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Title: THE EFFECT OF SELECTED POTASSIUM SALTS ON THE AVAILABILITY OF SOIL MANGANESE

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Incubation experiments with an acid poorly drained soil have shown that the application of neutral soluble salts influenced the level of extractable Mn. The application of a salt which lowered the soil pH either increased the extractable Mn or retarded the oxidation and/or fixation of extractable Mn. This effect was independent of the applied salt, although salts which had the greatest effect on soil pH generally had the largest effect on extractable Mn. Comparisons of K_2SO_4 with KNO_3 at equivalent concentrations of K and with K_2SO_4 at different ionic strengths showed a small but nonsignificant effect of ionic strength on the level of extractable Mn. This indicated that the solubility of the Mn oxides was largely pH dependent and that ionic strength considerations were of secondary importance.

The effect of the Cl salt was over and above that of the general salt effect. The application of KCl always released more extractable Mn than either the KNO_3 or the K_2SO_4 treatment. This was not a

strict pH effect since the KNO_3 and KCl treatments always had the same effect on soil pH. It was also not an ionic strength effect since the relative ionic strength of the K_2SO_4 treatment was 1.5 times greater than that of the KCl treatment, and biological activity was not a factor in well aerated conditions.

To explain the Cl effect, a hypothesis has been presented in which Cl would function in an oxidation-reduction reaction. In these reactions, Cl could act either as the electron donor or as an electron bridge between the reductant and oxidant. Evidence that would support this hypothesis was:

1. The similarity between the effect of KCl and KBr on extractable Mn, i.e., the KBr treatment released more extractable Mn than the KCl according to theory.
2. Theoretical considerations of some of the conditions which were possible in the soil system showed that both Cl and Br had the potential to reduce the lower Mn oxides under those conditions.
3. The pH dependence of the Cl effect.

The Effect of Selected Potassium Salts on the Availability of Soil Manganese

by

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INTRODUCTION

Manganese is considered as one of the micronutrients which are needed for plant growth. Very small quantities are needed for normal growth, and where appreciable quantities appear in an easily available form, Mn toxicity may develop. It is known to serve as an activator of certain enzyme systems and is thought to be involved in N transformations in both soils and plants. Manganese is absorbed by plants in the divalent form and has been found to concentrate in the regions of highest physiological activity.

Soil Mn has generally been considered to exist in three valence states: (1) the divalent Mn which is soluble and may be present as an adsorbed cation or as an ion in the soil solution, (2) trivalent Mn which supposedly exists as highly reactive oxides, and (3) tetravalent Mn which exists as a relatively inert oxide. These three forms are believed to be in dynamic equilibrium in soil systems.

Because of the dynamic nature of soil Mn, a relatively large number of variables influence its availability. Soil acidity, aeration, and biological growth are probably the three most important factors which have an influence. These variables are not independent of each other. An example of this is that increasing the soil pH does not necessarily lower toxic amounts of Mn unless aeration is adequate.

Increasingly greater amounts of fertilizer materials are being applied to increase available plant nutrients because of improved varieties and a greater demand for larger yields. These kinds of practices put special emphasis on obtaining knowledge of how these fertilizer materials react with the soil system. The effect of commonly used anions on the availability of soil Mn has been largely ignored in this respect.

For these reasons a soil chemistry approach has been used in this study to attempt to gain additional understanding of the mechanisms by which anions influence the availability of soil Mn. Potassium salts have been used as the carrier for the anion because of the wide spread use of K fertilizers.

LITERATURE REVIEW

Manganese Distribution

Robinson (1929) has observed that the majority of the soils found in the United States contain from 0.001 to 1.27 percent Mn, although tropical soils may contain as high as 15 percent Mn. He found that most of the H_2O_2-soluble Mn in soils did not occur in the clay or colloidal fractions but in the silt and sand size fractions. This distribution has also been reported by Wahhab and Bhatti (1958) who showed that there was relatively little increase in total Mn with increasing amounts of clay. The distribution of total soil Mn in a given soil profile was found to be dependent upon the reducing-oxidizing conditions in the profile and/or soil pH by Daniels, Brasfield, and Riecker (1962). They found that the $Na_2S_2O_4$-extractable Mn changed very little with depth of Brunizems but generally reached a maximum in the A_2 or B_2 horizons for other soil types. The amount of Mn extracted by $Na_2S_2O_4$ has been commonly referred to as "free Mn".

Pure Mn oxides or hydroxides have rarely been found as secondary minerals in soils. Taylor, McKenzie, and Norrish (1964) have studied the mineralogy of some Australian soil separates and have found that the specific Mn minerals of lithiophorite, birnessite, hollandite, todorokite, and pyrolusite could be identified. All of these were found to contain varying amounts of Ni, Co, Mg, Ba, Al, K, Na, Fe, and Ca. Lithiophorite occurred in neutral to acidic soil horizons; whereas, birnessite was most commonly found in the alkaline horizons. All of the minerals isolated were in the clay size fraction thus making their surface reactions very important. Hydrous oxides of Mn and Fe are also common in acid soils and solution systems. Nodules of MnO_2 admixed with Fe oxide are frequently found on the floors of ocean basins and in soils. Coatings of mixed oxides have also been found on clays and other minerals (Hem, 1963b). Whether Mn was present in soils as the oxide, as a constituent of silicates or other minerals, or was held by adsorption on the surfaces of the exchange complexes would probably depend on numerous factors which vary from one soil to another.

Factors Affecting the Availability of Mn

Several excellent reviews have been written recently which have assessed the role of Mn in plant nutrition and in the soil system. The general chemistry of the micro-nutrients in soils has been covered by Hodgson (1963). Mulder and Gerretsen (1952), and Anderson (1964) have discussed the role of Mn from a nutritional view. They covered such topics as the Mn content in plants to the functional aspects of Mn in plant metabolism. A conference was held in 1957 (Lamb, et al., 1958), which was concerned with the trace elements, Co, B, Va, Mn, Zn, Fe, and their role in plant nutrition, animal nutrition, and photosynthesis. An ample review of the literature relating to the estimation of available soil Mn was also presented.

The availability of Mn at any given time depends very little on the total amount present but rather on the present or prior environment in the soil system. In general, any process which causes reducing conditions increases the available Mn, and any process which results in an oxidizing environment reduces the level of available Mn (Piper, 1931; Snider, 1943; Sherman and Harmer, 1942).

The relationship between oxidation potential or redox potential (En)-a measure of the system's ability to accept or give up electrons-and pH has been discussed by Hem (1963a) for pure Mn oxide systems. A more general study of the applications of stability-field diagrams has been compiled by Garrels and Christ (1965). Such diagrams may also be utilized to give an indication of the factors affecting the solubility of the Mn oxides and the most stable assemblage of such under given conditions.

Stability-field Diagrams

The Eh-pH, or stability-field diagram, is a graphical means of showing how the conditions of redox potential and hydrogen ion concentration control the specific dissolved ions and solid mineral species of an element in an aqueous environment. The literature contains numerous examples of the use of such diagrams in studies relating to geologic applications, oceanography, and limnology. In preparing such diagrams certain basic assumptions have to be made and should be considered when making interpretations. The fundamental equations used are those dealing with dissolved and solid-phase species and these are assumed to be at equilibrium. In systems which are not at equilibrium they are still useful to indicate limiting conditions. The natural system generally involves much more complex compounds, and the aqueous phase generally contains other constituents in addition to those species dealt with in the preparation of the Eh-pH diagram. In general, these minor deviations cannot be satisfactorily evaluated.

The concentration of the dissolved species which are used are the effective chemical "concentrations" (activity) rather than the concentrations which can be measured by chemical analysis. In dilute solutions the actual concentrations are almost equal to the activity, but as the amount of dissolved material increases, the activity decreases. The actual concentration can be converted to the activity if the activity coefficient is known. The activity coefficient may be estimated by the use of the Debye-Huckel theory, but accurate conversions of concentrations to activities are questionable in highly mineralized solutions.

The diagrams which are usually prepared are for systems at a pressure of one atmosphere and at a temperature of 25°C. They are strictly applicable under these conditions, although pressures of a few atmospheres and temperatures of 10° or 15° C above or below 25°C do not seriously affect the results.

The standard electrode potential for a given reaction can be calculated from the standard free energy changes. Relating this value to changes in pH and in the activities of the oxidized and reduced species allows the calculation of the boundary between the species where an oxidative or reductive step is involved. The boundaries for those species whose stability field does not involve an oxidation or reduction reaction can be calculated from equilibrium constants and are represented by vertical lines on the stability diagrams.

The distributions of the mineralogical Mn species in stability field diagrams are generally given for the conditions under which water is stable. Water is oxidized with the liberation of gaseous oxygen above a line whose redox potential at pH 0.0 and 14.0 is 1.23 and 0.40 volts respectively. Water may be reduced at Eh values less than 0.0 volts at pH 0.0 and -0.82 volts at pH 14.0. It assumed that Eh-pH conditions beyond the water-stability boundaries are not likely to occur in nature in an aqueous medium. An Eh value considerably above or below these limits is necessary, however, to cause water to decompose at an observable rate.

Figure 1 shows the fields of stability for four solid phases and three dissolved species of Mn (Hem, 1963a). Interfering anions and cations are absent. The solid lines represent the positions of the boundaries where the effective concentration of the dissolved species of Mn was 0.01 ppm (1.8×10^{-7} molar). The dashed line represents the position of this boundary if the effective concentration of Mn^{++} was increased to 100 ppm (1.8×10^{-3} molar). The boundary line along which

$$Mn^{+++} + e^{-} \rightleftharpoons Mn^{++} \tag{1}$$

is above the upper water-stability limit. The other highly oxidized species of Mn such as permanganate are only stable outside the water-stability boundaries. It should be noted that the boundary between Mn^{++} and $MnOH^{+}$ is not dependent upon the Mn^{++} concentration but on the pH. This boundary has been indicated by a dotted line.

Increasing the activity of the dissolved Mn^{++} increases the area of the stability fields for the solid Mn species. This change is also accompanied by a change in the pH and/or Eh. If either the pH or the Eh were increased, precipitation of Mn^{++} would occur when either reached a stability boundary for a given mineral species if the dissolved activity of Mn^{++} exceeded the theoretical activity at this boundary. That is, the activity of the dissolved Mn^{++} species can never be greater than the activity for whose stability field boundary

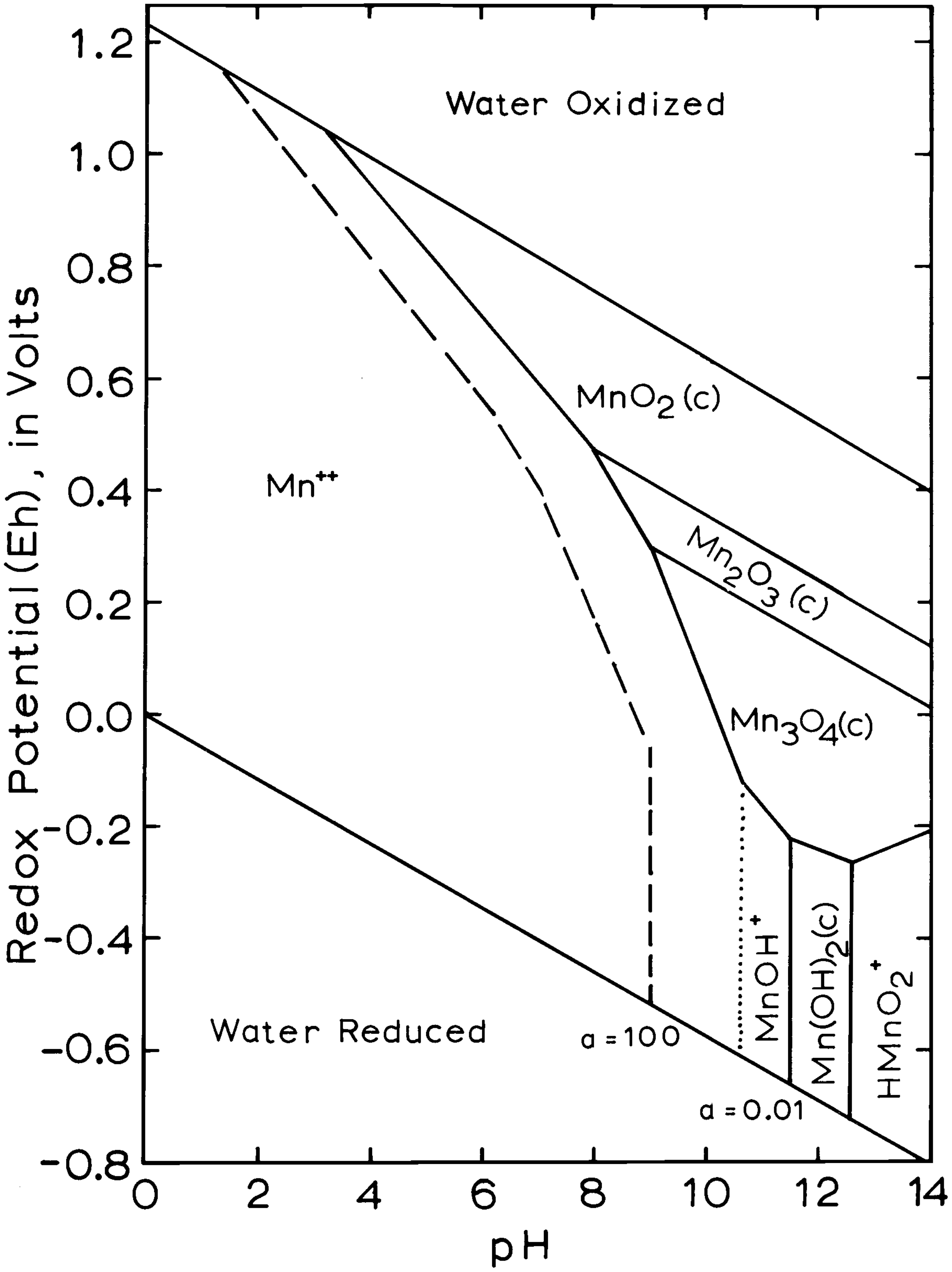

Figure 1. Stability fields of Mn species in an aqueous environment, free of interfering ions. (Hem, 1963a). Dissolved Mn at 0.01 and 100 ppm.

falls on the given pH and Eh values. An example would be at a pH of 8.0 and an Eh value of 0.20 volts. At that point precipitation would occur if the effective concentration of Mn^{++} was greater than 100 ppm (Figure 1). Therefore, the effective concentration of Mn^{++} at that point may be smaller than 100 ppm but never greater.

A more realistic stability-field diagram for natural systems would be one in which a gas phase was in contact with an aqueous phase and the amount of CO_2 in that gas was taken in consideration. Figure 2 represents a system exposed to air which contains CO_2 at a partial pressure of 3.8×10^{-4} atmosphere. This value for CO_2 is probably lower than that found in soil systems but, nevertheless, its use will give an indication of how CO_2 might affect the relationships between Mn species. Consideration has only been given to the pH range most likely found in the surface environment.

The boundaries for the $MnCO_3$ species must be located by considering both the HCO_3^- and H_2CO_3 species. At a pH of 6.4, half the total carbonate species will be present as HCO_3^- and half as undisassociated $H_2CO_{3(aq)}$. At a pH of 5.4, the HCO_3^- form only accounts for 10 percent of the total dissolved carbonate. This results in an increase in the solubility of $MnCO_3$ as the pH decreases. The dissolved carbonate increases as the pH increases and as a result the stability field for $MnCO_3$ occupies a large area which includes the fields of $Mn(OH)_2$, $HMnO_2^-$, and most of the Mn_3O_4.

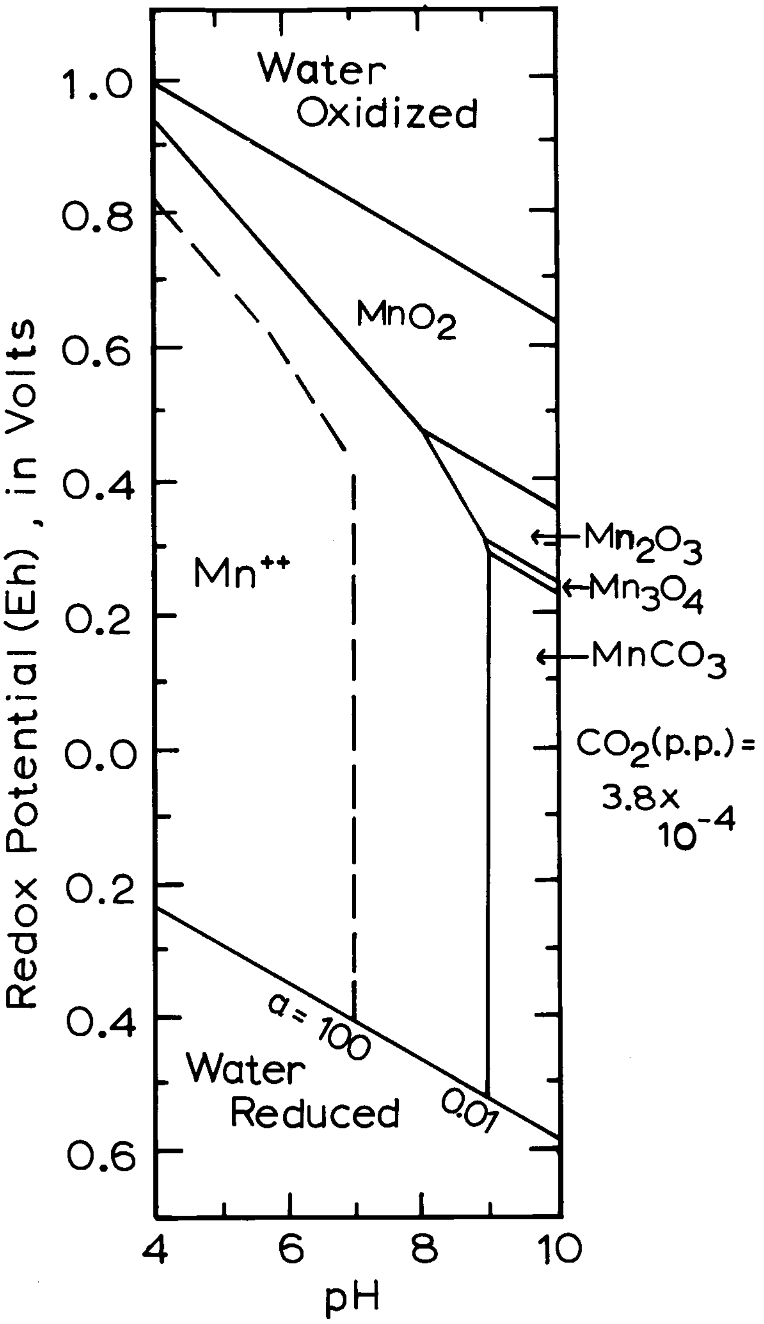

Figure 2. Stability fields of Mn species in an aqueous environment for the pH range of 4.0 to 10.0 and at a constant partial pressure of $CO_2 = 3.8 \times 10^{-4}$ atmosphere, free of any other interfering ions. (Hem, 1963a). Dissolved Mn at 0.01 and 100 ppm.

The net effect of the presence of the CO_2 is to decrease the activity of Mn. Figure 1 has indicated that the effective concentration of Mn may be as great as 100 ppm at a pH of 9.0, whereas in the presence of CO_2, a pH of 7.0 or less was necessary (Figure 2). In acidic soils the influence of the CO_2 must be extremely low if the soils are well aerated. In poorly aerated soils, however, the partial pressures of CO_2 would be higher and the pH should approach 7.0 because of H_2CO_3 equilibrium. This combined effect could cause some precipitation of Mn^{++} as $MnCO_3$ if the dissolved activity of Mn^{++} exceeded a boundary condition. It is doubtful, however, if the activity of Mn^{++} would ever reach the concentrations necessary to cause precipitation of $MnCO_3$ in acidic soils except under prolonged submerged conditions.

The addition of ions which form stable complexes with Mn^{++} causes the activity coefficient to decrease in proportion to the amount of Mn^{++} complexed. The measured chemical concentration of dissolved Mn^{++} may then increase if the solubility-product and mass action laws are valid. Some of the ions that have been shown to form complexes with Mn^{++} and which may be present in soil systems are shown below. The equilibrium constants for the complexing reactions have been shown by Hem (1963a) and Sillén and Martell (1964). Bicarbonate is thus able to form complexes with Mn^{++}. Half of any Mn^{++} present

Ion	K_{eq}
HCO_3^-	63
SO_4	190
Cl^-	1
NO_3^-	1
$P_3O_9^{\equiv}$	3.7×10^3

in natural water would be complexed where the concentration of HCO_3^- was 940 ppm. Sulfate is able to form a stronger complex with Mn^{++} than HCO_3^- and neither NO_3^- nor Cl^- form complexes at the concentrations found in natural systems. Phosphate ions show a strong tendency to form complexes with Mn^{++} and certain forms form Mn-phosphate compounds which are relatively insoluble. Soils also contain organic ions which are capable of forming complexes with Mn^{++} (Schnitzer and Skinner, 1967).

This stability diagram approach for Mn in soil systems has generally met with little success because of the physical problems involved in measuring both Eh and pH values and the mixed redox systems present in soil systems. Some success has been achieved with these measurements in characterizing the chemical changes which are taking place in flooded or submerged soils (Mukhopadhyay, Fisher, and Smith, 1967; Ponnamperuma, Tianco, and Loy, 1967) and in comparisons between normal and inundated soils (Quispel, 1947). Starkey and Wight (1946) in a careful study of the environmental relations between aerated and waterlogged soils were able to show a correlation between Eh and the amount of Fe corrosion.

Mechanisms of Mn^{++} Oxidation

Data on the kinetics of oxidation-reduction reactions involving the +2, +3, and +4 forms of Mn are very limited. In general, these reactions have been shown to be slower than similar ones involving Fe (Hem, 1963a), which are generally rapid at the pH's of most natural waters. The oxidation of Mn^{++}, however, has been considered to be rapid enough under favorable conditions to reach equilibrium in natural systems.

The conditions under which Mn precipitates in natural systems are not known with any certainty. Chemical precipitation of $MnSO_4$ has been shown to begin at a pH of 8.5 when titrated with $Ca(OH)_2$ (Mehlich, 1957). Hem (1963a, 1963b) has also shown that solutions of Mn^{++} were stable only below a pH of 8.5. Manganese precipitation has been shown to take place at pH's below this value in the presence of an exchange complex. Hemstock and Low (1953) found that Mn^{++} would oxidize and precipitate on the surfaces of montmorillonite to a pH as low as 5.5. The freshly precipitated hydrous oxides of Fe and Al have also been shown to influence the oxidation process (Mehlich, 1957).

Manganese may also be coprecipitated with Fe in natural systems. Iron precipitates at pH's lower than Mn and forms coatings of $Fe(OH)_3$ on the surfaces of particles. Once a thin layer of this hydrous oxide was formed, it could participate in the following reaction with Mn^{++}.

$$2Fe(OH)_3 + Mn^{++} + 2H^{+} \rightleftharpoons MnO_2 + 4H_2O + 2Fe^{++} \qquad (2)$$

The equilibrium constant for this reaction, $10^{-5.67}$, shows that this reaction is normally displaced to the left. However, if the activity of Fe^{++} were very low and the activity of Mn^{++} relatively high, some displacement of $Fe(OH)_3$ by MnO_2 could occur. The negatively charged MnO_2 surface would tend to attract more $Fe(OH)_3$, and the process would be repeated to build up a deposit of two substances. Thus, the precipitation of Mn^{++} may be expected even though the activity of Mn^{++} in solution was below the point where oxide precipitation would be expected if Fe was absent.

Biological reactions are also possible explanations for the oxidation of Mn^{++}. Bromfield and Skerman (1950) have found that organisms of the genera <u>Corynebacterium</u>, <u>Chromobacterium</u>, and <u>Flavobacterium</u> would oxidize Mn^{++} on soil extract agar. They also found that certain fungi could readily oxidize Mn and concluded that they were probably important in acid soils.

A careful inspection of Figures 1 and 2 shows that Mn^{++} is thermodynamically unstable in the presence of gaseous O_2. Manganese dioxide is the only solid phase which would be stable in the normal pH range of oxygenated aqueous systems. Identification of Mn oxide deposits that are exposed to the atmosphere generally substantiate the formation of this oxide. This oxide has also been found as a specific mineral in soils (Nikiforoff and Drosdoff, 1943; Taylor, McKenzie, and Norrish, 1964), as coatings on clays and other minerals (Hemstock and Low, 1953; Hem, 1963a), and admixed with Fe oxides in concretionary forms. It has been found by Bricker (1965), however, that the most highly oxidized Mn oxide that could be synthesized using air, oxygen gas, or hydrogen peroxide was γ-MnOOH. The MnO_2 oxide was only formed by acidifying suspensions of this oxide or Mn_3O_4. This would create some doubt as to whether MnO_2 was formed directly or by disproportionation in natural systems.

