
42	6.31	8.91	12.30	15.80	0.00	0.00
49	9.33	13.50	19.90	19.90	1.58	0.17
56	6.76	8.51	19.50	31.60	0.89	0.23
63	0.17	0.35	16.90	0.45	5.62	2.51
70	3.16	7.24	10.90	14.10	0.17	0.00

## APPENDIX IIIA

Calculated Values of  $(\text{Mn}^{2+})$  Based on  
 the  $\text{Mn}_2\text{O}_3 - \text{Mn}^{2+}$  System ( $E^\circ = 1.443$ )  
 $\text{Log} (\text{Mn}^{2+}) = 16.95 (E^\circ - \text{Eh} - 0.177\text{pH})$

Number of Days after Saturation	Calculated $(\text{Mn}^{2+})$ for Each of the Soils (Molarity x $1 \times 10^{-5}$ )					
	Red River	Tarno	Lakeland	Newdale	Stockton	Plum Ridge
3	0.01	0.27	2.57	0.12	0.04	0.10
7	2.14	0.32	1.17	24.50	6.31	0.003
14	8.32	2.88	302.00	N.V.	0.14	0.03
21	3.02	0.83	446.00	N.V.	1.32	11.70
28	2880.00	758.00	34600.00	18.20	3.02	0.04
35	63.10	3.63	N.V.*	26900.00	155.00	4070.00
42	2.45	4.26	56.20	1.69	0.45	0.18
49	7.58	12.00	50.10	38000.00	8.51	0.01
56	66.10	6.76	148.00	N.V.	4.26	0.07
63	0.93	0.23	5.01	0.27	1.32	0.31
70	4.26	2.14	5.25	7.41	0.26	0.54

\*N.V. = Negative value obtained.

APPENDIX IIIB  
 Measured Values of  $[\text{Mn}^{2+}]$  in Soil Solutions

Number of Days after Saturation	Measured $[\text{Mn}^{2+}]$ for Each of the Soils (Molarity $\times 1 \times 10^{-5}$ )					
	Red River	Tarno	Lakeland	Newdale	Stockton	Plum Ridge
3	0.00	0.22	0.36	1.26	0.39	0.77
7	1.77	2.82	6.31	7.58	1.26	0.18
14	4.26	4.46	9.33	20.40	0.14	0.36
21	4.89	7.08	15.10	26.90	3.46	1.44
28	5.88	7.76	19.00	30.90	8.91	1.26
35	1.82	3.55	13.50	16.90	5.75	19.00
42	7.24	11.20	15.10	14.10	2.18	1.82
49	7.08	11.20	18.20	35.50	6.31	3.31
56	7.76	8.71	19.90	25.10	5.01	2.29
63	0.29	5.49	14.80	4.57	11.70	5.88
70	6.31	9.55	14.10	15.80	2.75	2.75

## APPENDIX IVA

Fe Extracted with DTPA-TEA from Soils Planted to Flax

Soils	Water Regimes*	Fe Extracted (ppm)	
		First Harvest	Second Harvest
Red River	W <sub>1</sub>	12	14
	W <sub>2</sub>	13	15
Tarno	W <sub>1</sub>	22	26
	W <sub>2</sub>	23	28
Lakeland	W <sub>1</sub>	10	12
	W <sub>2</sub>	10	12
Newdale	W <sub>1</sub>	11	13
	W <sub>2</sub>	11	13
Stockton	W <sub>1</sub>	39	40
	W <sub>2</sub>	39	35
Plum Ridge	W <sub>1</sub>	6	7
	W <sub>2</sub>	6	7

\*W<sub>1</sub> = 100% of Field CapacityW<sub>2</sub> = 150% of Field Capacity

## APPENDIX IVB

Fe Extracted with DTPA-TEA from Soils Planted to Oats

Soils	Water Regimes*	Fe Extracted (ppm)	
		First Harvest	Second Harvest
Red River	W <sub>1</sub>	13	15
	W <sub>2</sub>	13	14
Tarno	W <sub>1</sub>	29	23
	W <sub>2</sub>	23	23
Lakeland	W <sub>1</sub>	10	10
	W <sub>2</sub>	10	11
Newdale	W <sub>1</sub>	10	11
	W <sub>2</sub>	10	13
Stockton	W <sub>1</sub>	40	48
	W <sub>2</sub>	38	48

\*W<sub>1</sub> = 100% of Field CapacityW<sub>2</sub> = 150% of Field Capacity

## APPENDIX IVC

Mn Extracted with  $\text{NH}_4\text{OAc}$  + Quinol  
from Soils Planted to Flax

Soils	Water Regimes*	Mn Extracted (ppm)	
		First Harvest	Second Harvest
Red River	$W_1$	189	190
	$W_2$	196	199
Tarno	$W_1$	70	68
	$W_2$	68	68
Lakeland	$W_1$	66	66
	$W_2$	67	66
Newdale	$W_1$	200	202
	$W_2$	198	204
Stockton	$W_1$	177	179
	$W_2$	174	172
Plum Ridge	$W_1$	48	47
	$W_2$	50	49

\* $W_1$  = 100% of Field Capacity

$W_2$  = 150% of Field Capacity

## APPENDIX IVD

Mn Extracted with  $\text{NH}_4\text{OAc}$  + Quinol  
from Soils Planted to Oats

Soils	Water Regimes*	Mn Extracted (ppm)	
		First Harvest	Second Harvest
Red River	$W_1$	196	202
	$W_2$	191	204
Tarno	$W_1$	66	71
	$W_2$	66	72
Lakeland	$W_1$	64	66
	$W_2$	64	69
Newdale	$W_1$	199	212
	$W_2$	195	209
Stockton	$W_1$	174	180
	$W_2$	176	179

\* $W_1$  = 100% of Field Capacity

$W_2$  = 150% of Field Capacity