Fertilizer Materials and Soil Amendments

The influence that fertilizer materials and soil amendments have on the availability of Mn can generally be related to pH changes, to effects on the redox potential of the soil system, and to changes in the microbiological population.

Fertilizer treatments which lowered the soil pH always increased the uptake of Mn by plants and in some cases caused Mn toxicity in some greenhouse studies done by Berger and Gerloff (1947). Soil acidity, soluble Al, or a deficiency of Ca, Mg, or Fe were not contributing factors in their studies. Available soil Mn and the Mn content found in plants were increased by the addition of $(NH_4)_2SO_4$ and NH_4NO_3, both acidic forming fertilizers (Funchess, 1918; Lingle and Wight, 1961).

The reaction of $Ca(H_2PO_4)_2$ with a soil system lowered the soil pH near the fertilizer granule from 5.5 to 1.48 (Lindsay and Stephenson, 1959). In this process compounds of Fe, Al, Mn and Ca were dissolved and then were precipitated as the soil-fertilizer solution moved outward from the fertilizer granule. Initially, the Mn was probably reduced to the Mn^{++} form and later precipitated as the phosphate before oxidation could have taken place. These Mn^{++}-phosphates are slightly soluble, and as a result the Mn content of plants has been shown to be increased (Messing, 1960; Page, Schofield-Plamer, and MacGregor, 1963). A later study by Messing (1965) has shown that this superphosphate effect was dependent on the initial soil pH if the soil was steam sterilized. In alkaline soil systems the soil pH was decreased and the Mn uptake increased, but in acidic soils the Mn content of the plant was decreased and very little pH change occurred. No attempt was made to correlate these differences to either the biological effect or to the changes resulting from the steam-sterilization treatment.

The application of elemental S always increased the amount of soluble Mn in all of the soils studied by Funchess (1918). Forsee

(1954) has also shown that the application of S decreased the fixation of applied Mn on organic soils. He contributed this to a lowering of the soil pH and to a release of available electrons from the biological oxidation of the applied S. This effect of S has been shown by Vara and Frederick (1952) to be largely the result of the biological oxidation of the added S. In pure cultures, ten times more soluble Mn was formed when S was oxidized by <u>Thiobacillus</u> <u>thiooxidans</u> than when the same acidity was produced by the addition of H_2SO_4. There was some indication, however, that the lower pH facilitated the formation of the soluble Mn.

The reports that deal with the effect of increasing pH on decreasing the amount of available Mn and thus reducing the plant uptake of Mn are voluminous. In general, materials which cause an increase in soil pH have been used to correct the soil acidity problems associated with excessive amounts of available Al and Mn. These materials have the greatest effect on the water-soluble and exchangeable fractions of soil Mn (Adams, and Weir, 1957; Messing, 1960; Christensen, Toth, and Bear, 1950; Messing, 1965; Sherman and Fujimoto, 1946).

The theory of nonavailability of Mn at the higher pH values as a result of the formation of insoluble oxides was found to be incompatible with soil experiments relating soil pH to water-soluble Mn (Page, 1962). It was suggested that the formation of Mn-complexes with the organic matter may account for the curvilinear relationship between pH and water-soluble Mn. No attempt was made, however, to exclude the biological factor in these studies.

The additional Ca supplied by the liming material may have also had an antagonistic effect on Mn absorption. Calcium has been found by Williams and Vlamis (1957) to reduce the Mn content of barley. Maas (1967) in work done with excise barley roots has shown that Ca promotes the absorption of Mn at low concentrations but inhibited Mn absorption at higher concentrations. It should be mentioned that the above work was done with solution systems and not under field conditions; nevertheless, this may be part of the mechanism by which lime reduces Mn uptake.

An effect of fertilizer materials on the relative number of Mn oxidizing and reducing organisms has been shown by Timonin (1950, 1965). He found that various N-compounds affected the intensity of the oxidation of applied Mn^{++}. Asparagine and urea enhanced Mn^{++} oxidation; whereas, $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ depressed the activity of the Mn-oxidizing flora. Potassium nitrate and $NaNO_3$ appeared to have very little effect. These results may partially explain the effects that were obtained from applications of N-sources by Lingle and Wight (1961).

Organic Matter and Biological Effects

Readily decomposable organic matter has been shown to increase the amount of available Mn in soil systems (Hurwitz, 1948; Christensen, Toth, and Bear, 1950; Sanchez and Kamprath, 1959). This influence was generally limited to its period of decomposition in limed soils, but in non-limed soils the higher Mn levels remained after the bulk of the organic matter had decomposed. The increases which have resulted from the addition of the organic matter were probably the result of the depletion of gaseous O_2 by the increased microbial activity and from the production of reduced products. It should be noted that this type of Mn-reduction could take place either directly or indirectly. A thorough literature review has failed to indicate that a microorganism has been isolated which could reduce Mn directly in the presence of adequate O_2.

Manganese dioxide has also been found to act as an electron acceptor in the absence of gaseous O_2 when an oxidizable organic substrate was present (Hochster and Quastel, 1952). This is probably the mechanism by which a majority of the increase in available Mn arises when soils become water-logged.

Microbiological oxidation of Mn^{++} has been found to take place on soil agar plates which had a final pH range of 4.8 to 8.0 (Leeper and Swaby, 1940; Dhawan, Singh, and Bhatnagan, 1950). The intensity of oxidation was found to increase as the pH increased up to 8.0. Most of the organisms which have been shown to oxidize Mn^{++} have been fungi although the isolation medium no doubt had a large influence on this selection. In some soils, apparently the oxidation of Mn^{++} has been due to this biological mechanism entirely (Mann and Quastel, 1946).

Aeration Influence

The increase in available Mn upon waterlogging has been usually attributed to the scarcity of available oxygen (Pearsall, 1950). Incubation studies have shown that regardless of the soil pH, flooding always increased the exchangeable Mn fraction in the soil and the Mn content of alfalfa (Graven, Attoe, and Smith, 1966). In the absence of a source of easily decomposable organic matter, the Mn mobilization was considerably slower at a soil pH of 4.7 than 7.3. If organic matter were added, flooding mobilized more Mn in the acid than in the neutral soil. Liming has also been shown to promote the immobilization of this released Mn^{++} upon the resumption of normal soil moisture conditions.

Effect of Halide Salts

A study of the conditions necessary for the "poisonous" action of Cl was conducted as early as 1902 by Wheller and Hartwell (1903).

They found that the application of either $CaCl_2$ or NH_4Cl to an acidic soil caused a severe yield reduction of both potatoes and barley when compared to equivalent concentrations of either $CaSO_4$ or $CaCO_3$. This depressing effect was corrected when a liming material was used in conjunction with the Cl salt. The injurious effect does not appear to be of the "salt injury" type because of the low concentrations of salt used (approximately 180 pounds Ca per acre, broadcasted). Since liming eliminated the effect, it would appear to be due to the acidic conditions present being aggravated by the Cl salt. It is unfortunate that no plant or soil analyses were made in that study.

A comprehensive study was made by Sherman, McHargue, and Hageman (1943) in an attempt to determine the influence of halides on the oxidation of added Mn^{++} in both acid and alkaline soils. Manganese(II) was added to the soil system at a rate of 200 ppm and then incubated 72 hours before the halide salts were added. The systems were then incubated an additional 72 hours before the halide salt effect was evaluated. In the acidic soil, pH 4.1, both I^- and Cl^- had no effect on the Mn^{++} oxidation rate, F^- caused a considerable increase in the oxidation rate, and the effect of Br^- was not conclusive. In the alkaline soil, pH 7.4, I^- retarded the oxidation rate, both F^- and Br^- increased the natural capacity of the soil to oxidize Mn^{++}, and Cl^- had no apparent effects. It is interesting to note that Cl^- had no effect in both the alkaline and acidic systems. The authors also did not make any attempt to separate the biological effects from the chemical effects. In a later study by Fujimoto and Sherman (1948) it was observed that neither KCl or $CaCl_2$ had any significant effects on the level of available Mn in a steam-sterilized soil. Steam-sterilization, however, has been shown to release large amounts of available Mn, so that the susceptible fraction of Mn may have already been dissolved before the salt treatments were applied. It is also possible that most of the added Mn^{++} may have been oxidized before the halide salts were added, since Page (1962) has observed a significant decrease in available Mn within two hours after increasing the pH of a soil-solution system.

Other researchers have applied large amounts of $CaCl_2$, KCl, or NaCl in studies designed to ascertain toxic factors in acidic soils. Adams and Weir (1957) have indicated that the application of $CaCl_2$ had little or no effect on any form of soil Mn although their reported levels of available Mn appear to be high enough to be toxic to plant growth initially. Foy (1964) has shown that the addition of $CaCl_2$ caused severe yield decreases of alfalfa which were associated with increased Mn toxicity symptoms, increased Mn uptake by the plants, and large increases of exchangeable Mn on acidic soils of the Southeastern United States. The addition of 400 pounds of KCl or NaCl increased the Mn content approximately 200% in an unlimed soil (York, Bradfield, and Peech, 1954). They did not, however, include non-halide salts in their study for comparative purposes.

A different aspect of the halide effect on Mn availability has been given by Leonard and Steward (1959) and Stewart and Leonard (1963). Working with citrus trees, it was found that the application of $CaCl_2$ with $MnSO_4$ in small concentrated piles around each tree corrected the Mn-deficiency symptoms. An increase in the Mn content of the leaf tissue was also associated with this treatment. The application of $MnSO_4$ singlely or the oxides of Mn with or without $CaCl_2$ did not correct the Mn-deficiency symptoms. The beneficial effect of Cl was found on both an acidic (pH 6. 1) and an alkaline (pH 7. 7) soil.

Additional evidence has been presented recently which has indicated that the application of halogen containing salts increased the availability of Mn in soil systems and the uptake by Mn by plants. Hamilton and Lathwell (1965) have studied the influence of salts associated with phosphates on the movement of Mn in soil solutions. All salts increased the amount and distance which Mn was diffused away from the fertilizer layer; however, chloride salts were particularly effective in causing this diffusion. The effect of the salts associated with $Ca(H_2PO_4)_2$ was much greater than those which were associated with $(NH_4)_2HPO_4$. This was apparently not a strict pH effect, since the presence of the salts in association with $Ca(H_2PO_4)_2$ in every case ameliorated the extreme acidity produced in the layer of soil around the fertilizer band. There was no definite relationship between salt-associated pH and the amount of available Mn present for any of the salt comparisons.

A significantly greater amount of Mn was taken up by oats when a chloride salt was added to either $Ca(H_2PO_4)_2$ or $(NH_4)_2HPO_4$ (Hamilton, 1966). Similar responses were obtained from either KCl or NH_4Cl on this neutral soil (pH 7.0). Jackson, Westermann, and Moore (1966) have also observed that the application of Cl^- from either KCl or $CaCl_2$ increased the Mn uptake by bush beans and caused the appearance of Mn-toxicity symptoms on an acid soil (pH 4.9). Increasing the level of Cl increased the level of Mn in all cases. The application of lime always reduced the Mn content and, in most cases, eliminated the Cl effect.

OBJECTIVES

The apparent influence that Cl^- containing fertilizers have on the availability of Mn would have a direct effect on the method of application of the salt where either a potentially Mn toxicity or a deficiency condition existed. Very little factual information was found in the literature which showed an effect of Cl^- without being in association with some other salt and which attempted to determine the mechanism or mechanisms of this phenomenon. This inadequate knowledge has prompted the initiation of this study with the following specific objectives:

1. To substantiate that Cl salts do affect the availability of Mn in soil systems differently than other neutral, soluble salts.
2. To attempt to determine how Cl functions in this process by studying the
   a. biological influence and the
   b. salt effect

   in relation to other anion salts with the same cation carrier.

GENERAL METHODS AND MATERIALS

Soil Characteristics and Preparation

The soil experiments were conducted with the A_p horizon of the Dayton soil, a depositional Planosol found in the Willamette Valley (Parsons and Balster, 1967). They have typically dark gray, friable, silt loam surface horizons and dark grayish brown, very firm, clayey B horizons up to depths of 36 inches. These two horizons are usually underlain by a brown massive silty clay loam. The soil is mottled to the surface, and a perched water table occurs above the clayey subsoil during the rainy season. Iron-manganese concretions occur throughout the profile and are concentrated in the lower part of the A_2 horizon.

The texture of the laboratory sample was determined by the hydrometer method and by a wet sieving procedure involving the use of centrifugation for the removal of the clay fraction. The latter method will be described in the discussion of the Mn distribution. Analyses by both methods, however, gave a texture of silt loam.

The moisture holding capacity was determined by lightly packing the soil into a ringed tube assembly. Water was then added at the top of the tube so that the soil column did not become completely moistened lengthwise. The moisture was then allowed to equilibrate for 24 hours before the tube was broken into sections for a moisture determination. By using this method, the moisture holding capacity of the laboratory soil sample was 24 percent moisture on an oven dry weight basis. Core samples of this soil, however, have retained 34.7 percent moisture at 0.3 bar tension (Oregon Agricultural Experiment Station, April 1966).

Soil samples were taken from the Jackson farm 2 1/2 miles west of Lebanon, Oregon, on State Highway 34. The chemical soil analyses for the three individual samples are given in Table 1. All of the methods used for the soil analyses except that method used for the determination of extractable Mn were those used by the Oregon State University Soil Testing Laboratory (Alban and Kellogg, 1959). Extractable Mn was determined on the freshly sampled soil as described under chemical measurements.

Table 1. Soil chemical characteristics of the laboratory bulk samples at the time of field sampling.

			meq/100 g				
Sample	pH	ppm P	K	Mg	Ca	Mn	CEC
1967s	4.8	10.0	0.24	0.9	2.5	0.183	11.3
1967f*	5.8	22.5	0.53	2.3	6.8	0.047	12.0
1968w	4.8	10.0	0.20	1.3	3.0	0.794	11.5

*This soil sample had been previously limed.

All samples were air-dried to approximately 10-15 percent moisture and then screened through a quarter-inch screen. All concretions which did not pass through were hand selected and placed back into the screened soil. The soil samples were then stored in plastic lined containers until used. Very little moisture was lost by this method; however, extractable Mn increased slightly during storage.

The soil sample was separated into the various soil separates for a Mn distribution analyses by the following method:

> One-hundred grams of oven-dry soil were shaken for one hour with 200 ml of distilled water. This mixture was then centrifuged for 4.0 minutes at 750 rpm. The supernatant containing the clay was then decanted off and saved. This process was repeated until approximately two liters were collected or until very little clay was being removed. Shaking was continued for only 5 minutes after the initial step. The remaining soil particles were wet sieved through the respective sieve sizes. The particles passing through the 50 micron sieve were collected as the silt fraction.

The respective size fractions were then placed in porcelain evaporating dishes and heated at 550°C for four hours to remove organic matter. The samples were then weighed to determine the portion of each size fraction in the original 100 gram sample (Table

2). The amount of clay was found by the difference.

Table 2. Percentage distribution of acid-H_2O_2 soluble and total Mn and relative distribution of Mn in the various soil separates. (Soil contained 0.128 percent Mn).*

	Soil separate						
			Sand (microns)				
	Clay	Silt	50-100	100-250	250-500	500-1000	>1000
% H_2O_2 Soluble Mn	0.102	0.046	0.144	0.292	0.258	0.318	0.998
% Total Mn/ Separate	0.155	0.063	0.173	0.360	0.352	0.520	1.388
Grams of separate/ 100 g soil	21.7	68.6	2.0	1.9	2.1	2.1	1.6
mg Mn/separate	33.6	43.2	3.4	6.5	7.6	11.1	22.9
% Total Soil Mn	26.2	33.7	2.6	5.1	5.9	8.7	17.8

*Average of two replications.

Each size fraction was finely ground and a 0.250 gram sample was then treated with H_2O_2 according to a dissolution method described by Taylor, McKenzie, and Norrish (1964). The remaining residue was washed and then treated with a HNO_3-$HClO_4$ digestion mixture for two hours. Manganese in both fractions was determined by an atomic absorption spectrophotometer. The results are shown in Table 2.

In general as the size of the particle increased, the percentage of Mn increased. This was particularly evident in the sand fractions.

Visible observation had indicated that a large portion of the individual grains were of a concretionary nature. Somera (1967) found that concretions which were larger than 170 microns contributed 8.3 percent of the total soil mass of the top eight inches of the Dayton soil and that these contained 0.81 percent free Mn. Earlier studies by Drosdoff and Nikiforoff (1940) and Nikiforoff and Drosdoff (1943) have found total Mn concentrations similar to those found in this study.

Experimental Procedures

General

The following is a discussion of the general procedures which were used in conducting the soil-salt experiments. Information which pertains to individual experiments has been discussed under each experiment or given in the Appendices.

For the majority of the experiments, 300 grams of soil (corrected for included moisture) were placed in an one liter Erlenmeyer flask, and a preweighed amount of salt was added. The soil-salt system was then thoroughly mixed, and distilled water was added to raise the soil moisture up to near the determined moisture holding capacity. The flasks were then plugged with a cotton plug and placed in a controlled temperature water bath. The flasks were not shaken for 24 hours to allow the moisture to become evenly distributed but were shaken daily thereafter. At each sampling interval ten grams of soil, on an oven-dried basis, was taken for both the Mn extraction procedure and the pH measurement. Each soil-salt treatment was maintained at the same moisture level for the duration of the experiment. All treatments had two replications.

The salt concentrations were calculated by considering the area that might have been affected by the diffusion of the fertilizer material away from the point of band placement. The amount of fertilizer material per inch of banded row was determined by assuming a 30 inch row spacing, that all the material was banded, and that this material was applied at a rate of 60 pounds of K per acre. The grams of soil affected by this amount of fertilizer material were calculated by assuming a given volume of soil and a bulk density of 1.45 g/cm^3. These calculations are shown in Table 3. All salts were of reagent grade quality and had been ground to pass a 250 micron sieve before application. A concentration term, meq K/100 g, will be used when referring to the different areas of salt diffusion in the Results and Discussion section.

Biological

A simple sterilization procedure has long been sought which would cause the least amount of chemical change in soil systems. Ethylene oxide has been used as a soil sterilant (Dalton and Hurwitz,

Table 3. A sample of the respective values used in calculating the amount of salt applied per 300 grams of soil for 60 pounds of K banded per acre in 30 inch rows.

Salt	Total g/acre ($\times 10^4$)	g/inch of row	Grams of salt/300 g soil (area of salt diffusion)		
			1 in^2	4 in^2	16 in^2
KCl	5.190	0.248	3.12	0.78	0.20
KBr	8.304	0.397	4.98	1.24	0.31
KNO_3	7.037	0.336	4.22	1.05	0.26
K_2SO_4	6.070	0.290	3.64	0.91	0.23

Diffusional area	g soil/linear inch of row*	Linear inches of row/300 g soil	meq K/100 g
1 in^2	23.9	12.57	13.98
4 in^2	95.6	3.14	3.48
16 in^2	382.4	0.78	0.87

*A bulk density of 1.45 g/cm^3 was assumed.

1948; Allison, 1951) and was shown to have little if any effect on extractable Mn. Propylene oxide which has similar sterilization features but better handling properties was used as the sterilant in this study. A preliminary study (Skipper and Westermann, 1968) indicated that the increase in extractable Mn from the use of this material was approximately 1/3 of that amount caused by autoclaving. Gamma irradiation has also been shown to increase the available Mn in some soils (Salomius, Robinson, and Chase, 1967).

Propylene oxide's mode of action has been reported to be as an alkylation agent of active groups on proteins (Bartlett and Zelazany, 1967). Materials of this type are also effective for the inactivation of spores (Phillips, 1942).

Twenty-five grams of soil on an oven-dried basis were weighed into a 125 ml Erlenmeyer flask. The soil contained 10-15 percent moisture. Two ml of propylene oxide were then added, the flask was stoppered with a cotton plug, and it was covered with Saran wrap. The flasks were placed in a 27°C water bath for 48 hours after which time the Saran wrap was removed and the temperature of the water bath increased to 45°C to facilitate the removal of the residual vapors. The flasks remained in the 45°C water bath for 48 hours before being removed for the initiation of the soil-salt experiments. All procedures which involved handling and removal of the sterilant were carried out under a ventilated hood.

Nutrient broth has been used as the sterility test medium in this study because both aerobic and anaerobic growth can be observed and because of the simplicity of the method. This method consisted of transfering 0.3-0.5 grams of soil from each flask into each nutrient broth tube. The transfer was made with a stainless steel spatula which had been flamed after dipping it into a 95 percent ethanol solution. Two tubes were treated for each sample flask. The inoculated tubes were then incubated in a polysterene container at 27°C for 10 days before checking for contamination.

All water blanks, acids, and bases that were used in the sterilization experiments were steam autoclaved for 30 minutes. The amount of salt that was needed for the treatment of each flask was weighed into separate aluminum foil packages and then dry sterilized at 180°C for three hours. The moisture level of the soil in the flasks was adjusted after the addition of the salt materials. Two flasks per treatment were removed at each sampling interval, sampled for sterility test, and then sampled for the Mn extraction and pH measurement.

The effect of the salt treatments on the number of Mn-oxidizing organisms was evaluated by plating soil dilutions of 10^{-2} and 10^{-4} on soil extract agar pour plates. The soil extract agar was made according to a method used by Broomfield and Skerman (1950). The plates were incubated at room temperature for 14 days before evaluation.

Chemical Measurements

All pH measurements were made on a 1:2, soil:water, suspension using a standard saturated calomel reference electrode and a standard glass electrode. The soil was thoroughly mixed with the distilled water and allowed to set one-half hour before determination. The reference electrode was calibrated with two pH buffer solutions immediately prior to making the measurements. No appreciable amount of drift was detected in the time interval needed for a given set of analyses.

Methods for estimating available soil Mn have generally been developed for the estimation of a single Mn fraction. Four possible forms of Mn which have been proposed to exist in soils are (1) the Mn^{++} ion in the soil solution or on the exchange complex, (2) a highly reactive colloidal form which probably decomposes in acid soils to MnO_2, (3) a hydrated form of MnO_2 or Mn_3O_4 which could contain both Mn^{++} and Mn^{+++}, and (4) a relatively inert MnO_2 oxide. Extractions made with salt solutions are thought to contain the soluble and exchangeable fraction and perhaps some Mn which has been released from fractions (2) and (3). It has been assumed that the soluble and exchangeable fractions constitute that Mn which was immediately available to plants and the reducible Mn that part which may become available to the plant over a period of time (Hoff and Mederski, 1958).

A number of different extracting solutions have been used for estimating available Mn. Boken (1958) and Page (1964) have shown that the amount of Mn extracted by $Ca(NO_3)_2$ and $Mg(NO_3)_2$ increased with time and that the Mn^{++} ion behaved as a typical divalent cation. The Ca salt usually extracted more Mn than the Mg salt. Apparently the smaller hydrated radii of the Ca^{++} allowed it to more easily penetrate the interlayer and interpore areas where Mn^{++} was being held as an exchangeable cation. Neutral NH_4Ac (Sherman, McHargue, and Hodgkins, 1942) and weak acidic solutions (Hoff and Mederski, 1958; Hammes and Berger, 1960) have also been used to estimate plant available Mn. Easily reducible Mn has generally been evaluated by weak reducing agents such as hydroquinone (Sherman, McHargue, and Hodgkins, 1942).

Normal $Mg(NO_3)_2$ was used as the major extracting solution in this study. Neutral N NH_4Ac was used in one experiment (Appendix 7). A comparison of the Mn extracted by these two salt solutions is shown in Table 4. The total amount of Mn extracted by the $Mg(NO_3)_2$ solution was greater than that for the NH_4Ac solution. The majority of the Mn, however, was extracted by the first three portions of each salt solution, and decreasingly smaller amounts of Mn were extracted with each new extraction solution. The $Mg(NO_3)_2$ solution was chosen on the basis of (1) being an unbuffered salt, it should closely assume the pH of the soil and thus avoid secondary precipitation reactions and

(2) the apparent inability of NO_3^- to form complexes with Mn^{++}.

Table 4. A comparison of the amount of Mn extracted by two extracting solutions in four consecutive 30 ml portions from 10 grams of soil.*

Salt Solution		Consecutive extraction (1)	(2)	(3)	(4)	Total µg Mn/10 g
N NH_4Ac, pH 7.0	µg Mn	720	129	53	29	931
	% of total	77.4	13.8	5.7	3.1	---
N $Mg(NO_3)_2$	µg Mn	900	269	125	86	1380
	% of total	65.2	19.5	9.1	6.2	---

*Average of two replications.

The Mn fractions were extracted by the following procedures:

Extractable Mn. Thirty ml of a N salt solution were added to ten grams of soil, corrected for moisture and salt content, in a 250 ml wide-mouthed polypropylene bottle. The sample was shaken for ten minutes, centrifuged, and the supernatant was decanted off through a filter paper into a 100 ml volumetric flask. This process was repeated three times for each sample. The flask was brought up to volume and the Mn in the combined filtrate was determined as extractable Mn.

Easily reducible Mn. To the soil residue, after the removal of the extractable Mn fraction, 100 ml of a N salt solution plus 0.2 percent hydroquinone were added. The sample was shaken for one hour and the supernatant was filtered. The Mn in the filtrate was determined as easily reducible Mn.

Water-soluble Mn. Twenty ml of distilled water were added to ten grams of soil on an oven-dried basis. This system was thoroughly mixed and filtered by a Buchner funnel. The soil sample was then leached with 4-20 ml aliquots of distilled water. The Mn in the combined leachates was analyzed for water-soluble Mn.

Exchangeable Mn. This fraction was determined by taking the difference between the water-soluble fraction and the extractable fraction.

The Mn content of the extracts was determined directly by an atomic absorption spectrophotometer. A preliminary study, involving evaporation of the extract and digestion with HNO_3 and $HClO_4$, had indicated that it was not necessary to acid-digest the extract before determining the Mn content.

The redox potential (Eh) was measured with electrodes of platinized Pt and by using the saturated calomel electrode as the reference. The general Pt electrode construction and method of platinizing was patterned after those described by Quispel (1947). The electrodes were standardized in distilled water, a poorly poised system, and in Zobell's solution, a well poised system (Zobell, 1946). Electrodes that had potentials more than 20 millivolts from the mean in the water system were rejected. It was found that the reproducibility of electrodes in well poised systems was not an indication of reproducibility in poorly poised systems.

Manganese Oxide Studies

An excellent study of the stability relationships of the $Mn-O_2-H_2O$ system has recently been done by Bricker (1965). The freshly precipitated Mn oxides in this study were prepared by the methods used in that study. Manganous hydroxide was precipitated from a solution of $MnCl_2$ and $MnSO_4$ by the slow addition of dilute KOH. The $Mn(OH)_2$ was then oxidized to $\gamma-Mn_2O_3$, Mn_3O_4, and possibly β-MnOOH with CO_2 free air. The precipitated oxides were washed with distilled water until a negative Cl^- test was obtained and dried overnight at 100°C. An x-ray diffraction pattern was then run using Ni filtered Cu(Kα) radiation. The diffraction peaks obtained from these oxides have been compared with known oxide patterns in Table 5. Pure reagent grade MnO_2 was used as the well crystallized Mn oxide.

In the MnO_2 studies (Appendices 8 and 9), reagent grade salts were added to a 5 percent by weight MnO_2-H_2O system. Each of the individual flasks were aerated with air which had been purged of CO_2 by passing it through dilute solutions of NaOH. For the other MnO_2 system, the flasks were aerated with CO_2 and O_2 free N_2 gas. The trace amounts of O_2 were removed by bubbling the N_2 gas through a vandyl sulfate solution (Meites and Meites, 1948). Samples for Mn analyses were taken through a 0.5 micron millipore filter and directly analyzed by atomic absorption spectrophotometer. The dilute acid or base of the respective salts were used to control pH.

Table 5. X-ray diffraction data for known Mn oxides and for the synthetic oxides used in this study.

Mn_3O_4 (Bricker, 1965)		γ-Mn_2O_3 (Bricker, 1965)		Mn-oxides (This study)	
d[1]	I[2]	d	I	d	I
4.92	8	4.92	7	4.92	5
3.08	8	3.08	9	3.09	4
2.87	2	2.88	2	2.87	2
2.76	9	2.76	9	2.76	9
2.48	10	2.49	10	2.48	10
2.36	4	2.36	3	2.35	2
2.03	6	2.04	6	2.03	7
1.83	5				
1.57	4	1.57	3	1.57	3
1.54	9	1.54	8	1.54	4

[1] Crystal spacings in angstroms.

[2] Relative intensity of x-ray peaks.

A similar experimental procedure was used for the experiments involving the freshly precipitated Mn oxides. A concentration of 0.1 gm of precipitated oxide was used per 100 ml of salt solution and a HAc-NaAc buffer was used for controlling pH.

Statistical Methods

A statistical evaluation of the treatment effects was first attempted by linear regression analysis. The procedure was modified by using the reciprocal value of the independent variable, time, since the level of extractable Mn should reach an equilibrium value for a given set of conditions. The predicted values, however, did not correlate satisfactorily with the experimental observations, and a close reexamination of the experimental incubation curves indicated that the observations followed a non-linear function. For these reasons, the treatment effects were evaluated by an analysis of variance, utilizing a time X treatment factorial design. The hypothesis that there was no effect of treatments on extractable Mn was then evaluated. This is a test of significant differences between treatment means instead of the differences between means for a given time of extraction.

It should be noted that the duplicate observations for a given treatment did not generally overlap with those for another treatment. This was especially true for the observations at 10 and 15 days where most of the comparisons between treatments have been made in this dissertation.

Thermodynamic Considerations

Redox Equations

The following basic relationships of chemical thermodynamics have been utilized in this study.

$$\Delta F^\circ = -RT \ln K_{eq} \qquad (3)$$

$$\Delta F^\circ = -nFE^\circ \qquad (4)$$

$$E_h = E^\circ + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \qquad (5)$$

$$\Delta F^\circ = \Sigma\Delta F^\circ_f \text{ (products)} - \Sigma\Delta F^\circ_f \text{ (reactants)} \qquad (6)$$

The symbols were defined as follows:

ΔF° = standard free energy change in chemical reactions in kilogram-calories

R = universal gas constant

T = temperature in degrees Kelvin

ln = logrithm to the base "e"

n = number of electrons appearing in the redox equation

F = Faraday constant

E° = standard potential in volts

Eh = redox potential in volts

$\frac{a_{ox}}{a_{red}}$ = activities of oxidized and reduced species as expressed in mass action or redox equations.

ΔF°_f = standard free energy of formation for substances involved in the mass action or redox equations

K_{eq} = equilibrium constant.

The standard oxidation potentials were calculated from the respective half-cell electrode potentials. The half-cell potentials for the Mn-oxides were calculated from the free energy values given by Bricker (1965). All other half-cell potentials were taken from the Handbook of Chemistry and Physics, 40th Edition (1959). The redox potentials (Eh) were calculated by evaluating the activities of the components in a given redox reaction through the Nernst equation (Equation 5). All oxidation potentials were given for standard state conditions.

Activities

The relationship between activity, activity coefficient, and molar concentration was evaluated by the Debye-Hückel theory. The ionic strength of a given solution was calculated from

$$\mu = 1/2 \, \Sigma_i C_i Z_i^2 \qquad (7)$$

where μ was the ionic strength, C_i was the molar concentration of the ith ion, and Z_i its charge. The effect of ionic strength on the activity coefficient (γ) of Mn^{++} was evaluated by Equation 8 as a first approximation, where Z_i is the charge of the ion, μ is the ionic

$$\log \gamma_i = - \frac{A Z_i^2 \sqrt{\mu}}{1 + a_i^\circ \beta \sqrt{\mu}} \qquad (8)$$

strength according to Equation 7, and A and B are constants characteristic of the solvent at a specified temperature and pressure. For aqueous solutions at 25°C and one atmosphere pressure, A and B are 0.5042×10^8 and 0.3281×10^{-8} respectively. The quantity a_i° has a value dependent upon the "effective diameter" of the ion in solution. This value for Mn^{++} has been given as 6×10^{-8} (Garrels and Christ, 1965). The activity (a_i) of the Mn^{++} ion could then be calculated from this activity coefficient and the molar concentration by

$$a_i = \gamma_i m_i \tag{9}$$

The activity of pure solids and liquids have an activity of one by definition.

The activity of water in solutions was calculated from Equation 10, where P_{H_2O} was the vapor pressure of the water in the electrolyte solution and $P^\circ_{H_2O}$ the vapor pressure of pure water at a specified temperature. The value for P_{H_2O} was calculated from Raoult's

$$a_{H_2O} = \frac{P_{H_2O}}{P^\circ_{H_2O}} \tag{10}$$

law (Equation 11) where x_A is the mole fraction of the solvent.

$$P_{H_2O} = x_A P^\circ_{H_2O} \tag{11}$$

The vapor pressure of pure water at 25°C has been given as 23.75 mm Hg (Garrels and Christ, 1965). It should be recognized that Raoult's law only applies to dilute solutions and in such cases the mole fraction is equivalent to the activity.

RESULTS AND DISCUSSION

Extractable Mn as Influenced by Various K Salts

Preliminary Study

A preliminary field study was initiated when it had become apparent that banded applications of Cl salts were increasing the Mn content of bush beans and sweet corn (Westermann, 1965). All fertilizer materials were hand-banded at a depth of two inches at rates that were comparable to those used in the field fertility experiments. The treatments were placed on limed and non-limed areas. Soil samples that closely approximated the square inch of soil around the fertilizer band were taken on the 7th and 19th day after placement and analyzed for extractable Mn. A summary of the treatment effects has been shown in Table 6 for the second extraction interval.

Extractable Mn levels at the time the experiment was started were 0.01 and 0.09 meq Mn/100 g for the limed and non-limed areas respectively. Comparison of the K salts, KCl and K_2SO_4 showed that more extractable Mn was found in the KCl treatment. This occurred in the presence and absence of both $Ca(H_2PO_4)_2$ and lime. The application of $Ca(H_2PO_4)_2$ had little effect when applied singlely, but when either KCl or K_2SO_4 was added, a much larger amount of extractable Mn was observed. This observation supported the results of Hamilton and Lathwell (1965) who studied the influence of salts associated with $Ca(H_2PO_4)_2$ on the movement of Mn away from the fertilizer band.

Table 6. Influence of banded fertilizer materials on N $CaCl_2$ extractable Mn in the presence and absence of lime. Samples were extracted 19 days after the treatments were applied.[1]

Treatment	meq Mn/100 g soil LO[2]	L1[2]	Average
Control	0.12	0.06	0.09
KCl	0.15	0.10	0.12
K_2SO_4	0.09	0.03	0.06
$Ca(H_2PO_4)_2$	0.09	0.05	0.07
KCl + $Ca(H_2PO_4)_2$	0.20	0.14	0.17
K_2SO_4 + $Ca(H_2PO_4)_2$	0.16	0.08	0.12

[1] Complete information regarding the experimental conditions, treatments, and results has been tabulated in Appendix 1 for this experiment. Treatments were not replicated.

[2] LO, L1 = zero and three ton of hydrated lime added respectively.

In view of these observations and the apparent lack of information concerning the effect of Cl on the availability of soil Mn, a laboratory investigation was initiated. This study was limited to K salts since K fertilizers are widely used and the anion effect was the primary interest.

Soils with Low Extractable Mn

The primary objective of this experiment was to compare the effects of KCl, KNO_3, and K_2SO_4 on extractable Mn. In order to obtain a soil sample that had an initial level of extractable Mn which would approximate the level that was normally found in these soils during the growing season, a sample was taken in the early fall months from a previously limed area. This sample was designated as 1967f. The bulk of the sample was air-dried to 10-15 percent moisture and an incubation experiment was started. An effective salt concentration that corresponded to 13.98 meq K/100 g of soil was used (Table 3). The effect of KCl, KNO_3, and K_2SO_4 on the level of extractable Mn across time has been shown in Figure 3.

It was found that the salt treatment had very little effect on the amount of extractable Mn when the soil was extracted immediately after the salt application. For this reason, the amount of extractable Mn found in the control treatment was used as the zero point for all treatments in a given experiment.

The application of any salt prevented the decrease in the extractable Mn which occurred in the control treatment. Apparently the initial level of extractable Mn was unstable with respect to the experimental conditions, and without the added salt an oxidation or fixation process was taking place. It has been observed that when a

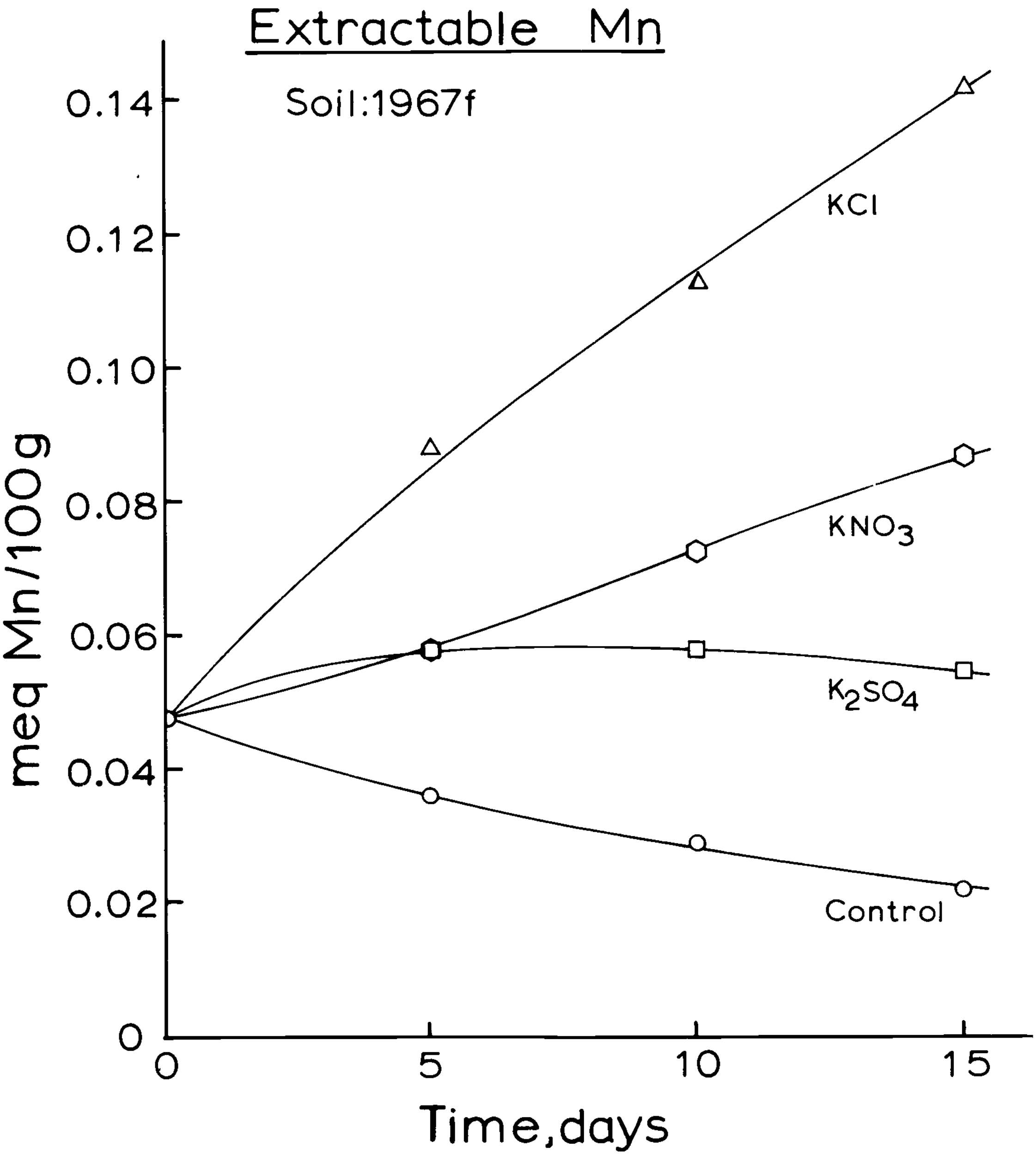

Figure 3. The effect of KCl, KNO_3, and K_2SO_4 on N $Mg(NO_3)_2$ extractable Mn in a soil with a low initial level of extractable Mn (Experiment 16-68).

soil was air-dried that the available Mn was increased (Fujimoto and Sherman, 1945). Upon remoisting the soil to its field capacity the available Mn then gradually dropped to the level it was before air-drying. This process was contributed to a hydration-dehydration of the Mn-hydrous oxide complex.

The behaviour of the KCl and KNO_3 treatments was very different than that of the K_2SO_4. Initially, the K_2SO_4 treatment caused a slight increase in the extractable Mn. It then appeared to become stabilized, although some Mn oxidation has possibly occurred by 15 days. The level of extractable Mn increased with every period of incubation for both the KCl and KNO_3 treatments. The increases, however, resulting from the KCl treatment were approximately twice those from the KNO_3 treatment. The KCl treatment was 2.6, 1.6 and 6.5 times greater than the K_2SO_4, KNO_3, and control treatments respectively at 15 days. Measurements of extractable Mn after 20 days of incubation showed that this trend continued for at least that period.

Soil with High Extractable Mn

The objective of this experiment was to determine what effect the K salts would have on the level of extractable Mn in a soil with a high initial level. The soil sample (1968w) was taken from the field when wet from the winter rains and was dried enough to facilitate handling and screening. The level of extractable Mn was much higher than in any of the other soil samples used in this study (Table 1). Field observations have indicated that extractable Mn levels of this magnitude were reached only during the winter months on these soils (Oregon Agricultural Experiment Station, April 1967).

Comparison of the KCl and K_2SO_4 treatments in Figure 4 leaves little doubt that more extractable Mn was released in the presence of Cl^-. The largest observed difference occurred after 15 days of incubation. It was also quite apparent that the KCl salt had not reached an equilibrium state at that point. The extractable Mn increased at a linear rate after the first initial period in the KCl treatment, similar to that shown in Figure 3. Both the K_2SO_4 and control treatments were apparently approaching an equilibrium point when the experiment was terminated. Although the experimental points for the K_2SO_4 treatment were erratic, the difference between the two salts, KCl and K_2SO_4, was becoming progressively larger.

Increasing the concentration of the salt in the soil system increased the amount of extractable Mn. The effect of increasing the concentration of KCl is presented in Figure 5. There was not a linear relationship between salt concentration and the level of extractable Mn at 15 days. Each step increase in salt concentration was a four-fold increase, _i.e._, from 0.87 to 3.48 meq K/100 g and from 3.48 to 13.98 meq K/100 g.

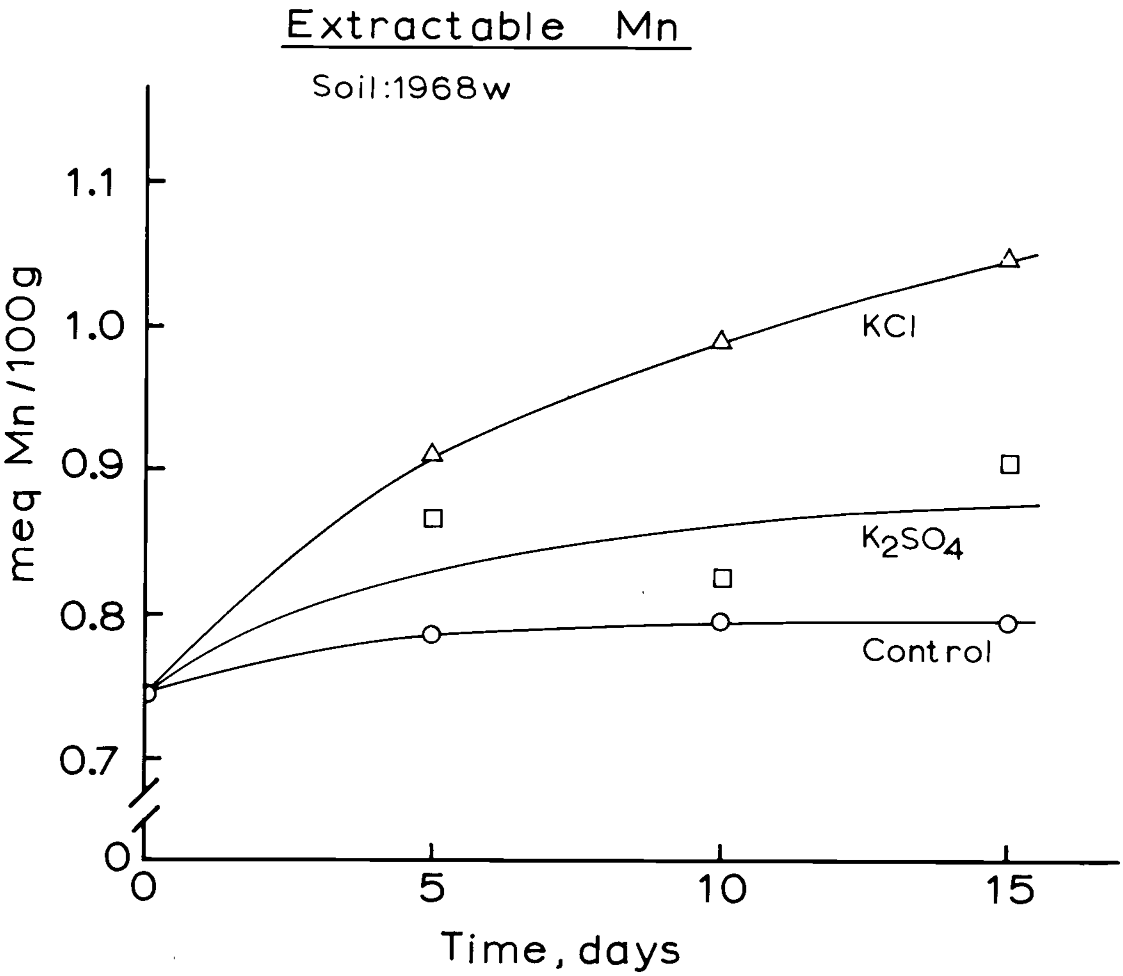

Figure 4. The effect of KCl and K_2SO_4 on N $Mg(NO_3)_2$ extractable Mn in a soil with a high initial level of extractable Mn (Experiment 12-68).

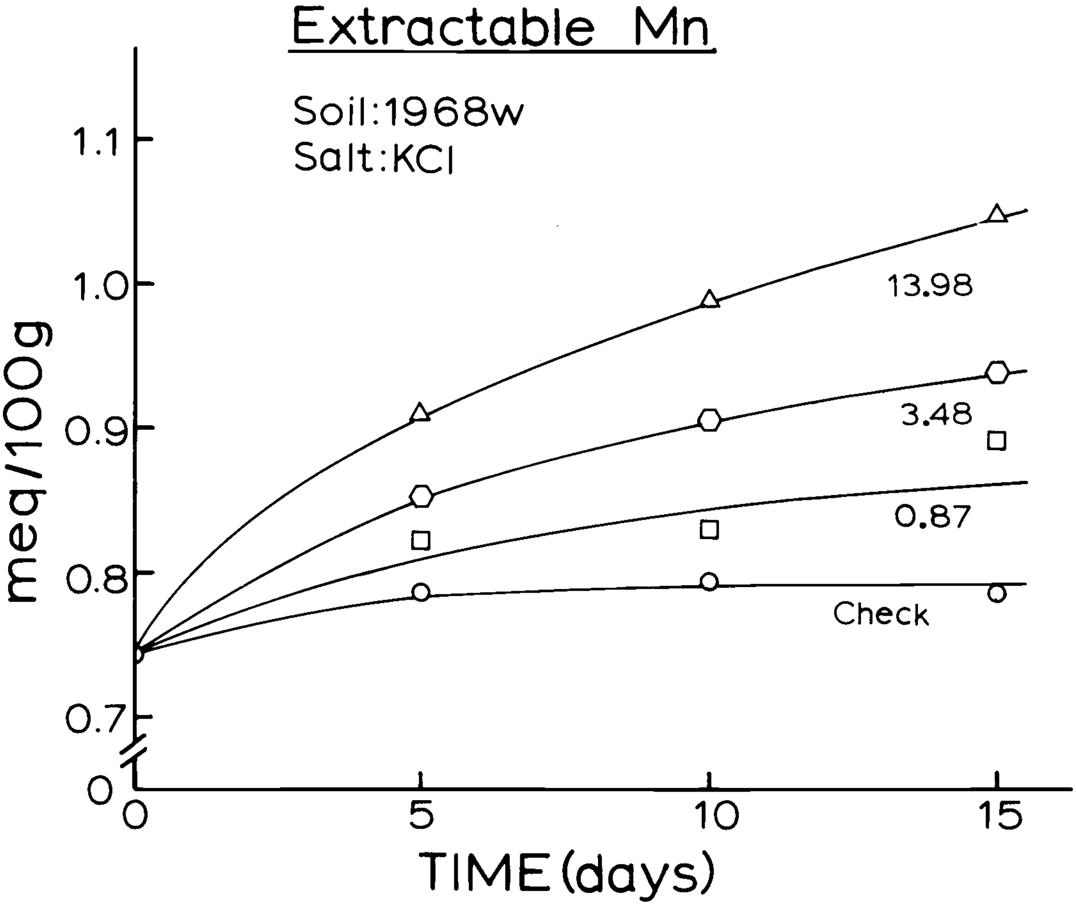

Figure 5. The effect of different salt concentrations (meq K/100 g) on N $Mg(NO_3)_2$ extractable Mn. (Experiment 12-68).

A comparison of the extractable Mn level found at 15 days showed that the KCl treatment was always greater than the K_2SO_4 treatment at an equivalent concentration of K.

	Salt Concentration (meq K/100 g)		
Salt	0.87	3.48	13.98
KCl	0.892*	0.939	1.048
K_2SO_4	0.823	0.859	0.903

*meq Mn/100 g

The level of extractable Mn for the K_2SO_4 at a concentration of 13.98 meq K/100 g was the only K_2SO_4 treatment which surpassed any of the KCl treatments. This concentration was, however, 16 times greater than that of the lower KCl treatment. Even at the lower salt concentration both salts treatments had more extractable Mn than was found in the control treatment.

Comparison of K Salts on the Other Mn Fractions

An attempt was made to determine if the increased level of extractable Mn could be related to a change in the easily reducible Mn fraction and if the relationships between Mn fractions were the same for all the K salts used.

The total available soil Mn has been differentiated into the water-soluble, exchangeable, and easily-reducible forms. The latter form was evaluated by using a N salt solution containing 0.2 percent hydroquinone. Hydroquinone has been considered to extract the highly reactive forms of Mn_2O_3 and some of the more reactive forms of Mn_3O_4. The electrode potential for hydroquinone in acid solution indicated that it was a stronger reducing agent than F^-, Cl^-, or Br^-.

	E (volts)	
$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2H^+ + 2e^-$	-0.699	(12)
$2F^- \rightleftharpoons F_2 + 2e^-$	-2.87	(13)
$2Cl^- \rightleftharpoons Cl_2 + 2e^-$	-1.36	(14)
$2Br^- \rightleftharpoons Br_2 + 2e^-$	-1.06	(15)

The amount of Mn found in the various fractions has been shown in Table 7 for the 15 day sampling interval for experiment 12-68. The extractable Mn fraction has been taken as the sum of the water-soluble and exchangeable fractions. Total available Mn was the sum of the extractable and the easily reducible Mn.

The application of either KCl or K_2SO_4 reduced the amount of exchangeable Mn and increased the water-soluble fraction. These two changes, however, were not equal. That is, the increase in the water-soluble fraction was larger than the decrease in the exchangeable fraction. This would suggest that the salts were dissolving some precipitated form(s) of soil Mn. In general, the easily reducible fraction was decreased from the addition of the salt. This decrease was not, however, equal to the increase which occurred in the

Table 7. Part a. The influence of KCl and K_2SO_4 on the Mn fractions after 15 days of incubation for 1968w soil sample. *

Treatment	Salt concentration (meq K/100 g)	Mn fraction (meq Mn/100 g)				Total available Mn
		Water-soluble	Exchangeable	Extractable	Easily-reducible	
Control	----	0.022	0.764	0.786	0.644	1.430
KCl	0.87	0.120	0.772	0.892	0.517	1.409
	3.48	0.362	0.577	0.939	0.517	1.456
	13.98	0.675	0.373	1.048	0.444	1.492
K_2SO_4	0.87	0.124	0.699	0.823	0.612	1.436
	3.48	0.263	0.596	0.859	0.546	1.405
	13.98	0.537	0.366	0.903	0.532	1.435

Part b. Comparisons of the changes which occurred in the extractable and easily reducible Mn fractions after 15 days incubation. *

Treatment	Salt concentration (meq K/100 g)	Increased Extractable Mn	Decreased easily-reducible Mn	Easily-reducible extractable ratio
KCl	0.87	0.106	-0.127	1.19
	3.48	0.153	-0.127	0.83
	13.98	0.262	-0.200	0.75
				0.92 ave.
K_2SO_4	0.87	0.037	-0.032	0.86
	3.48	0.073	-0.098	1.34
	13.98	0.117	-0.112	0.96
				1.06 ave.

*Complete experimental details have been given in Appendix 2. Average of two replications.

extractable Mn fraction for any given treatment. These calculations have been based on the control treatment.

A comparison of the changes which occurred in the extractable and easily-reducible Mn fractions generally showed that the KCl salt decreased the easily-reducible fraction to a greater degree than the K_2SO_4 salt. The effect of the KCl treatment was not, however, entirely related to a greater release of Mn from this fraction since the ratio of decreased easily-reducible to that of the increased extractable Mn was generally less than one. This ratio was closer to one for the K_2SO_4 treatment. Another experiment gave ratio values of 0.68 and 0.77 for the KCl and K_2SO_4 salts respectively. These results would indicate that the KCl treatment was affecting some other form of soil Mn than those which were influenced by the K_2SO_4 treatment.

The amount of total available Mn did not appear to be affected by the salt treatment (Table 7). There was, however, a tendency for larger amounts with increasing salt concentrations.

The changes which took place in the three Mn fractions with incubation time have been illustrated in Figure 6. Only the control treatment has been drawn to zero time since the complete graphing of the salt treatments would have confused the results. Initially, there was a very rapid drop in the exchangeable Mn fraction and a corresponding increase in the water-soluble with the addition of the

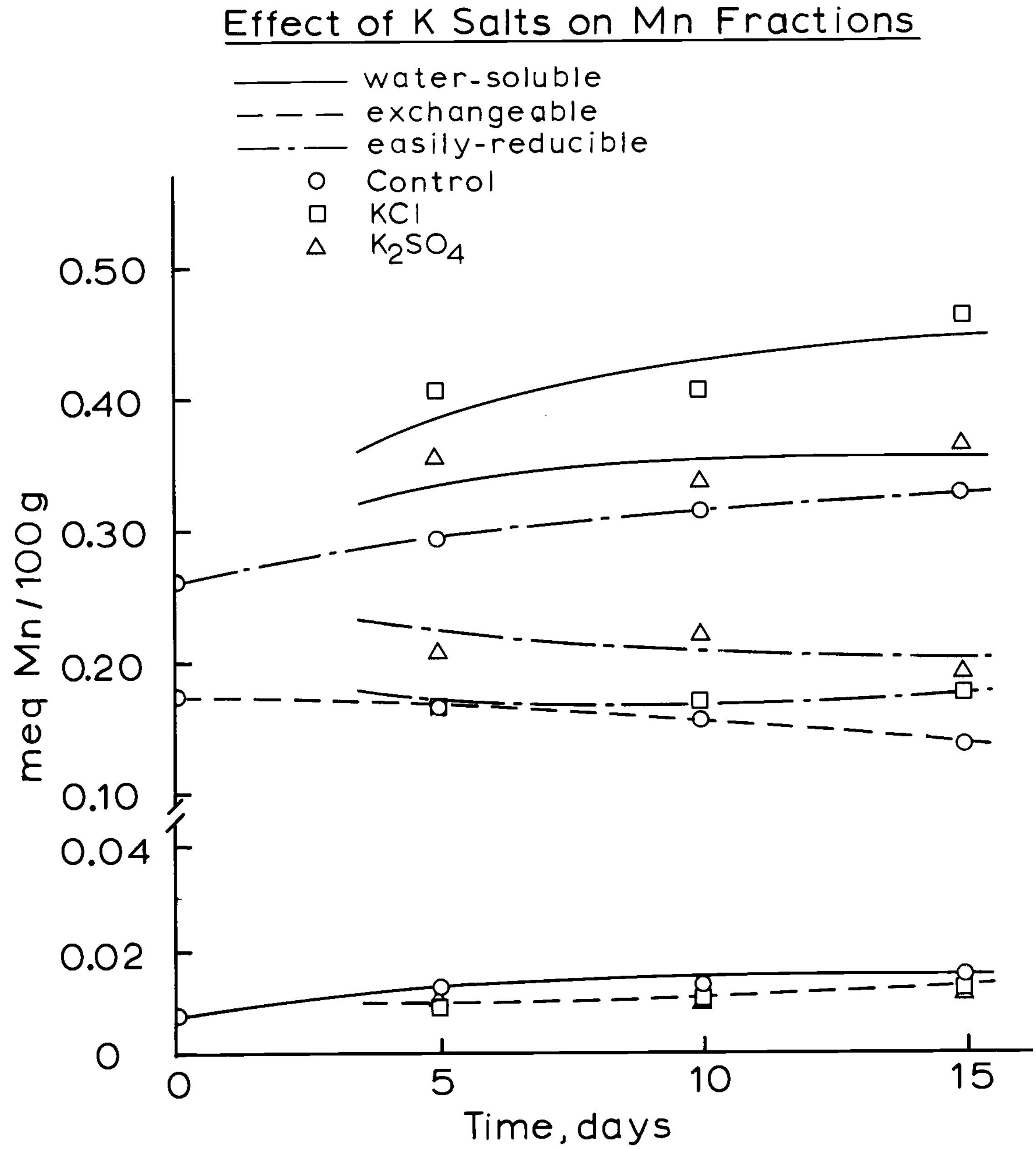

Figure 6. The effect of KCl and K_2SO_4 on the different soil Mn fractions where 25 grams of the 1968w soil was placed in 50 ml of one ionic strength salt solution. (Experiment 7-66).

salt treatments. After this period of adjustment the exchangeable fraction for the two salts, KCl and K_2SO_4, remained constant and nearly equivalent to the water-soluble fraction of the control treatment.

The exchangeable Mn fraction for the control treatment decreased with time which corresponded to an increase in the easily reducible fraction. This indicated that Mn^{++} was being oxidized and precipitated in the easily reducible fraction in the absence of an added salt.

A decrease in the easily reducible fraction and an increase in the water-soluble fraction occurred in both salt treatments. Two important differences, however, existed between the two salt treatments. First, the water-soluble fraction for the KCl treatment increased at a faster rate than that for the K_2SO_4 treatment, and secondly, the KCl treatment contained less easily reducible Mn than the K_2SO_4 treatment at all times of sampling. These differences were not equal. That is, the increases observed in the water-soluble Mn for the KCl treatment did not correlate as well to the decreases in the easily reducible fraction as those for the K_2SO_4 treatment.

The effect of the salts on extractable Mn appeared to be due mainly to the increased amount of water-soluble Mn. This was to be expected from mass action exchange laws since all treatments had equal amounts of K applied for a given concentration of salt.

It has been conclusively shown that the addition of KCl, KNO_3, and K_2SO_4 increased the level of extractable Mn and that this increase was larger in the presence of KCl. The following results and their discussion have been an attempt to determine which factors were responsible for the observed salt effects. The term salt effect has been used to include all chemical reactions and biological adjustments that take place in the soil system as a result of the addition of the salt material.

Investigation of the Salt Effects

Biological Influence

The addition of a salt to a soil system has the possibility of influencing the distribution and/or numbers of microorganisms. One such effect was the effect of nitrogenous compounds on the number of Mn-oxidizing organisms (Timonin, 1965). It was observed that the application of certain salts and carbon sources would prevent Mn deficiency from occurring in certain susceptible oat varieties. Timonin (1965) found that $Ca(NO_3)_2$ and $(NH_4)_2SO_4$ depressed the activity of the Mn oxidizing organisms while $NaNO_3$, urea, and KNO_3 had little apparent effect on their activity. It may be possible that the effect of the Cl salt may be by a similar mechanism. That is, it could alter the equilibrium between the Mn oxidizing and the Mn reducing organisms such that more extractable Mn would be the result.

A salt associated pH change may also cause a partial selectivity of organisms since most organisms have an optimum pH range. Manganese oxidation by organisms has been observed to occur on soil extract agar plates in the pH range of 4.8-8.9 (Dhawan, Singh, and Bhatnagan, 1950) although the intensity of oxidation increased as the pH increased up to 8.9. The lowering of the soil pH from the salt addition could then slow this process of biological oxidation.

An experiment consisting of KCl, K_2SO_4, and a control as treatments was prepared and sterilized. The salts were added after the soil sterilization process was complete in order to avoid possible salt-propylene oxide interactions. Two flasks per treatment were removed from the water bath, sampled for sterility, and then sampled for Mn extraction and pH measurements at each sampling interval. Moisture was maintained at 22 percent with repeated additions of sterilized water.

A sterility test indicated that no measureable recontamination had occurred in any of the sample flasks. This test was conducted by visual observation of inoculated nutrient broth tubes which had been incubated for ten days.

The effect of the sterilized treatments on the extractable Mn levels is shown in Figure 7. A plot of similar treatments from the non-sterile experiment has also been included for comparative purposes (also shown in Figure 3).

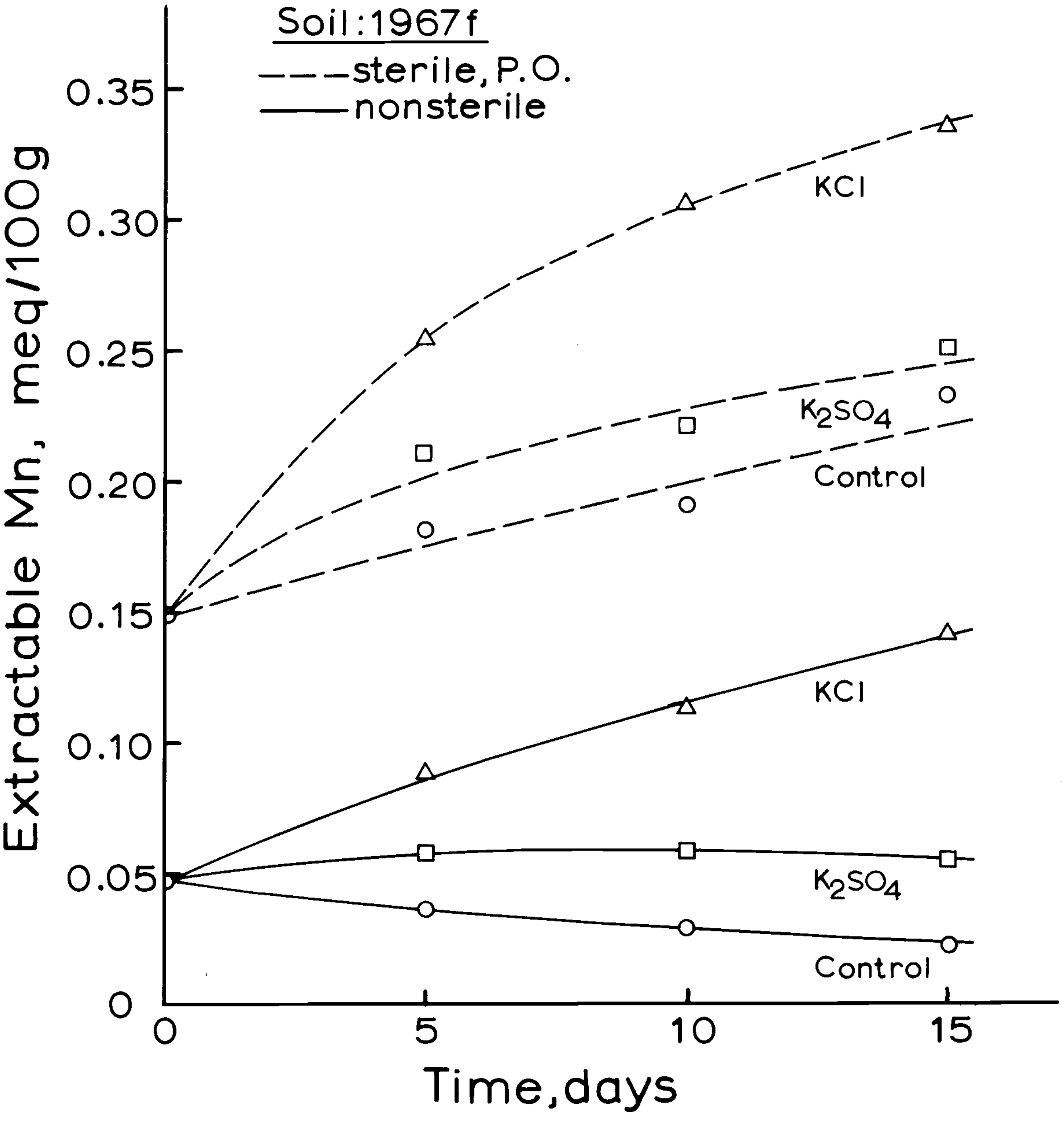

Figure 7. Comparison of the influence of KCl and K_2SO_4 on N $Mg(NO_3)_2$ extractable Mn in sterile and nonsterile soil systems. (Experiments 16-68 and 17-68).

The sterilization treatment increased the amount of extractable Mn by a factor of three in the control treatment at time zero. Propylene oxide had been observed by Skipper and Westermann (1968) to also increase the extractable Mn in the Dayton, Jory, and Woodburn soil series. A search of the literature has failed to produce any reference which cited a cause for this increase. It was, however, most probably due to a release of Mn from the organic matter and from a dissolution of some very easily reducible hydrous Mn oxides. The sterilization process also increased the soil pH from 5.56 to 5.76. This increase was probably the result of a labile H^+ becoming neutralized by attaching itself to the 0 at the unstable C-O bond in the propylene oxide molecule.

The extractable Mn levels were found to be more variable for the sterile than for the non-sterile system. This was especially true for the control and K_2SO_4 treatments. Comparisons of these two treatments showed that the extractable Mn increased with every incubation period in the sterile soil but remained constant or decreased in the non-sterile system. This might have been indicative of some residual propylene oxide although there was not any corresponding pH change.

The level of extractable Mn in the KCl treatment was greater than that found in either the K_2SO_4 or the control treatment at every sampling interval. This had also been observed in the non-sterile soil system. This treatment also increased the extractable Mn at a faster rate initially under the sterile conditions although it is doubtful if much significance should be placed on this because all treatments increased initially under this condition. The propylene oxide treatment could have affected the Mn oxides in such a way that they were more easily dissolved and/or reduced by the treatments.

Comparisons were made between the salt treatments and between the salt treatments and the control for both the sterile and non-sterile systems. The results of those comparisons have been given in Table 8. Comparisons were made from experimental values instead of points lying on the plotted curves.

Both systems gave treatment difference values which were very close together for both the extractable Mn and the pH changes. The difference in extractable Mn between the K_2SO_4 and control treatments showed that there was very little effect of K_2SO_4 after five days in either the sterile or non-sterile system. That is, the majority of effect of the K_2SO_4 treatment was apparently taking place in the first five days. The extractable Mn difference, however, became progressively larger with time when either the K_2SO_4 treatment or control treatment was compared with the KCl treatment. There was no increase after ten days in the sterile system although the absolute value for all treatments was still increasing after this date (Figure 7).

Table 8. Comparisons of the extractable Mn and pH differences between treatments in both sterile and non-sterile systems for the 1967f soil sample.*

		Days of incubation					
		5		10		15	
Comparison	System	Δ meq Mn	Δ pH	Δ meq Mn	Δ pH	Δ meq Mn	Δ pH
K_2SO_4-Control	sterile	0.029	-0.38	0.030	-0.31	0.017	-0.39
	non-sterile	0.022	-0.22	0.029	-0.38	0.033	-0.40
KCl-Control	sterile	0.073	-0.70	0.114	-0.78	0.101	-0.63
	non-sterile	0.052	-0.77	0.084	-0.62	0.120	-0.64
KCl-K_2SO_4	sterile	0.044	-0.32	0.084	-0.47	0.084	-0.24
	non-sterile	0.030	-0.25	0.055	-0.24	0.087	-0.24

*Differences between averages for two replications from Appendices 3 and 4.

The pH differences for these comparisons in the sterile and non-sterile systems were very similar. Little change occurred after the first five day period. There was some variation between the two systems for the KCl-K_2SO_4 comparisons, but these are probably within the experimental measurement error.

The most significant part of these comparisons was the similarity between the sterile and the non-sterile systems. There was little apparent change in the form of the incubation curves for the respective treatments when the system was sterilized prior to the incubation study. This occurred even though there was a pronounced effect of the sterilant on extractable Mn and soil pH. This would tend to indicate that the biological population was not in any way influencing the effect of salts on the level of extractable Mn. It also indicated that the sterilant, propylene oxide, was having very little effect on the soil Mn fraction that the salts were affecting.

An attempt was also made to determine if the salt treatments had an effect on the number of Mn oxidizing organisms. Duplicate dilution plates of 10^{-2} and 10^{-4} were prepared from the KCl, K_2SO_4 and control treatments (Appendix 2) on a Mn^{++} enriched soil extract agar. The soil extract agar was chosen because it should approximate those conditions found in the soil system. The dilution plates were incubated for 20 days before being evaluated. The presence of a darker brownish colored area around a colony of organisms was taken to be indicative that that organism was able to oxidize Mn^{++}.

Treatment	Approximate number of Mn-oxidizers per gram of soil
Control	1700
KCl	1200
K_2SO_4	1500

The number of Mn oxidizing organisms was found to be low in comparison with other reported results. Timonin (1946) found between 8,000 and 9,000 Mn oxidizers in a soil where oats were susceptible to Mn deficiency. The acidic nature of this soil (1968w) probably has accounted for the smaller numbers of Mn oxidizers since most biological oxidation of Mn has been found to occur in the pH range of 5.5 to 8.9. The pH of these soils was 5.0 or below where the salts had been added.

There was a 10 to 30 percent reduction in the number of organisms capable of oxidizing Mn due to the salt additions. These levels also corresponded to the amount of extractable Mn found in these treatments (Figure 4). It is, however, doubtful if much significance should be placed on these differences because of the variability between plate counts and the salts could have suppressed the entire biological population.

The similarity between the sterile and non-sterile soil systems has shown that the biological population was probably not responsible for the effect of salts on the level of extractable Mn. This would indicate that a chemical mechanism(s) was responsible for the salt effects in well aerated soil systems.

Chemical Salt Influence

Effect of Soil pH. The effect that pH has on Mn availability can best be visualized by considering the effect of pH changes on known Mn oxides. Both MnO_2 and MnOOH (γ-Mn_2O_3) were used for this illustration. The oxidation-reduction reactions for these two oxides in an acidic environment have been given in equations 16 and 17. The equilibrium constant was calculated from the standard oxidation potential.

	E° (volts)	
$2MnO_2 + 4H^+ \rightleftharpoons 2Mn^{++} + 2H_2O + O_2$	0.001	(16)
$4MnOOH + 8H^+ \rightleftharpoons 4Mn^{++} + 6H_2O + O_2$	0.215	(17)

$K_{eq}(MnO_2) = 1.168$

$K_{eq}(MnOOH) = 3.39 \times 10^{14}$

A calculation was then made to determine the activity of Mn^{++} in solution at pH's of 4, 5, and 6. The activity of oxygen was set at 0.21 and one was used for the activity of water, MnO_2, and MnOOH. If the activity coefficient of Mn^{++} were assumed to be one, the effective concentration of Mn^{++} in solution was found to be increased 100 fold by each unit of a pH decrease. This would indicate that the effect of the added salt on soil pH could be a major factor influencing the amount of available Mn that would be present at equilibrium.

	pH		
Mn oxide	4	5	6
MnO_2	2.36×10^{-8}	2.36×10^{-10}	2.36×10^{-12}
MnOOH	6.35×10^{-5}	6.35×10^{-7}	6.35×10^{-9}

Concentrations of extractable Mn may also exceed these values because the activity coefficient would probably be less than one, the amount held on the exchange complex is also measured, and the Mn oxides in soils are probably mixed oxide systems.

The pH changes which occurred in the 1967f and 1968w soils have been given in Table 9. The soil pH was lowered immediately by the addition of all salts. The pH then changed very little, if any, during the period of incubation. The pH of the control treatment did, however, decrease in the 1967f soil. Increasing the concentration of either KCl or K_2SO_4 also decreased the soil pH.

The most significant observation was that the measured pH of the K_2SO_4 treatment was always higher than those for the other salts. This difference was present in all soil-salt experiments conducted in this study and has also been observed by Chao, Harward, and Fang (1965). The pH of the KCl and KNO_3 treatments was very similar throughout the experiment and was generally 0.3of a pH unit lower than the pH of the K_2SO_4 treatment.

Table 9. The effect of K salts on soil pH (Averages of two replications). *

Soil	Treatment	Salt concentration (meq K/100 g)	Days of incubation 5	10	15
1967f	Control	-	5.42	5.36	5.29
	KCl	13.98	4.65	4.74	4.65
	KNO_3	13.98	4.66	4.58	4.66
	K_2SO_4	13.98	4.90	4.98	4.89
1968w	Control	0	5.08	5.14	5.05
	KCl	0.87	4.63	4.70	4.58
		3.48	4.34	4.34	4.32
		13.98	4.06	4.12	4.08
	K_2SO_4	0.87	4.66	4.66	4.72
		3.48	4.54	4.56	4.56
		13.98	4.34	4.38	4.41

*See Appendices 2 and 3 for complete experimental details. Initial soil pH for the 1967f and 1968w soil samples was 5.56 and 5.12 respectively.

The KNO_3 treatment had a lower pH than the K_2SO_4 treatment and it also had a higher level of extractable Mn after 15 days of incubation (Figure 3). More extractable Mn was also found in the KCl treatment than in the K_2SO_4 treatment (Figures 3 and 4). The objective of the following series of experiments was to determine if the pH change that resulted from the salt addition was responsible for the changes that occurred in the extractable Mn. The amount of base or acid needed to adjust the pH of certain treatments was estimated from a curve constructed from the pH values obtained when different amounts of acid or base were added to a given salt treatment.

In the initial experiment of this series, the pH of the KCl treatment was adjusted with KOH to approximate the pH of the K_2SO_4 treatment. This required 0.4 ml of 0.1 N KOH per ten grams of soil which was adding only 2.5 percent more milliequivalents of K. The effect of this treatment on the extractable Mn is shown in Figure 8.

Raising the pH of the KCl treatment decreased the amount of extractable Mn in comparison to the uncontrolled KCl treatment. It still was, however, greater than that amount found in the K_2SO_4 treatment. The pH-KCl treatment appeared to prevent the decrease in the extractable Mn which occurred in the K_2SO_4 and control treatments. Unlike the KCl treatment the pH-KCl treatment did not significantly increase the extractable Mn except at 15 days. The lower pH of the KCl treatment was therefore partially responsible for the larger amounts of extractable Mn in that treatment.

The pH of the pH-KCl treatment closely approximated the pH of the K_2SO_4 treatment for the duration of the experiment.

	Soil pH (days)		
Treatment	5	10	15
Control	4.92	4.91	4.82
KCl	4.09	4.14	4.06
pH-KCl	4.45	4.46	4.30
K_2SO_4	4.41	4.49	4.38

The difference between the pH of the pH-KCl and K_2SO_4 treatments was probably within measurement error.

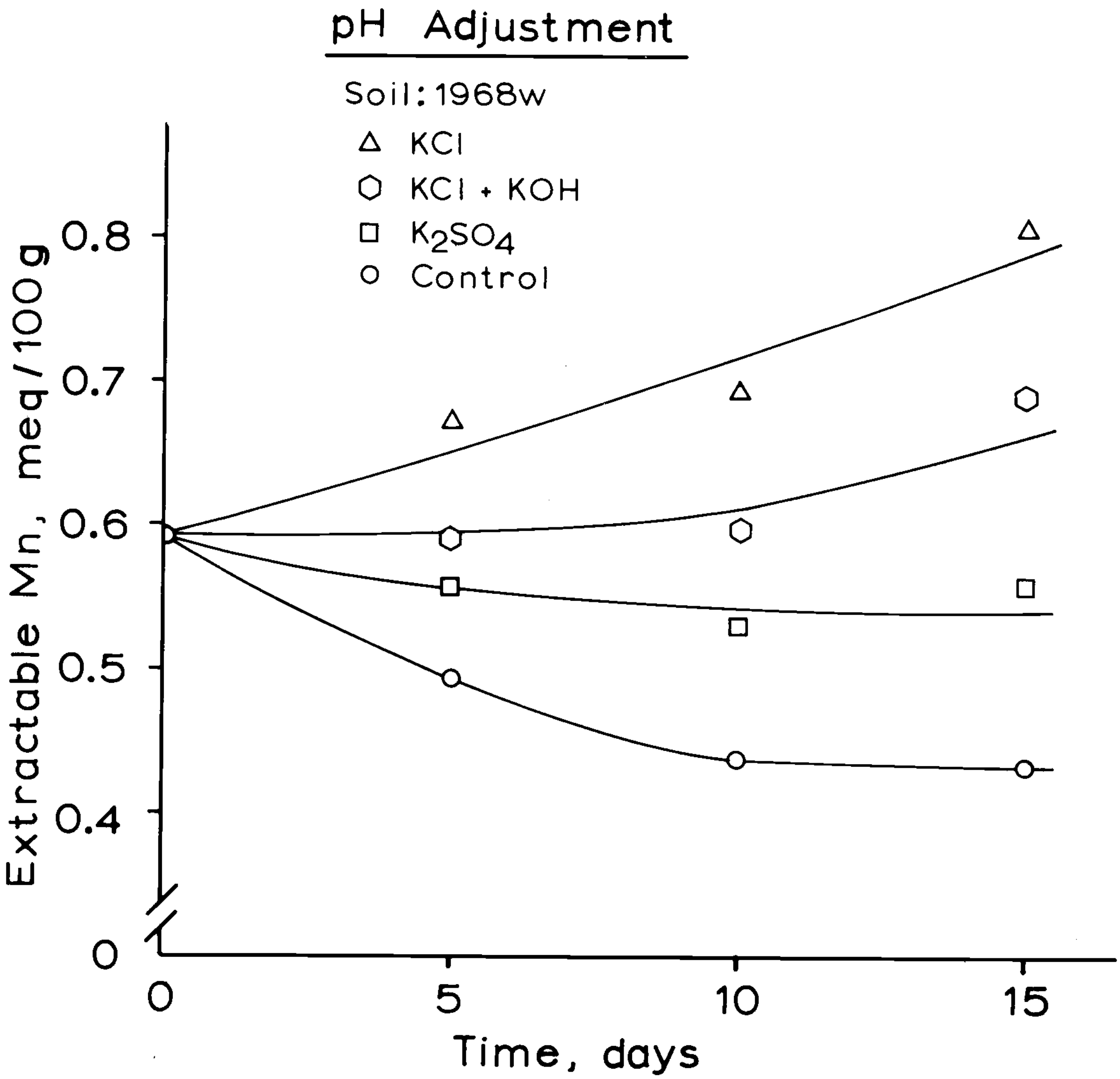

Figure 8. The effect of raising the soil pH in the KCl system to that of the K_2SO_4 system with 0.1 N KOH on N $Mg(NO_3)_2$ extractable Mn. (Experiment 15-68).

The next experiment was also conducted under non-sterile conditions, using the 1967f soil. The pH of the K_2SO_4 was decreased to the pH of the KCl and KNO_3 treatments. Approximately 0.3 ml of 0.1 N H_2SO_4 was found to be necessary to lower the pH of the K_2SO_4 treatment. This added only 2.3 percent more milliequivalents of $SO_4^=$.

The extractable Mn in the pH-K_2SO_4 treatment was nearly equivalent to that which was found in the KNO_3 treatment (Figure 9). The pH's of the KNO_3 and the pH-K_2SO_4 treatments were, however, identical and approximately the same as the KCl treatment. The main effect responsible then for the extractable Mn differences between KNO_3 and K_2SO_4 was the salt associated pH difference. The salt associated pH did not, however, account for the greater amounts of extractable Mn found in the presence of the KCl salt since both the KNO_3 and the pH-K_2SO_4 had the same soil pH as the KCl treatment.

The pH of all the control treatments in the non-sterile experiments generally decreased with time and since no attempt had been made to adjust the pH of the control, it was felt that perhaps the pH could be controlled easier where biological activity was not a factor. The last experiment of this series was then run under sterile conditions at equal pH's and equal relative ionic strengths. The pH adjustments were made after the systems had been sterilized and the salt additions had been made. An additional 3.7 percent more

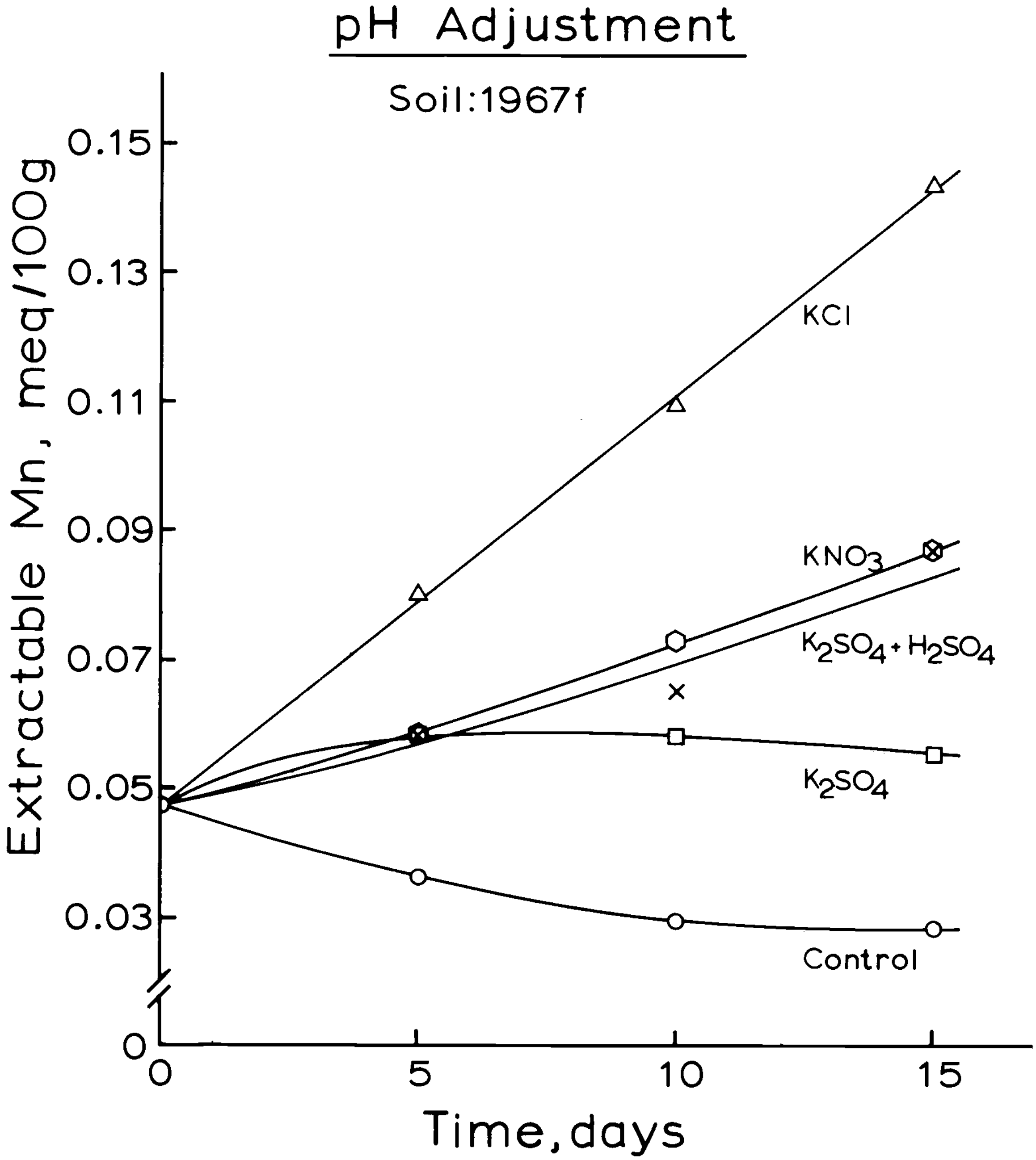

Figure 9. The effect of lowering the soil pH in the K_2SO_4 system to that of the KCl and KNO_3 systems with 0.1 N H_2SO_4 on N $Mg(NO_3)_2$ extractable Mn. (Experiment 16-68).

milliequivalents of $SO_4^{=}$ as H_2SO_4 were added to the K_2SO_4 treatment and the control treatment was raised to a relative ionic strength of 0.048 from the addition of 0.125 milliequivalents of H_2SO_4.

The decreased pH of all adjusted treatments had a pronounced effect on the amount of extractable Mn (Figure 10). The extractable Mn increased in every treatment with increasing incubation interval. A comparison of the KNO_3, pH-K_2SO_4, and KCl at equal pH's and ionic strengths (Figure 10) showed that the KNO_3 and the pH-K_2SO_4 always had similar levels of extractable Mn. The KCl treatment, however, contained more extractable Mn than any of the other treatments. Similar results were obtained in the non-sterile system (Figure 9).

The increases in extractable Mn from time zero to 15 days for the control and the KCl treatment were very similar to those which were obtained in Figure 7. The adjustment of the soil pH in the control treatment had a marked effect on the amount of extractable Mn. That is, a satisfactory separation of the salts (KNO_3 and K_2SO_4) and the control treatment did not occur where the soil pH's were equal (Figure 10).

The effect of salts on extractable Mn was shown to be related to the effect of the salts on soil pH. The lowering of the soil pH by the addition of the salts caused an increase in the level of extractable Mn which was proportional to the pH decrease. An additional

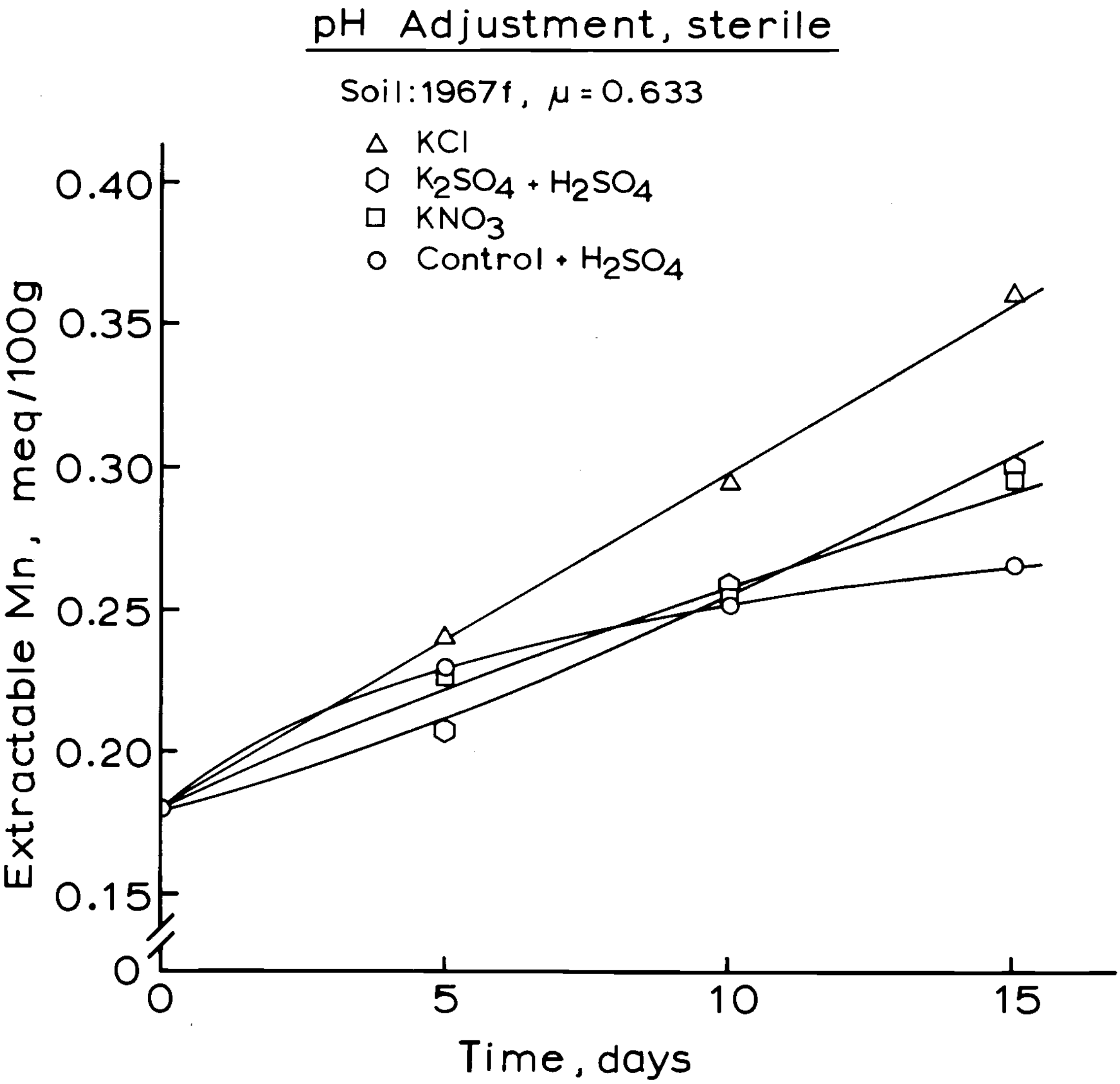

Figure 10. The effect of KCl, KNO_3, and K_2SO_4 on N $Mg(NO_3)_2$ extractable Mn in a propylene oxide sterilized soil system. All salts were applied to give the same relative ionic strength and the pH's of the K_2SO_4 and control treatments were adjusted with 0.1 N H_2SO_4 to those of the KCl and KNO_3 treatments. (Experiment 18-68).

chemical mechanism which may account for part of the salt effects is the effect of ionic strength.

Effect of Ionic Strength. The solubility of a difficulty soluble substance is increased by an increase in the ionic strength of the solution. This effect can be evaluated through the Debye-Hückel theory and the relationship between activity (a), activity coefficient (γ), and molar concentration. The solubility product of a slightly soluble substance is related to ion activities by

$$K_{s.p.} = (a_-)^x (a_+)^y \tag{18}$$

The activity is then related to the activity coefficient and the molar concentration by

$$a = \gamma m \tag{19}$$

In ideal or very dilute solutions, γ approaches the value of one and, therefore, the activity of a particular ion is equivalent to its molar concentration. In real solutions, γ is a measure of the deviation from ideality and generally is less than one.

The Debye-Hückel theory recognized that an excess of oppositely charged ions tended to preferentially surround an ion causing a stabilizing effect on that particular ion. For solutions less than 0.01 M, the relation between ionic strength and activity coefficient for a given ion has been given by

$$\log \gamma_i = - \frac{A Z_i^2 \sqrt{\mu}}{1 + a_i^\circ B \sqrt{\mu}} \qquad (8)$$

The theory then predicts that γ_i becomes smaller as the ionic strength increases. Thus, the molar concentration must become larger in order to maintain a constant ion activity if the solubility product relationship is to be obeyed.

At equal rates of K per acre the relative ionic strength of K_2SO_4 treatment was always 1.5 times larger than that for the KCl or KNO_3 treatment. When 60 pounds of K per acre were applied and the salt was considered to diffuse to an area of one square inch (13.98 meq K/100 g), the K salts had been given relative ionic strengths as calculated by Equation 7.

Salt	Relative Ionic strength	Theoretical γMn^{++}
KCl	0.633	0.238
KNO_3	0.633	0.238
K_2SO_4	0.942	0.224

Thus the K_2SO_4 treatment should have the greatest solubilization effect on the Mn oxides if the ionic strength effects were valid in these systems. This also assumes that the systems have reached equilibrium, that all the other factors which may influence the activity coefficient are equivalent, and that the salt systems have the same pH.

The absolute effect of ionic strength on the solubility of the Mn oxides in soil systems was very difficult to separate from the accompanying pH effect. Increasing the relative ionic strength always resulted in a lower soil pH value. An example of this effect has been shown below for the K_2SO_4 treatment. Similar results were obtained from the application of KCl (Appendix 2) except that the pH's of the KCl-soil system were always lower than those for the K_2SO_4.

meq K/100 g	Relative Ionic Strength	Soil pH
13.98	0.942	4.41
3.48	0.236	4.56
0.87	0.059	4.72
0.0	0.000	5.05

Comparisons of K_2SO_4 with the pH-KCl in Figure 8 and with either KCl or KNO_3 in Figure 9 have failed to show a significant effect of ionic strength. A comparison of K_2SO_4 at two different ionic strengths, 0.633 and 0.942, gave similar results (Table 10). Thus, the different effects of salts on the level of extractable Mn could not be explained by this mechanism. The ionic strength should have had an influence on the solubility of Mn but, apparently it was not detectable in these experiments.

Evidence has been presented which has shown that the effect of Cl on the level of extractable Mn cannot be explained by either a biological mechanism or by chemical salt effects, i.e., pH and ionic strength effects. The experimental observations have indicated that the dissolution of the Mn oxides by the Cl salt was partially pH dependent. This would indicate that the Cl effect might be due to an oxidation-reduction reaction. It would be informative to look at some of the redox reactions of Cl and Br with known forms of Mn oxides to determine if such reactions were feasible in soil systems. All of the standard oxidation potentials have been given for standard state conditions. A positive emf of the combined reaction would indicate that the reaction proceeds from left to right and a negative emf from right to left.

Table 10. The effect of ionic strength on the level of extractable Mn in sterile systems and at equal soil pH's. Ionic strength changes from the addition of K_2SO_4. (Appendix 6).

Relative ionic strength	Days of incubation 5		10		15	
	pH	meq Mn	pH	meq Mn	pH	meq Mn
Control	5.44	0.229	5.30	0.251	5.18	0.265
0.633	5.40	0.207	5.26	0.259	5.19	0.299
0.942	5.35	0.225	5.09	0.272	5.09	0.294

<u>MnO_2</u> E° (volts)

$$MnO_2 + 4H^+ + 2Cl^- \rightleftharpoons Mn^{++} + 2H_2O + Cl_2 \qquad -0.128 \qquad (20)$$

$$MnO_2 + 4H^+ + 2Br^- \rightleftharpoons Mn^{++} + 2H_2O + Br_2 \qquad 0.165 \qquad (21)$$

γ-Mn_2O_3

$$2\ MnOOH + 6H^+ + 2Cl^- \rightleftharpoons 2Mn^{++} + 4H_2O + Cl_2 \qquad 0.184 \qquad (22)$$

Bixbyite

$Mn_2O_3 + 6H^+ + 2Cl^- \rightleftharpoons 2Mn^{++} + 3H_2O + Cl_2$ 0.095 (23)

γ-Manganite

$2MnOOH + 6H^+ + 2Cl^- \rightleftharpoons 2Mn^{++} + 4H_2O + Cl_2$ 0.135 (24)

Mn_3O_4

$Mn_3O_4 + 8H^+ + 2Cl^- \rightleftharpoons 3Mn^{++} + 4H_2O + Cl_2$ -0.708 (25)

The combined standard oxidation potential for reactions 21 through 24 indicates that the halide electrode (Cl or Br) has a greater tendency to give up electrons with respect to the Mn oxide electrode. The net result is that it is possible for both Cl^- and Br^- to reduce the Mn oxides where the emf is favorable and when the reaction components are at unity activity (standard state conditions). Similar reactions are not directly applicable to soil system because all components would not have unity activity values. Nevertheless, this may be part of the mechanism responsible for the effect of salts on extractable Mn.

Effect of KBr

The half-cell electrode potentials for the halides in an acidic solution have been given below. They have been written according to the American Convention where a negative value indicates that they are better oxidizing agents than the hydrogen ion.

	F	Cl	Br	I
E° (volts)	-2.87	-1.36	-1.06	-0.54

The electrode potentials for the halides show that there is an increasing thermodynamic tendency for the system to give up electrons from F to I. Bromide and iodide are both weaker oxidizing or stronger reducing agents than Cl. If indeed the greater amounts of extractable Mn found in the presence of Cl were due to an oxidative-reductive type of reaction, then the application of a Br or I salt should have a similar or even greater effect on the amount of extractable Mn. An experiment was conducted that compared the effect of a KCl or KBr treatment on the level of extractable Mn. The results have been shown graphically in Figure 11 for two different concentrations of salt.

Both KCl and KBr increased the extractable Mn level with every period of incubation. The amount of extractable Mn found in the K_2SO_4 treatment at the highest salt concentration (13.98 meq K/100 g) was lower than that found in either the KCl or the KBr treatment at 3.48 meq K/100 g (Appendix 2). The KBr treatment did not, however, have the same effect on extractable Mn that the KCl treatment had. At the lower salt concentration, the amount of extractable Mn was higher in the KBr treatment at all times of sampling. This difference was also greater at 15 days than at 5 days. For the first 5 days of incubation the KCl and KBr treatments had apparently the

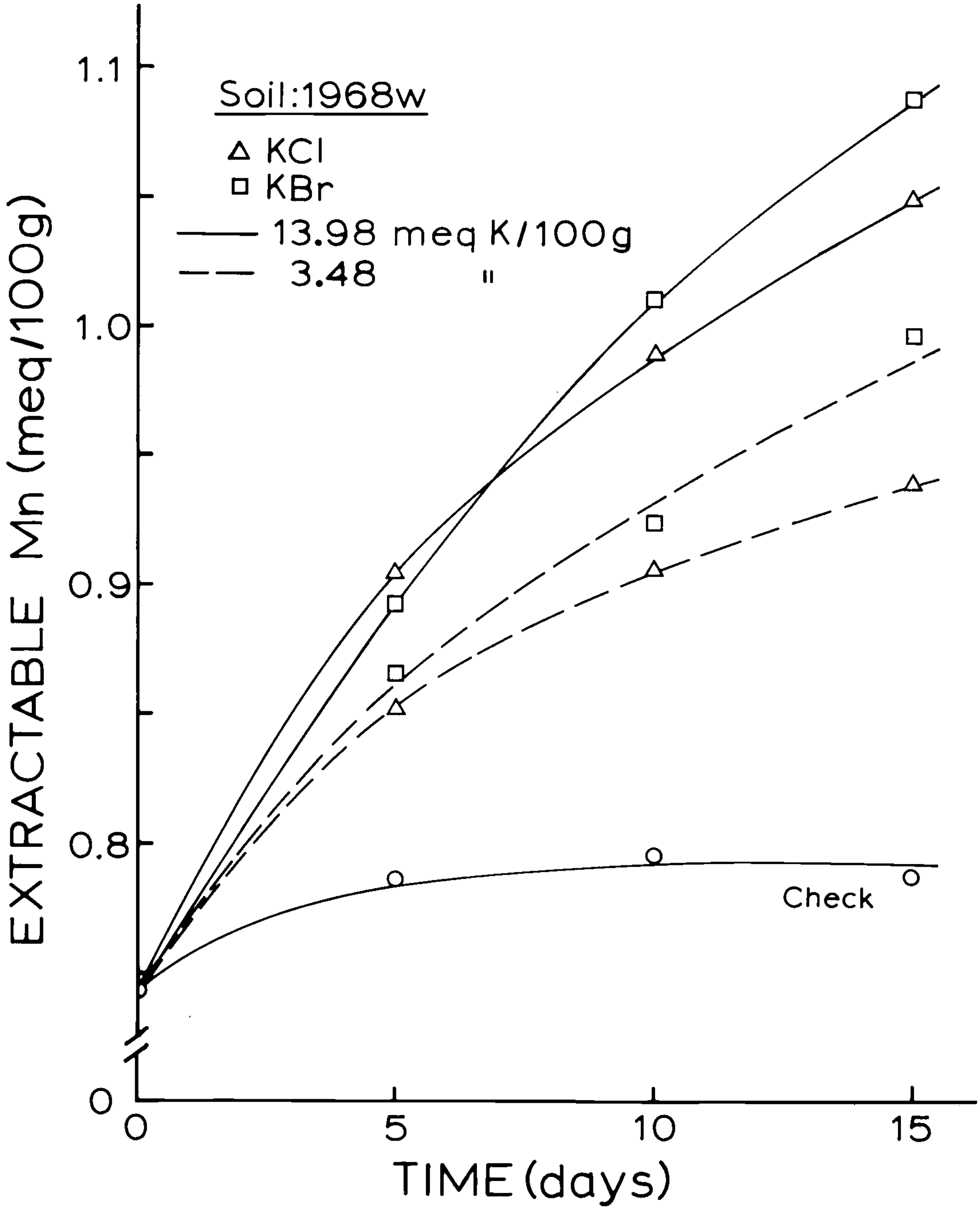

Figure 11. A comparison of the effect of KCl and KBr on N $Mg(NO_3)_2$ extractable Mn at two different salt concentrations. (Experiment 12-68).

same effect on the extractable Mn levels at a salt concentration of 13.98 meq/100 g. The extractable Mn for the KBr treatment did, however, exceed that for the KCl treatment at 10 and 15 days.

The effect that these two salts, KCl and KBr, had on the soil pH was identical. Both KCl and KBr lowered the pH of the soil system one full pH unit at the higher salt concentration; that is, from 5.05 to 4.05. There was, however, little difference between the salt associated pH for the K_2SO_4 treatment at 13.98 meq K/100 g and that for either KCl or KBr at 3.48 meq K/100 g. The relative ionic strengths for KCl and KBr were also equal at equivalent concentrations of K.

The greater release of extractable Mn in the presence of KBr than in the presence of KCl is strong evidence that an oxidation-reduction mechanism was responsible for the effect of Cl. This would be in addition to that effect which would occur from the salt material itself. Since some Mn oxides have been suggested as possible sources of the released Mn and that these reactions have been shown to be feasible at standard state conditions, experiments were then conducted with some synthetic Mn oxides to determine what effects the K salts would have on their solubility under experimental conditions.

Effect of K Salts on Selected Mn Oxides

The initial oxide experiment was conducted with MnO_2 since it is the only stable Mn oxide in an oxygenated environment. An additional experiment was conducted with some freshly precipitated Mn oxides. Their preparation has already been discussed under General Methods and Materials.

MnO_2 Study

The objective of this experiment was to determine and attempt to characterize the effect of K salts on the solubility of MnO_2. All treatments were maintained at pH 4.0 and were continuously aerated with 21 percent O_2. The results have been shown graphically in Figure 12.

The Mn^{++} concentration in solution was increased by all salt treatments. The effects of the KCl and KNO_3 treatments on the solubility of MnO_2 were similar. Both salts had approximately three times more Mn^{++} in solution than the control treatment after 59 days incubation. The amount of Mn found in solution for the KCl treatment was, however, consistently greater than that found in the KNO_3. The similarity of the two treatments, KCl and KNO_3, would tend to indicate that both were affecting the solubility of MnO_2 by the same mechanism. Potassium sulfate's behavior was noticeably different

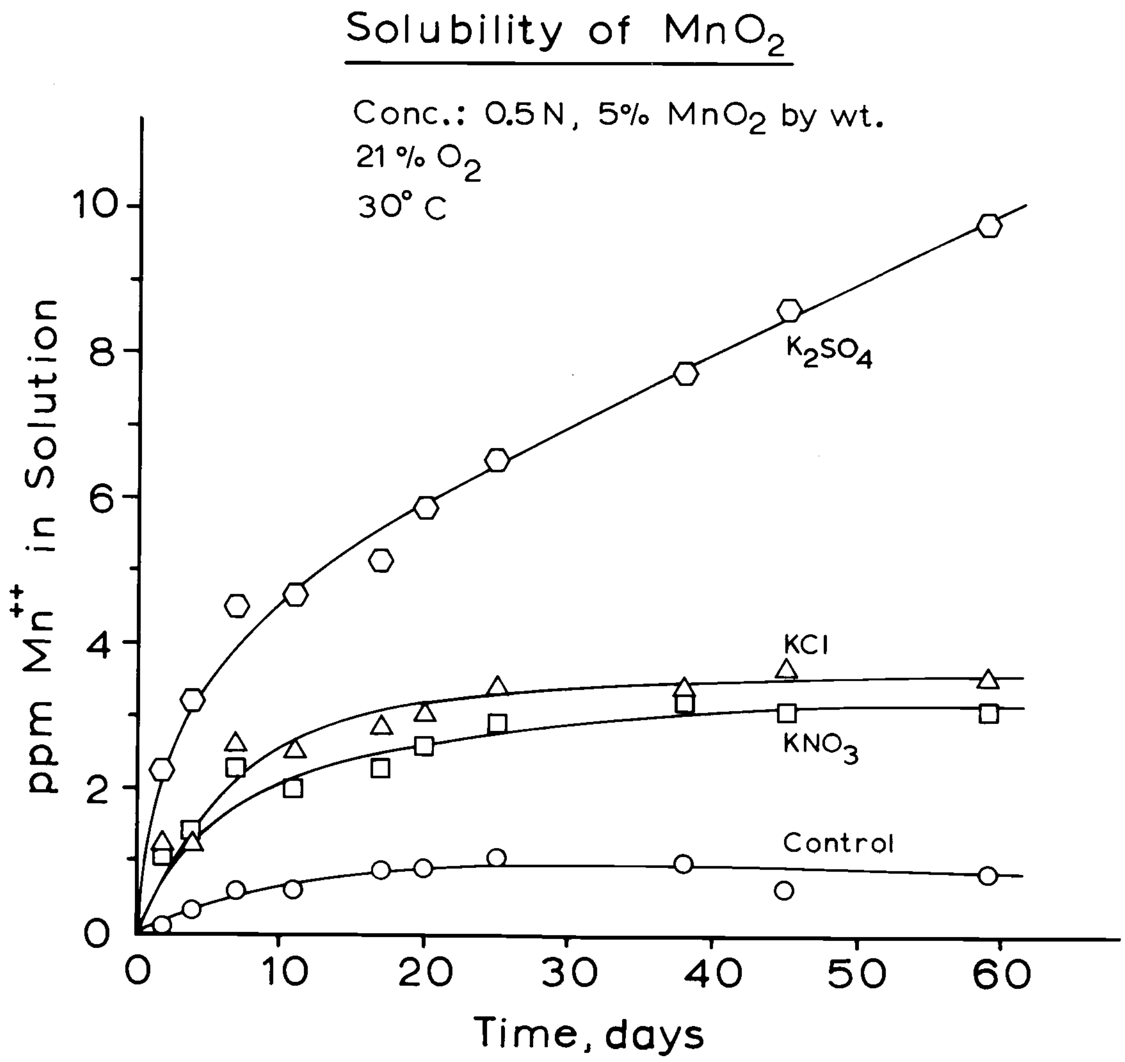

Figure 12. The effect of KCl, KNO_3 and K_2SO_4 on the solubility of MnO_2 in an aqueous environment at a constant pH of 4.0. (Experiment 1-66).

from the other two salts. The Mn^{++} in solution was greater than that in either the KCl or the KNO_3 treatment at each sampling interval. This difference also became progressively larger. Initially, the K_2SO_4 treatment caused a rapid increase in soluble Mn to approximately 20 days. At this point the increase in Mn was linear up to the termination of the experiment. All the other treatments were apparently at or very near to being at equilibrium at that time.

One of the possible explanations for these salt effects is the effect of ionic strength on the solubility of a slightly soluble substance. For these considerations the activity coefficient of the solution Mn^{++} in the control treatment has been assumed to be one since it was a dilute solution, and the theoretical activity coefficient of solution Mn^{++} for the salt treatments has been calculated by using the Debye-Hückel theory as a first approximation (Equation 8). The theoretical concentration of solution Mn^{++} in the salt treatments was then determined by assuming that the activity of solution Mn^{++} would be equal in all solutions at equilibrium. The activity of the solution Mn^{++} in the control treatment was used for the equilibrium value.

The results of these calculations and the observed concentration of Mn^{++} in the KCl and KNO_3 treatments were similar. The experimental results of the K_2SO_4 treatment, however, did not lend

Treatment	Theoretical $\gamma_{Mn^{++}}$	Theoretical $a_{Mn^{++}}$	Observed ppm Mn^{++}
Control	1.0	1.3	0.9
KCl	0.254	3.5	3.5
KNO_3	0.254	3.5	3.1
K_2SO_4	0.227	4.0	9.5

itself to this treatment. Another factor which would have an influence on the activity coefficient of Mn^{++} in the K_2SO_4 treatment would be the ability of $SO_4^{=}$ to form a complex with Mn^{++}. The equilibrium constant for the complexing reaction (Equation 26) has been given as 190 (Hem, 1963a).

$$SO_4^{=} + Mn^{++} \rightleftharpoons MnSO_{4(aq)} \tag{26}$$

The majority of the solution Mn^{++} in the K_2SO_4 treatment would have been complexed since $SO_4^{=}$ was not limiting (0.5 normal). If the activity of Mn^{++} is the same in all solutions at equilibrium, then the concentration of soluble Mn^{++} must be greater in the K_2SO_4 treatment because of the complexing effect. The other anions, Cl^- and NO_3^-, have been shown not to form complexes with Mn^{++}. Thus, the effect of these two salts was apparently an ionic strength effect and the Cl^- ion did not appear to be able to cause a reduction of MnO_2 in this system.

Redox potentials were also measured in this experiment. Selected values have been used for this illustration and the average values are the averages for all times of sampling (Table 11). The redox potential of the KCl treatment was consistently 50-60 millivolts lower than any of the other treatments. This would indicate that the KCl treatment could contain more Mn^{++} in solution before precipitation would begin (Figures 1 and 2). There would also be a greater tendency for the Mn oxides to be reduced in this system. All of the other treatments had approximately the same Eh value for a given time of measurement. The precise meaning of the lower potential in the KCl treatment cannot be satisfactorily evaluated because of the possible influence of a liquid junction potential error.

Table 11. The influence of different K salts on selected redox potentials in a MnO_2-H_2O system. Averages of six readings.*

	Elapsed time (days)			
Treatment	2	20	59	Average
Control	625	616	562	609
KCl	568	548	466	541
KNO_3	636	610	546	604
K_2SO_4	622	622	587	614

*Readings are given in millivolts. See Appendix 9 for complete experimental details.

The measured potentials were, however, not applicable to either the MnO_2-O_2-H_2O or the O_2-H_2O system. Based on the amount of solution Mn^{++} and/or the pH in the control, the theoretical redox value should have been 0.004 volts for the MnO_2-O_2-H_2O system and 1.017 volts for the O_2-H_2O system. The measured redox potentials (Table 11) were apparently a mixed potential of these two systems. They could have also been affected by the "irreversible oxygen potential" (Garrels and Christ, 1965).

The changes in Mn^{++} concentration were probably not detectable by the technique used in the Eh measurements. A 100-fold change of Mn^{++} concentration would be needed to change the Eh value 50 millivolts in the MnO_2-O_2-H_2O system at pH 4.0. Measurements of Eh at their best are reproducible to within 20 millivolts, and a more realistic value for natural systems would probably be 40-50 millivolts.

Freshly Precipitated Mn Oxide Study

In view of the failure to observe the Cl effect on MnO_2 an attempt was made to determine if this effect would occur in a system containing relatively freshly precipitated Mn oxides. No attempt was made to obtain pure Mn oxide species. The freshly precipitated oxides probably contained β-MnOOH and Mn_3O_4 as the principle Mn oxides since they were always formed upon the rapid oxidation of $Mn(OH)_2$ according to Bricker (1965). The oxide, γ-Mn_2O_3, was probably present in trace amounts since the oxides were precipitated in an oxygenated system.

A 0.1 gram sample of the freshly precipitated oxides was weighed into 100 ml of a NaAc-HAc buffer system and allowed to set one week to come to equilibrium. At the end of this period a preweighed amount of salt was added to give a concentration of one ionic strength. The flasks were then stoppered with cotton plugs and placed in a water bath at 25°C.

The amount of Mn^{++} in solution was still increasing, and each flask contained different amounts of dissolved Mn^{++} at the time the experiment was initiated. In order to take these two factors into account the changes which occurred in dissolved Mn^{++} have been plotted on a percentage change basis in Figure 13. The differences shown were due entirely to differences between salts since each system contained equal amounts of buffer solution.

The effects that the two salts, KCl and K_2SO_4, had on the solubility of these oxides were similar to those which had been observed when MnO_2 was used. The increase that resulted from the KCl treatment was approximately half of the K_2SO_4 effect. The K_2SO_4 treatment, however, had the same ionic strength as the KCl treatment. This indicated the difference between these two salts was probably due to the complexing ability of the $SO_4^{=}$ ion. On the basis of ionic strength, the KCl and K_2SO_4 treatments should have increased the soluble Mn^{++} 46 percent.

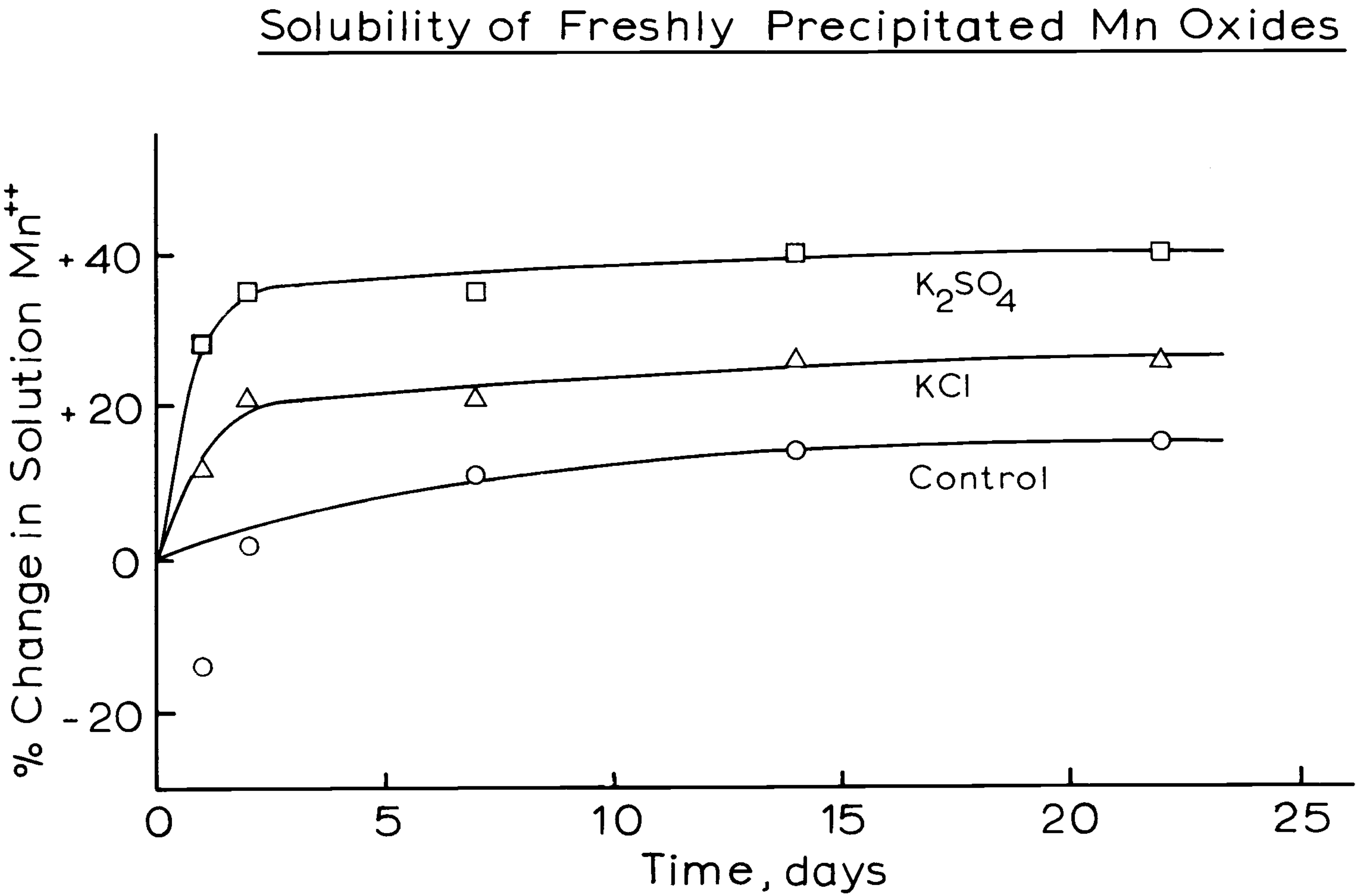

Figure 13. The effect of KCl and K_2SO_4 at one ionic strength on the solubility of some freshly precipitated Mn oxides in aqueous solution system buffered at pH 4.0 by HAc-NaAc. (Experiment 14-68).

The behavior of the salts were not the same in the soil and in the synthetic oxide systems. In the latter systems, the K_2SO_4 treatment released a greater amount of soluble Mn^{++} than either the KCl or the KNO_3 treatment. The effects of the different salts, however, could be satisfactorily explained by ionic strength considerations and no evidence was found that would indicate that these oxides were being reduced by Cl. This would suggest that the Cl ion was affecting some other form of Mn in the soil system. These experiments also indicated that the ability of an anion to form a complex with Mn was an important factor affecting the dissolution of the Mn oxides.

Other Factors which Influenced the Salt Effect

Effects of Air-drying

The process of air-drying has been shown by other authors to increase the level of extractable Mn (Fujimoto and Sherman, 1945; Jones, 1957; Hammes and Berger, 1960; Walker and Barber, 1960). The origin of this released Mn is not known, although it has been contributed to either a release from the hydrous oxides or from a partial selection of the microbiological population. Since soil samples are generally air-dried before being analyzed, an attempt was made to determine if this process had an effect on the Mn fraction(s) that the salts were influencing, especially the Cl sensitive form.

The effect that air-drying had on the initial soil pH and extractable Mn levels is shown in Table 12. The extractable Mn was increased in both soils. In the 1968w soil sample it was increased 1.4 times, whereas the increase was 5.5 fold for the 1967f sample.

Table 12. The effect of air-drying on extractable Mn and soil pH in the 1967f and 1968w soil samples.

	1967f		1968w	
	moist	air-dried	moist	air-dried
pH	5.56	5.11	4.98	5.05
meq Mn/100 g	0.047	0.258	0.590	0.823

The pH did not appreciably change in the 1968w sample but decreased in the 1967f sample from air-drying. A possible explanation for these pH changes would be that upon drying some of the inorganic and organic materials became oxidized releasing H^+ ions in the process. The soluble organic fraction has been shown to be increased from air-drying (Birch, 1959) which corresponded to a drop in soil pH.

The pH differences between the salt treatments and the control which were present in the previous experiments (Table 8) were also present in the air-dried system. The pH of the KCl treatment was approximately 0.3 of a pH unit lower than the pH of the K_2SO_4 treatment. Potassium sulfate lowered the pH of the soil system 0.4 of a pH unit from the control treatment. These effects were similar in both soil samples.

The effects that air-drying had on the salt affected extractable Mn is shown in Figure 14 for the 1967f soil. Similar results were also obtained for the 1968w soil but will not be discussed here. The control treatments were altered by the air-drying process. That is, in the moist soil systems Mn fixation was apparently taking place while in the air-dried systems the extractable Mn increased in the control treatments. Stevenson (1956), Lebedjantzev (1924), and Birch (1959) found that the process of air-drying caused a sharp decrease in the number of microorganisms. It is possible that the microorganisms which were affected were the organisms which could oxidize Mn^{++}. Jones (1957) showed that if Mn^{++} was added to both moist and air-dried soil samples that the extractable Mn^{++} for the air-dried soil remained constant; whereas, oxidation of the added Mn^{++} occurred in the moist soil. This would indicate that the air-drying process either inhibited the capacity of the organisms to oxidize Mn^{++} or removed those organisms which were capable of such.

The salt effects were also affected by the air-drying process. In both soils, 1967f and 1968w, the addition of the salts to the remoistened air dried soils caused an increase in the extractable Mn. Part of this increase was, however, not related to the salts since the extractable Mn also increased in the control treatments upon

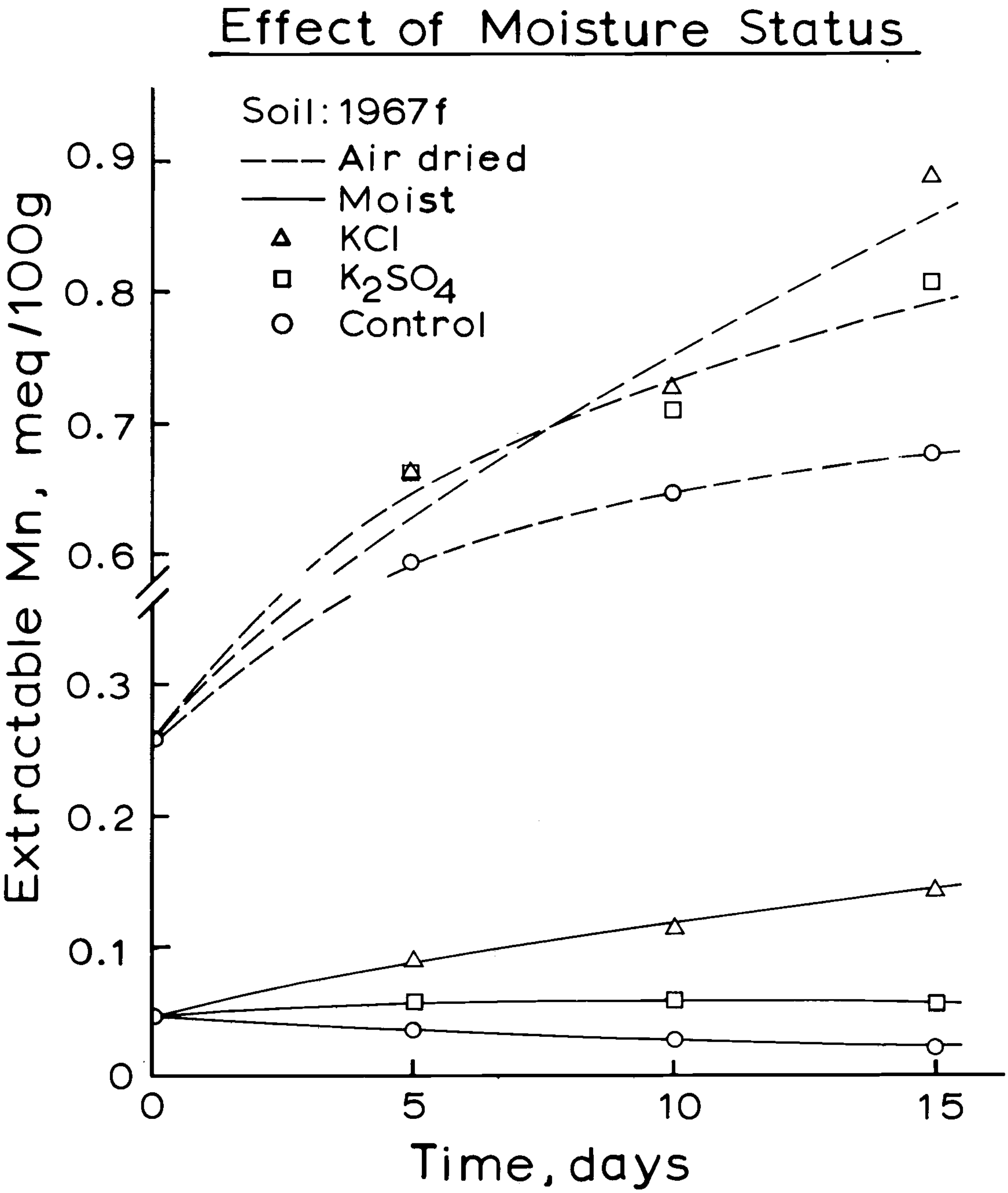

Figure 14. The effect of an air-drying pretreatment on the release of N $Mg(NO_3)_2$ extractable Mn by KCl and K_2SO_4. (Experiment 16-68).

remoistening. The main difference between the moist and air-dried system was that K_2SO_4 caused a decrease of extractable Mn in the former but increased it in the latter system. The air-drying process apparently caused a conversion of the form of Mn which was sensitive to the Cl ion. Since air-drying has been considered to be an aging process, it could have converted the reactive oxides to nonreactive forms.

Effect of Oxygen Partial Pressures

Oxygen has been shown to be one of the factors controlling the availability of soil Mn. At partial pressures which were near to that of the atmosphere, Mn was appreciably oxidized by oxygen at pH's greater than 8.0 (Hem, 1963b; Bricker, 1965). Other than this strict chemical effect it can also serve as an electron acceptor in the processes of aerobic cell respiration. Where oxygen was limiting in pure cultures MnO_2 served as an electron acceptor (Hockster and Quaster, 1952).

An attempt has been made to determine whether oxygen was necessary for the occurrence of the salt effect on the availability of soil Mn. Special emphasis was also placed on determining whether the Cl effect would be enhanced or depressed under reduced partial pressures of oxygen. In these experiments two soil samples, 1967s and 1967f, were used. The systems were continuously aerated with

0, 6, and 21 percent oxygen-nitrogen gas mixtures. No attempt was made to remove the trace amounts of CO_2 since biological activity was present in all systems. The Mn fractions were evaluated with N NH_4Ac in the 1967s sample instead of the usual N $Mg(NO_3)_2$. The results of these experiments have been shown in Figures 15 and 16.

Decreasing the partial pressures of oxygen increased the level of extractable Mn (Figure 15). In the absence of oxygen, the extractable Mn increased at a linear rate up to the last time of extraction for both soil systems (Figures 15 and 16). The highest partial pressures of oxygen, however, decreased the amount of extractable Mn. The intermediate level of oxygen, six percent, increased the extractable Mn for the first five days and then appeared to remain at this level for the remainder of the experiment. It should be noted that not all extractable Mn measurements fell on the plotted curve for the intermediate level of oxygen.

The effect of salts on the extractable Mn levels was influenced by the partial pressures of oxygen. A comparison of the different salt effects for systems at 0 and 21 percent oxygen has been shown in Figure 16. At zero percent oxygen the level of extractable Mn was increased independently of the salt, the ionic strength effects, and the pH effect. The relative increase of extractable Mn in any of the salt treatments at zero percent oxygen was, however, greater than that which occurred at 21 percent oxygen. Similar results were also

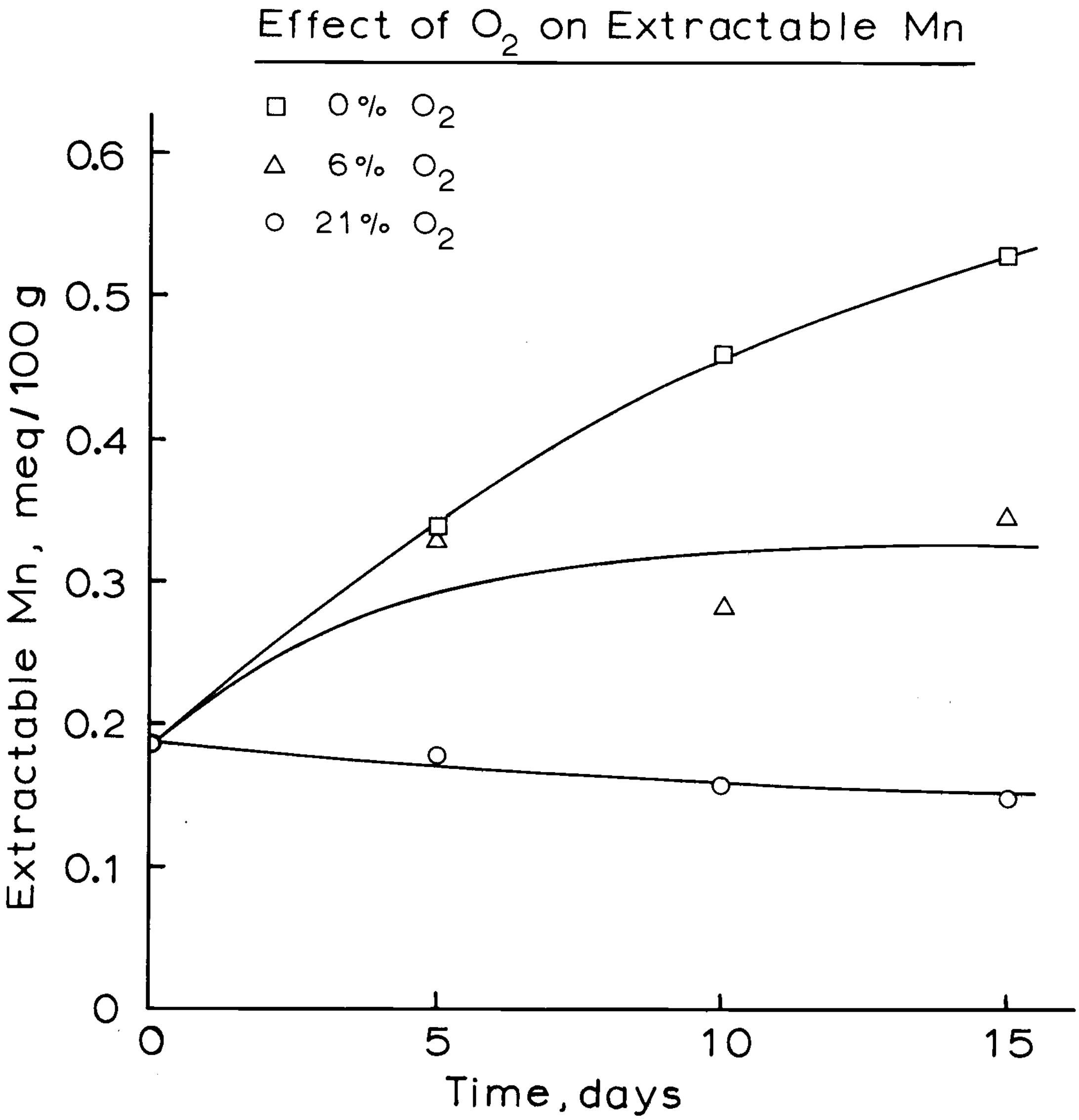

Figure 15. The effect of percent oxygen in the aeration gas on neutral N NH_4Ac extractable Mn. (Experiment 7-67).

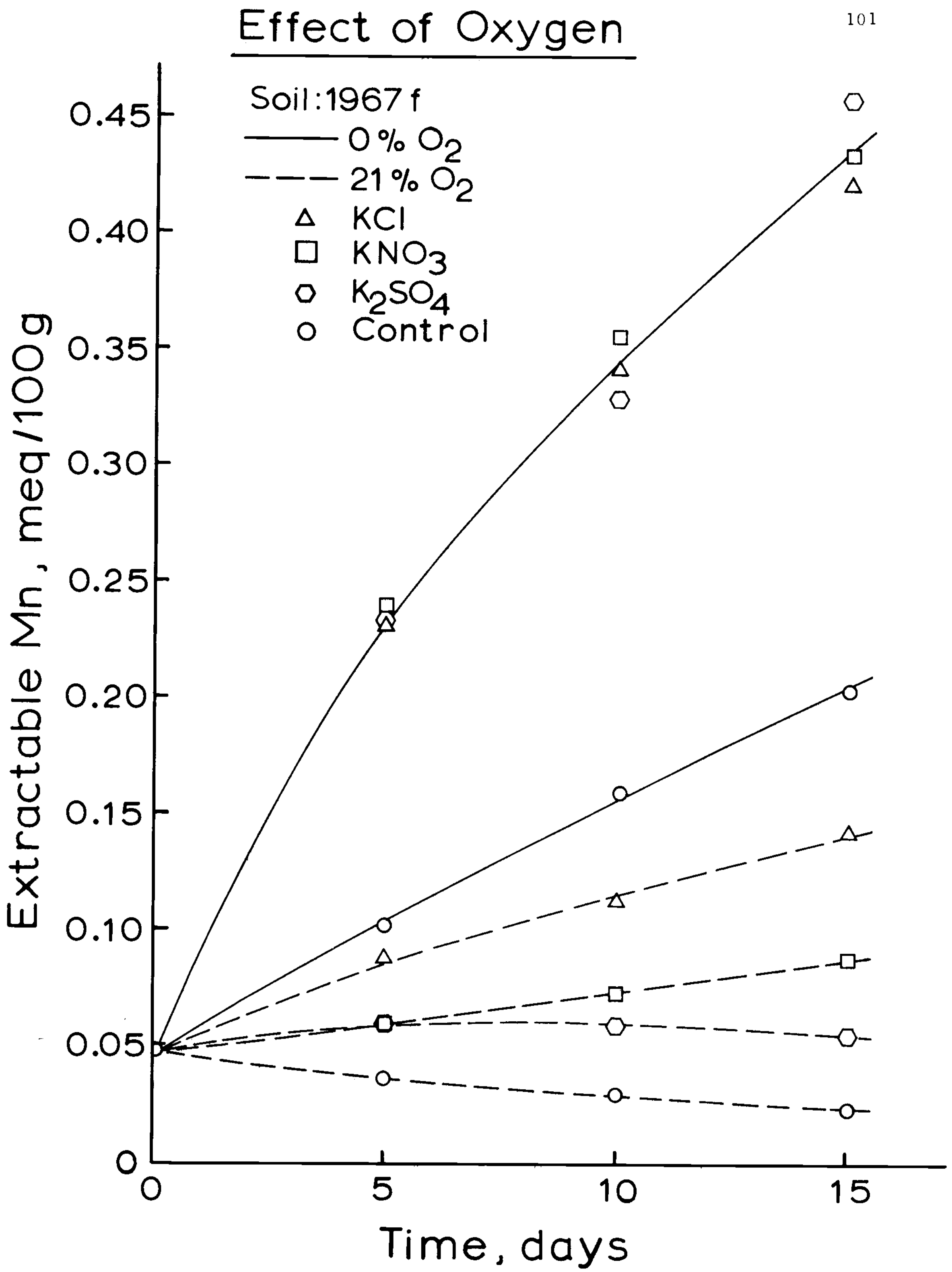

Figure 16. The effect of KCl, KNO_3, and K_2SO_4 on the level of N $Mg(NO_3)_2$ extractable Mn in 0 and 21 percent oxygen systems. (Experiment 16-68).

observed for the 1967s soil sample (Appendix 7).

The effects that the lower partial pressures of oxygen had on the extractable Mn level were probably very similar to those effects which would result from waterlogging a soil system. The effect of the salts on the level of extractable Mn was enhanced by the lower partial pressures of oxygen. This was especially true for the system which was aerated with zero percent oxygen.

Sulfate and nitrate may be biologically reduced in soils that are deficient of oxygen. Under these conditions MnO_2 may also serve as an electron acceptor; however, in the absence of an organism that can use MnO_2, the reduced products of $SO_4^=$ and NO_3^- could reduce the Mn oxide. Equations 27, 28, and 29 have been written as redox reactions involving assumed reduction products and MnO_2.

	E° (volts)	
$MnO_2 + NO_2^- + 2H^+ \rightleftharpoons NO_3 + Mn^{++} + H_2O$	2.170	(27)
$MnO_2 + SO_3^= + 2H^+ \rightleftharpoons SO_4^= + Mn^{++} + H_2O$	1.060	(28)
$3MnO_2 + H_2S + 6H^+ \rightleftharpoons H_2SO_3 + 3Mn^{++} + 3H_2O$	0.639	(29)

The standard oxidation potentials of these equations indicate that the reduction of MnO_2 by NO_2^-, $SO_3^=$, and H_2S was thermodynamically feasible. This may be part of the mechanism which accounts for the lack of difference between salts in Figure 16 at zero percent oxygen.

The effect of Cl on the extractable Mn level was not observed at the lower partial pressure of oxygen. Chloride is only a weak reductant and probably not effective under anerobic conditions where stronger reducing agents may be present. In sterile conditions the Cl effect may be detectable because these stronger reducing agents may not be formed.

GENERAL DISCUSSION

General Salt Effect

In retrospect there are three basic types of salt associated changes which could have influenced the amount of extractable Mn. The first and most important change is the pH change. The solubility of the Mn oxides as predicted by redox equations is very pH dependent. Increasing the pH increases the tendency for systems to become oxidized and thus the redox potential would be increased. If the pH is lowered, the opposite effects occur. The second change would be strictly a concentration effect. That is, the solubility of a slightly soluble substance being increased from the addition of a strong electrolyte. This effect is independent of the pH effect although pH changes may influence the rate of dissolution. Salts may also have an affect on the biological population.

The majority of the changes which occurred in this study were the results of pH changes. Theoretical calculations have shown that the solution activity of Mn^{++} can be changed by a factor of 100 when the pH is changed by one unit. All of the salts that were used in this study decreased the soil pH. This resulted in either slowing the oxidation and/or fixation of extractable Mn or it increased the amount of extractable Mn. The K_2SO_4 treatment generally dropped the pH

0.3-0.4 pH units whereas the KCl, KNO_3, and KBr treatments lowered the measured soil pH 0.7-1.0 pH units. In every case more extractable Mn was found in the latter treatments. Lowering the pH of the K_2SO_4 treatment to that of the other treatments caused the extractable Mn of the pH-K_2SO_4 treatment to be increased to that of the KNO_3 treatment (Figure 9). Also, lowering the pH of the control treatment to that of the KNO_3 treatment increased the extractable Mn of the control treatment. The extractable Mn in the control treatment was then almost as great as that amount found in the KNO_3 and pH-K_2SO_4 treatments (Figure 10). However, adjustments of soil pH failed to account for all of the Cl effect.

Some clarification of the possible causes of the salt associated pH changes would appear to be relevant since there the pH differences between salts accounted for the majority of the extractable Mn differences.

The lowering of the soil pH upon salt addition was apparently not a simple effect of a cation exchange for the hydrogen or hydronium ion. If this were true, all salt-associated pH's would have been the same because the amounts of K supplied were equivalent. Part of the effect of salt on pH may be explained from the replacement of Al^{+++}, Fe^{+++}, hydroxy-Al, and hydroxy-Fe polymers by the added cation (Chang and Thomas, 1963; Thomas and Coleman, 1964). These ions are not stable in acid soil systems and tend to hydrolyze and precipitate as nonexchangeable hydrous oxides. During this process H^+ ions are released. This could be represented by the following Equation where R is any Al, Fe, or possibly Mn hydrous oxide. The acidity released by this process should also be equal for every salt treatment.

$$nK^+ + R_{x\ clay} + yH_2O \rightleftharpoons R_x(OH)_y\text{-clay}K_n + yH^+ \qquad (30)$$

The strengths of adsorption of the anions are not equal. Sulfate is more strongly held than either Cl^- or NO_3^- which are apparently equivalent (Mattson, 1931; Chang and Thomas, 1963; Harward and Reisenauer, 1966). Among other factors the amount of $SO_4^=$ adsorption taking place has been shown to be proportional to the amounts of hydrous Fe or Al oxides (Chao, Harward, and Fang, 1964). The anion exchange could be represented by the Equation 31 where x may be any anion. Since $SO_4^=$ is more strongly held than NO_3^- or Cl^-,

$$R_n(OH)_n\text{-clay} + mx^{-y} \rightleftharpoons R_n[(OH)_{n-m}\ mx]\text{-clay} + mOH^- \qquad (31)$$

the equilibrium for the above reaction would be shifted more towards the right for the $SO_4^=$ than for either Cl^- or NO_3^-. The degree to which the soil pH was changed would then depend upon the combined effects of Equations 30 and 31.

Another possible mechanism which has been overlooked in the literature but may account for part of the pH difference between K_2SO_4 and KCl is the second ionization constant of sulfuric acid. The ionization constant for Equation 32 has been given as 2.0×10^{-2}. The

$$HSO_4^- \rightleftharpoons H^+ + SO_4^= \qquad (32)$$

consideration of this ionization constant would theoretically increase the soil pH from 3.81 to 4.87 for a system which contained 0.21 molar K_2SO_4. Applications of this equilibrium to soil-salt systems usually, however, gave calculated pH's which were higher than those observed.

In pH measurements, an electric current is transported across the liquid junction by Cl^- migrating from the saturated KCl solution in the calomel electrode and by hydrogen and other cations present in the test solution migrating into the saturated KCl. If the flow of current were reversed, anions would then migrate into the KCl solution while K^+ would migrate out of the saturated KCl solution into the test solution. Therefore, the corresponding changes are irreversible if the flow of current were reversed. The pH measurements could have then been subjected to liquid junction potential errors between the electrolyte solutions. A critical evaluation of these effects is not possible because ion mobilities and transference numbers are valid only for infinite dilute conditions. However, comparative evaluations between salts within a given system or adjustment of soil pH for a given soil would be valid.

All variables which were salt affected must be kept constant in order to evaluate the ionic strength effect. The application of salts at different ionic strengths to soil systems always caused different pH changes and if equivalent amounts of K per acre were applied, the relative ionic strength of the K_2SO_4 treatment was 1.5 times greater than that of the KCl and KNO_3 treatments. The application of K_2SO_4 at different ionic strengths, however, failed to show a significant effect on the extractable Mn (Table 10) when the pH was controlled. A comparison of KNO_3 and K_2SO_4 at the same pH also did not show an effect of ionic strength. There was, however, an ionic strength effect in the synthetic Mn oxide systems (Figures 12 and 13) at constant pH.

The salt effects that have been measured in this study were not influenced by the biological population where systems were well aerated. The differences between salts, however, were absent in poorly aerated conditions. This may be attributed to either a direct effect from the lack of oxygen or to an indirect effect caused by the biological population. It is impossible to differentiate between these two effects in this study since a sterile salt-soil system was not studied under poorly aerated conditions.

Chloride Effect

The level of extractable Mn was always greater in the KCl treatment than in the KNO_3 or K_2SO_4 treatments. This effect of Cl was not due to a pH effect since the pH of the KNO_3 and the KCl treatments were equal at equivalent amounts of K. Decreasing the pH of the K_2SO_4 treatment to that of the KCl or KNO_3 also failed to increase the level of extractable Mn in the pH-K_2SO_4 treatment to that of the KCl. The increased ionic strength of the soil solution was not a factor which accounted for the Cl effect. The relative ionic strength of the KNO_3 treatment was equal to that of the KCl since they are both 1:1 salts and they both had a lower relative ionic strength than K_2SO_4. On the basis of the sterility experiment, it would also appear that the larger amounts of extractable Mn were not influenced by an effect of Cl on the biological population.

Since the effect of Cl on extractable Mn was not explained by any of the general salt effects, the reduction of a form of Mn oxide by Cl^- is proposed. Evidence for this hypothesis was given in the KBr treated soil (Figure 11). Bromide by having a lower oxidation potential should have a greater thermodynamic tendency to reduce the higher Mn oxides than Cl^-. Experimental observations indicated that the KBr treatment contained a higher level of extractable Mn than the extractable KCl treatment, where the only known variable was the anion added.

Some additional evidence which would support the hypothesis that Cl was reducing Mn would be the redox measurements in the synthetic MnO_2 system. The redox potential in the Cl treatment was consistently lower than that which was measured in any of the other treatments. This would indicate that the potential for reducing the Mn oxides would be greater in this system than in the others.

All redox reactions in acidic and alkaline conditions are very pH dependent. Theoretical considerations have shown that the activity of the dissolved Mn^{++} species can be changed 100 fold by a one unit change in pH. Experimental observations in this study have shown that when the pH of KCl treatment was raised to that of the K_2SO_4, there was a corresponding decrease in extractable Mn (Figure 8). This extractable Mn was, however, still greater than the amounts found in the K_2SO_4 treatment.

It should be recognized that the standard oxidation potentials for redox reactions are for conditions in which the reaction components are at standard state conditions. Standard state conditions are where all reaction components have an activity of one. To apply such reactions to soil systems the activities must be estimated for the solution species and gases involved. These are then used with the Nernst equation to estimate the redox potential for the two combined half-cells. It should be pointed out that the results of such calculations only give the thermodynamic tendency or feasibility for the occurrence of the reaction. It does not give any information on the kinetics of the reaction. The following will be an attempt to determine the feasibility of Cl^- reducing some of the Mn oxides in soil systems.

The Nernst equation (Equation 3) would be modified as Equation 33 for a general mass action equation where A and B are the reactants

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(a_D)^d (a_C)^c}{(a_A)^a (a_B)^b} \quad (33)$$

and C and D are the reaction products. Substitution of the necessary activities and other values in the Nernst equation from Equation 22

$$2MnOOH + 6H^+ + 2Cl^- \rightleftharpoons 2Mn^{++} + 4H_2O + Cl_2 \qquad \frac{E^\circ \text{ (volts)}}{0.184} \quad (22)$$

gives

$$E = 0.184 - \frac{0.05915}{2} \log \frac{(a_{Mn^{++}})^2 (a_{H_2O})^4 (a_{Cl_2})}{(a_{MnOOH})^2 (a_{H^+})^6 (a_{Cl^-})^2} \quad (34)$$

The MnOOH reaction with Cl^- has been chosen because the redox potential was favorable at standard state conditions.

The effect that substituting different activities for the reaction components on the redox potential is illustrated in Table 13. The activity of MnOOH has been assumed to be one for all cases. The amount of water-soluble Mn^{++} which was found in the soil has been set to be equivalent to the initial activity of solution Mn^{++} before the salt addition.

For the initial calculation (case B) a soil pH of 4.0 and an activity of Cl^- of 0.633 was assumed. Aqueous solutions at 25°C which are saturated with respect to Cl_2 contain 0.061 moles per liter of Cl_2. This has been used as an approximation of the activity of $Cl_{2(aq)}$ with the realization that the actual activity of $Cl_{2(aq)}$ may be very much less. Substituting these values into Equation 34 gave a redox potential of -0.135 volts. This value indicated that the reaction would remain as MnOOH and Cl^- under these conditions.

Table 13. The effect of different activities of the reaction components of Equation 22 on the redox potential at 25°C.

Case	Reaction component (activity)					Redox Potential (volts)
	H^+	Cl^-	Mn^{++}	H_2O	Cl_2	
A*	1	1	1	1	1	0.184
B	1×10^{-4}	0.633	6.35×10^{-7}	1	0.061	-0.135
C	1×10^{-3}	4.77	6.35×10^{-7}	1	0.061	0.094
D	1×10^{-3}	4.77	6.35×10^{-7}	0.921	0.061	0.098
E	1×10^{-3}	4.77	6.35×10^{-7}	0.921	0.0061	0.175

*All reaction components are at standard state conditions.

It is, however, feasible that different conditions would exist in the soil system. The H^+ ion would be adsorbed and, therefore, its concentration and activity should increase at the surface of the exchange complex where the reduction reaction would probably occur. Also the pH that was used was the pH measured in a 1:2, soil:water, solution which would have caused some dilution of the H^+ concentration. The salts were also added dry and have a high probability of being next to the surface containing Mn oxides. Thus, the immediate area surrounding the salt granule may also be saturated with respect to the added salt. The redox potential was then recalculated with these changes being considered; that is, the pH lowered to 3.0 and a saturated KCl solution ($a_{Cl^-} = 4.77$). This gave a value of 0.094 volts which indicated that it was thermodynamically feasible for Cl^- to reduce MnOOH under these conditions.

The activity of water would not be one at saturated salt conditions due to the reduction of the vapor pressure by the added salt. By using Raoult's Law as a first approximation, the activity of water should be close to 0.921 when the molar concentration of Cl^- was 4.77. Substituting this value into the Nernst equation did not appreciably affect the redox potential (Case C _vs._ Case D).

An additional factor which has not been changed is the activity value assigned to Cl_2. It is difficult to visualize a solution saturated with respect to Cl_2 since Cl_2 will react with water and it may escape into the atmosphere as a gas. A ten-fold decrease in the activity of Cl_2 increased the redox potential by 0.077 volts (Case D _vs._ Case E, Table 13).

These calculations have shown that it is feasible for Cl^- to reduce MnOOH in soil systems without having to assume extreme conditions. Similar theoretical calculations showed that the reduction of MnOOH by Br^- was favorable even at a pH of 4.0 and at non-saturated salt conditions. It should be mentioned that it must be assumed that the reduction of the synthetic oxides by Cl^- was not feasible in those systems studied based on the above considerations.

The redox calculations have also been made for the well-crystalline Mn oxides. In soil systems the oxides which are commonly deposited on the surfaces of particles are largely amorphous in nature. This difference in crystallinity could decrease the stability of the higher Mn oxides allowing them to be more readily reduced.

The effects of anions on the chemical properties of the hydrous oxides in soils are not known. The adsorption of anions has been shown to change the isoelectric point of the soil colloidal complex (Maltson, 1931) although this effect was largely dependent on the strengths of adsorption of the anions. The degree to which the hydrous oxides of Mn will adsorb anions is not known although Fe and Al coatings have been shown to be related to $SO_4^=$ adsorption (Chao, Harward, and Fang, 1964). One could assume that the hydrous oxides of Mn preferentially adsorb Cl^- and Br^- over NO_3^- or $SO_4^=$. This may cause a deterioration or recrystallization of the hydrous oxide so that more "adsorbed" Mn^{++} would be released by KCl or KBr.

Recent evidence has been given which indicates that Cl^- catalyzes certain electron transfer reactions. In these reactions Cl^- functions as an electron bridge between the oxidant and reductant.

The reaction of Cr^{++} with a variety of ions of the type $(Co(NH_3)_5x)^{++}$ as oxidizing agents, has been shown to take place with a quantitative transfer of x to the reducing agents (Taube and Meyers, 1954). When x was Cl^-, the transfer took place without any exchange with the Cl^-, in solution. The authors concluded that the activated complex in the electron transfer reaction had a configuration which allowed x to make a bond simultaneously to both Cr^{++} and Co^{+++}. The reactions of the metal oxides of MnO_2, PbO_2, Tl_2O_3, Mn_2O_3, Co_2O_3, CeO_3, and Fe_2O_3 with aquated Cr^{++} and between Fe^{+++} and Sn^{++} were also accelerated by the presence of Cl^- (Gorin, 1936; Zabin and Taube, 1964). These affects were attributed to the smaller repulsive forces of the metal-Cl complexes, however, the electron transfer step would be across a Cl-briding molecule. The reduction of MnO_4^- by malonate and oxalate has also been shown to be catalyzed by halides (Kurian and Ghosh, 1966). The order of effectiveness was shown to be $I^- > Br^- > Cl^-$.

It is not difficult to visualize similar mechanisms which could be operative in soil systems. The presence of reduced organic radicals are common in soils and may only require the presence of Cl^- to be able to reduce some form of Mn oxide. Inorganic ions, such as Fe^{++}, can easily reduce MnO_2. In a pure system this reaction was faster in the presence of Cl^- than in the presence of $SO_4^=$ (Koch, 1957). An attempt was made, however, to detect Fe^{++}

in this study. The results showed that there was little if any Fe^{++} present in any of the treatments.

All salts were shown to decrease the level of easily reducible and exchangeable Mn fractions. The increase in the extractable Mn fraction was the result of a large increase in water-soluble Mn. In general, these results showed that the Mn found in the easily reducible fraction was indicative of changes which were occurring in the extractable Mn fraction. The increase in the extractable and the decrease in the easily reducible Mn fractions were closer to being equivalent for the K_2SO_4 and control treatments than for the KCl treatment. This might be indicative that the KCl treatment was affecting some form of Mn which was not being influenced by the K_2SO_4 treatment. It is also possible that the KCl treatment was affecting a form of soil Mn which was not being measured by the hydroquinone solution.

After the air-drying process there was no detectable differences between salts. This suggests that it caused a conversion of a form of Mn which was sensitive to Cl and supports the above hypothesis that Cl was affecting some form of soil Mn which was not influenced by either K_2SO_4 or KNO_3.

The process of air-drying may be considered as a factor which speeded up the rate of aging of the hydrous oxides. By removing the adsorbed water, the drying process could cause oxygen to diffuse into

into the hydrous oxide at a faster rate. The amorphous hydrous oxide would then become oxidized and more crystalline. In this process of reorganization some of the loosely held Mn^{++} would be released. Dessication may also cause a disproportionation of the lower Mn oxides to MnO_2. Two examples have been given in Equations 35 and 36.

E (volts)

$$Mn_2O_3 + 2H^+ \rightleftharpoons MnO_2 + Mn^{++} + H_2O \qquad 0.225 \tag{35}$$

$$2MnOOH + 2H^+ \rightleftharpoons MnO_2 + Mn^{++} + 2H_2O \qquad 0.314 \tag{36}$$

A second mechanism which may have influenced the salt reactions after air-drying is a change in the biological population. This process has been shown to release water-soluble organic matter and reduce the capacity of the soil to oxidize Mn^{++} by biological means (Jones, 1957). The remaining organisms would have utilized the soluble organic matter and indirectly, reduced some Mn oxides. No doubt this effect of biological growth could have masked any salt effect which occurred.

Both mechanisms are probably operative in soil systems that undergo cyclic wetting and drying. In some soils, however, one of the mechanisms may be predominant over the other. In this study the mechanism which was responsible for the lack of differences between salts was not evaluated. A comparison of sterile and non-sterile systems would have been necessary for this separation.

SUMMARY

Incubation experiments with an acid poorly drained soil have shown that the application of neutral soluble salts influenced the level of extractable Mn. The application of a salt which lowered the soil pH either increased the extractable Mn or retarded the oxidation and/or fixation of extractable Mn. This effect was independent of the applied salt, although salts which had the greatest effect on soil pH, generally had the largest effect on extractable Mn. Comparisons of K_2SO_4 with KNO_3 at equivalent concentrations of K and with K_2SO_4 at different ionic strengths showed a small, but nonsignificant effect of ionic strength on the level of extractable Mn. This indicated that the solubility of the Mn oxides was largely pH dependent and that ionic strength considerations were of secondary importance.

The effect of the Cl salt was over and above that of the general salt effect. The application of KCl always released more extractable Mn than either a KNO_3 or K_2SO_4 salt treatment. This was not a strict pH effect since the KNO_3 and KCl treatments always had the same effect on soil pH. It was also not an ionic strength effect since the relative ionic strength of the K_2SO_4 treatment was 1.5 times greater than that of the KCl treatment. Comparison of sterile and non-sterile soil systems also showed that the Cl effect was not caused by biological activity in well aerated conditions.

To explain the Cl effect, a hypothesis has been presented in which Cl would function in an oxidation-reduction reaction. In these reactions, Cl could act either as the electron donor or as an electron bridge between the reductant and the oxidant. Evidence which would support this hypothesis was:

1. The similarity between the effect of a KCl and a KBr treatment on extractable Mn, i. e., the KBr treatment released more extractable Mn than the KCl according to theory.
2. Theoretical considerations of some of the conditions which were possible in the soil system showed that both Cl and Br had the potential to reduce the lower Mn oxides under those conditions.
3. The pH dependence of the Cl effect.

The Cl effect was not present in poorly aerated soil conditions. Under these conditions stronger reducing agents than Cl may be formed which would mask any Cl effect.

The process of air-drying was also shown to eliminate the Cl effect. This suggested that Cl was affecting a form of soil Mn that was not being influenced by the other salts. Additional evidence for this effect was shown by the Mn fractionation data.

The results of studies with MnO_2 and freshly precipitated Mn oxides suggests that the Cl effect takes place on some other form of soil Mn. Since this form was shown to be changed by the air-drying process, it is suggested that a poorly crystalline form of Mn was present in the soil system which was sensitive to Cl and Br.

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APPENDICES

APPENDIX 1

Results of the preliminary field experiment 1964. The effect of banded fertilizer materials on N $CaCl_2$ extractable Mn and soil pH. Treatments were hand banded one week before sampling. Extractable Mn at the start of the experiment was 0.10 and 0.09 meq Mn/100 g in the absence and presence of lime respectively. Fertilizer rates were as follows: K = 100 pounds K/A, P = 26 pounds of P/A, N = 35 pounds N/A. No replications.

	Lime rate	Elapsed Time			
		7 days		19 days	
Treatment	T/A	meq Mn	pH	meq Mn	pH
Control	0	0.12	4.90	0.12	4.93
	3	0.02	6.25	0.06	5.45
KCl	0	0.17	4.45	0.15	4.63
	3	0.06	6.60	0.10	6.21
K_2SO_4	0	0.10	4.65	0.09	4.76
	3	0.07	5.15	0.03	6.83
$Ca(H_2PO_4)_2$	0	0.12	4.75	0.09	5.21
	3	0.07	5.35	0.05	6.39
$(NH_4)_2SO_4$	0	0.12	4.55	0.10	4.60
	3	0.07	4.80	0.07	5.75
KCl + $Ca(H_2PO_4)_2$	0	0.15	4.60	0.20	4.61
	3	0.09	5.45	0.14	6.14
K_2SO_4 + $Ca(H_2PO_4)_2$	0	0.12	4.45	0.16	4.55
	3	0.07	5.55	0.08	5.63
$(NH_4)_2SO_4$ + $Ca(H_2PO_4)_2$	0	0.13	4.55	0.11	4.72
	3	0.06	5.36	0.05	6.20

APPENDIX 2

Conditions, treatments, and results of experiment 12-68. The different K salts were applied at the noted concentrations. Incubation conditions were 25°C, 20% soil moisture, and 21% O_2. Extractable Mn was measured with N $Mg(NO_3)_2$. The soil, 1968w, contained 0.743 meq Mn /100g and had a pH of 5.12 initially. Averages of two replications.

		Elapsed Time (days)							
	Salt	5		10		15			
Treatment	concentration (meq K/100g)	meq Mn[1]	pH	meq Mn[1]	pH	meq Mn[1]	pH	WS[2]	ER[3]
Control	0	0.786	5.08	0.796	5.14	0.786	5.05	0.022	0.644
KCl	0.87	0.824	4.63	0.830	4.70	0.892	4.58	0.120	0.517
	3.48	0.853	4.34	0.906	4.34	0.939	4.32	0.362	0.517
	13.98	0.910	4.06	0.989	4.12	1.048	4.08	0.675	0.444
K_2SO_4	0.87	0.779	4.66	0.808	4.66	0.823	4.72	0.124	0.612
	3.48	0.824	4.54	0.775	4.56	0.859	4.56	0.263	0.546
	3.98	0.866	4.34	0.824	4.38	0.903	4.41	0.537	0.532
KBr	3.48	0.866	4.30	0.924	4.29	0.996	4.26	0.408	0.496
	13.98	0.892	4.08	1.010	4.10	1.087	4.04	0.717	0.444

[1] Extractable Mn, meq/100g.

[2] Water-soluble Mn, meq/100g.

[3] Easily reducible Mn, meq/100g.

APPENDIX 3

Conditions, treatments, and results of experiment 16-68. Salts were applied at a rate of 13.98 meq K/100g. The extractable Mn was measured with N $Mg(NO_3)_2$. Incubation conditions were 25°C and 22% soil moisture and was aerated with either 21% or 0% O_2. The soil, 1967f, contained 0.047 meq Mn/100g and had a pH of 5.56 under moist conditions and after air-drying it had a pH of 5.11 and 0.258 meq/100g extractable Mn. Averages of two replications.

			Elapsed Time (days)					
			5		10		15	
Treatment	Soil pre-treatment	Percent O_2	meq Mn	pH	meq Mn	pH	meq Mn	pH
Control	moist	21	,0.036	5.42	0.029	5.36	0.022	5.29
KCl	moist	21	0.088	4.65	0.113	4.74	0.142	4.65
KNO_3	moist	21	0.058	4.66	0.073	4.58	0.087	4.66
K_2SO_4	moist	21	0.058	4.90	0.058	4.98	0.055	4.89
pH-K_2SO_4*	moist	21	0.058	4.74	0.065	4.66	0.087	4.79
Control	moist	0	0.101	5.60	0.158	5.64	0.203	5.70
KCl	moist	0	0.232	4.80	0.341	4.82	0.420	4.80
KNO_3	moist	0	0.239	5.18	0.327	5.16	0.460	5.14
K_2SO_4	moist	0	0.233	4.84	0.355	4.90	0.433	4.98
Control	air-dried	21	0.596	5.40	0.648	5.48	0.677	5.52
KCl	air-dried	21	0.633	4.70	0.728	4.69	0.888	4.84
K_2SO_4	air-dried	21	0.633	5.08	0.710	5.03	0.804	5.12

*The soil pH was adjusted with 0.1 N H_2SO_4 to that of the KCl or KNO_3 treatment.

APPENDIX 4

Conditions, treatments, and results of experiment 17-68. The soil, 1967f, was sterilized with propylene oxide prior to adding the salt treatments. Incubation conditions were 25°C, 21% 0_2, and 22% soil moisture. The salts were applied at a rate of 13.98 meq K/100g. All treatments were found to be sterile throughout the experiment. The extractable Mn was measured with N $Mg(NO_3)_2$. Averages of two replications.

	Elapsed Time (days)							
	0*		5		10		15	
Treatment	meq Mn	pH	meq Mn	pH	meq Mn	pH	meq Mn	pH
Control	0.149	5.76	0.182	5.90	0.192	5.70	0.233	5.80
KCl	0.149	5.76	0.255	5.10	0.306	4.92	0.335	5.17
K_2SO_4	0.149	5.76	0.211	5.42	0.222	5.39	0.251	5.41

*After the stilization treatment, but prior to adding salts.

APPENDIX 5

Conditions, treatments, and results of experiment 15-68. Incubation conditions were 25°C, 21% O_2, and 22% soil moisture. A fresh soil sample, 1968w, was treated with 13.98 meq K/100g. The pH of the KCl treatment was raised with 0.1 N KOH to approximately that of the K_2SO_4 treatment. Averages of two replications.

	Elapsed Time (days)							
	0		5		10		15	
Treatment	meq Mn	pH	meq Mn	pH	meq Mn	pH	meq Mn	pH
Control	0.590	4.98	0.492	4.92	0.437	4.91	0.433	4.82
KCl	0.590	4.98	0.671	4.09	0.692	4.14	0.809	4.06
pH-KCl	0.590	4.98	0.580	4.45	0.597	4.46	0.692	4.30
K_2SO_4	0.590	4.98	0.576	4.41	0.550	4.49	0.533	4.38

APPENDIX 6

Conditions, treatments, and results of experiment 18-68. The soil, 1967f, was sterilized with propylene oxide prior to salt treatments. Incubation conditions were 25°C, 21% O_2, and 22% soil moisture. Salt was applied at a rate of 13.98 meq K/100g for the first four salt treatments. The latter two K_2SO_4 treatments were adjusted according to ionic strength (μ) considerations. The soil pH of the pH-K_2SO_4 treatments was adjusted with 0.1 N H_2SO_4. The soil pH and meq Mn/100g were initially 5.56 and 0.178 respectively. Average of two replications.

		Elapsed Time (days)					
		5		10		15	
Treatment	Relative μ	meq Mn	pH	meq Mn	pH	meq Mn	pH
Control	0	0.229	5.44	0.251	5.30	0.265	5.18**
KCl	0.633	0.240	5.24	0.294	5.18*	0.360	4.99*
KNO_3	0.633	0.225	5.21	0.253	5.18**	0.294	5.12*
pH-K_2SO_4	0.942	0.222	5.35	0.272	5.09	0.295	5.09
K_2SO_4	0.633	0.211	5.44	0.251	5.40	0.309	5.33*
pH-K_2SO_4	0.633	0.207	5.40**	0.259	5.26*	0.299	5.19**

* One replication was found to be contaminated.

**Two replications were found to be contaminated.

APPENDIX 7

Conditions, treatments, and results of experiment 7-67. Twenty-five grams of soil, 1967s, were treated with 50 ml of one ionic strength salt solution, then incubated at 25°C and aerated with N_2-0_2 gas mixtures. Extractable Mn was evaluated with neutral N NH_4Ac and easily reducible Mn was evaluated with neutral N NH_4Ac + 0.2% hydroquinone. Averages of two replications.[1]

		Elapsed Time (days)											
	Percent	5				10				15			
Treatment	0_2	WS[2]	E[3]	ER[4]	pH	WS	E	ER	pH	WS	E	ER	pH
Control	0	0.015	0.336	0.215	4.87	0.017	0.458	0.141	4.28	0.024	0.526	0.127	4.74
	6	0.022	0.328	0.276	4.61	0.017	0.279	0.268	4.48	0.020	0.342	0.276	4.51
	21	0.013	0.179	0.291	4.59	0.013	0.167	0.313	4.48	0.015	0.149	0.327	4.65
KCl	0	0.532	0.544	0.157	3.84	0.582	0.594	0.127	3.76	0.687	0.709	0.093	4.00
	6	0.497	0.511	0.206	3.96	0.486	0.502	0.144	4.07	0.572	0.585	0.122	3.98
	21	0.406	0.417	0.166	4.07	0.406	0.416	0.168	3.98	0.461	0.473	0.174	4.01
K_2SO_4	0	0.542	0.564	0.131	4.32	0.635	0.665	0.052	3.27	0.720	0.750	0.032	4.48
	6	0.541	0.565	0.214	4.42	0.476	0.496	0.160	4.39	0.658	0.692	0.176	4.41
	21	0.353	0.365	0.209	4.32	0.336	0.348	0.220	4.37	0.363	0.374	0.192	4.33

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[1] Soil initially had a pH of 4.82 and contained 0.008, 0.183, and 0.262 meq Mn/100g for the water-soluble, extractable, and easily reducible Mn fractions respectively.

[2] Water-soluble Mn, meq/100g.

[3] Extractable Mn, meq/100g.

[4] Easily-reducible Mn, meq/100g.

APPENDIX 8

Conditions, treatments, and results of experiment 1-67. Each system contained 5% MnO_2 by weight in a 0.5 ionic strength salt solution. Incubation conditions were 30°C and 0% O_2. The pH was adjusted with the acid of the anion and the base of the cation for each respective salt. Solution Mn^{++} is the average of two replications in ppm, whereas Eh is the average of four replications (two readings per flask) in millivolts.

				Elapsed Time (days)							
Treatment	pH			1	2	3	5	9	14	20	26
Control	4	ppm	Mn	1.33	1.60	2.50	3.25	8.60	14.45	15.70	19.20
			Eh	--	--	--	388	396	398	437	468
	6	ppm	Mn	0.21	0.15	0.10	(------------------ trace ------------------)				
			Eh	--	--	--	279	281	322	360	394
KCl	4	ppm	Mn	3.99	5.20	5.70	7.20	10.40	13.90	16.20	19.00
			Eh	--	--	--	457	438	428	472	482
	6	ppm	Mn	0.64	0.54	0.60	0.99	1.76	1.96	2.62	3.03
			Eh	--	--	--	291	358	340	355	380
K_2SO_4	4	ppm	Mn	3.32	4.00	5.05	6.40	8.00	11.20	12.70	15.60
			Eh	--	--	--	418	438	422	451	456
	6	ppm	Mn	0.44	0.42	0.52	0.74	0.96	1.11	2.74	2.47
			Eh	--	--	--	316	355	329	366	388
KNO_3	4	ppm	Mn	3.94	5.60	8.05	10.10	15.40	20.75	25.40	29.10
			Eh	--	--	--	--	450	419	444	448

APPENDIX 9

Conditions, treatments, and results of experiment 1-66. Each system contained 5% MnO_2 by weight in a 1N salt solution. Incubation conditions were 30°C, 21% O_2, and pH 4.0. The pH was adjusted with the acid of the anion and the base of the cation for each respective salt. The solution Mn^{++} is the average of two replications in ppm, whereas the Eh is the average of six replications (three readings per flask) in millivolts.

Treatment		Elapsed Time (days)									
		2	4	7	11	17	20	25	38	45	59
Control	Mn	0.14	0.34	0.62	0.66	0.92	0.92	1.08	1.00	0.64	0.86
	Eh	625	646	620	660	640	616	611	569	538	562
KCl	Mn	1.22	1.23	2.63	2.52	2.83	3.09	3.45	3.44	3.71	3.59
	Eh	568	570	540	611	544	548	531	520	514	466
K_2SO_4	Mn	2.24	3.21	4.51	4.68	5.16	5.88	6.56	7.76	8.64	9.80
	Eh	622	642	620	680	636	622	605	579	543	587
KNO_3	Mn	1.18	1.42	2.30	2.02	2.30	2.62	2.96	3.26	3.10	3.10
	Eh	636	630	611	666	634	610	594	566	542	546

APPENDIX 10

Conditions, treatments, and results of experiment 13-68. Incubation conditions were 25°C, 21% O_2, and 22% soil moisture. Each salt was applied at the rate of 13.98 meq K/100g. The moist salt, 1968w, initially contained 0.590 meq Mn/100g and had a pH of 4.98 which changed to 0.823 meq Mn/100g and pH 5.05 after air-drying. Averages of two replications.

		Elapsed Time (days)					
		5		10		15	
Treatment	Soil pretreatment	meq Mn	pH	meq Mn	pH	meq Mn	pH
Control	moist	0.492	4.92	0.437	4.91	0.433	4.82
	air-dried	0.848	4.96	0.797	4.98	0.823	4.74
KCl	moist	0.671	4.09	0.692	4.14	0.809	4.06
	air-dried	0.911	4.00	1.062	4.04	1.155	3.94
K_2SO_4	moist	0.532	4.36	0.550	4.44	0.568	4.32
	air-dried	0.802	4.36	0.903	4.42	1.026	4.32

APPENDIX 11

Conditions, treatments, and results of experiment 14.68. A 0.1 gram of freshly precipitated Mn oxide was placed into a 1.0 ionic strength salt solution, buffered at given pH by HAc-NaAc. Solution Mn^{++} is an average of two replications in ppm, whereas Eh is the average of four readings (two per flask) in millivolts.

	Initial		Elapsed Time (days)					
Treatment	pH		0	1	2	7	14	22
Control	3.2	Mn	62	74	76	78	80	80
		pH	3.24	3.26	3.24	3.22	3.35	3.42
		Eh	534	615	617	597	594	600
KCl	3.2	Mn	86	84	94	104	95	96
		pH	3.26	3.60	3.55	3.51	3.64	3.66
		Eh	538	584	590	576	574	578
K_2SO_4	3.2	Mn	70	79	87	88	91	91
		pH	3.26	3.70	3.66	3.59	3.72	3.75
		Eh	542	591	590	580	576	580
Control	4.0	Mn	170	92	109	112	115	116
		pH	4.00	4.00	4.00	3.91	4.01	4.06
		Eh	508	555	563	555	551	555
KCl	4.0	Mn	84	94	102	102	108	108
		pH	4.00	4.30	4.25	4.21	4.34	4.37
		Eh	510	546	540	534	531	533
K_2SO_4	4.0	Mn	96	123	133	133	138	139
		pH	4.00	4.31	4.25	4.20	4.34	4.37
		Eh	510	551	544	539	536	540
Control	5.0	Mn	78	88	88	96	106	104
		pH	5.04	5.10	5.02	5.00	5.13	5.16
		Eh	451	494	470	473	469	467
KCl	5.0	Mn	72	81	89	104	114	113
		pH	5.05	5.40	5.36	5.30	5.43	5.45
		Eh	456	470	448	452	445	446
K_2SO_4	5.0	Mn	59	83	98	102	108	111
		pH	5.04	5.32	5.29	5.26	5.40	5.40
		Eh	457	471	442	453	493	445

APPENDIX 12

Analysis of variance for experiments 16-68, 17-68, 15-68, 18-68, 12-68, and 1-66. All times of sampling have been involved in the analyses including those observations for zero time. Analyses have only been performed on the extractable Mn or solution Mn variable.

Experiment	Source	d. f.	Mean square	F
12-68	Treatment	8	0.02757	10.43
(Appendix 2)	Time	3	0.06597	24.52
	Interaction	24	0.00182	0.68
	Error	36	0.00269	
16-68	Treatment	11	0.40505	403.00
(Appendix 3)	Time	3	0.31822	316.60
	Interaction	33	0.02088	20.78
	Error	48	0.00100	
17-68	Treatment	2	0.01084	25.61
(Appendix 4)	Time	3	0.01660	39.52
	Interaction	6	0.00144	3.43
	Error	12	0.00042	
15-68	Treatment	3	0.05826	93.97
(Appendix 5)	Time	3	0.00491	7.92
	Interaction	9	0.00908	14.64
	Error	16	0.00062	
16-68	Treatment	5	0.01981	76.19
(Appendix 6)	Time	3	0.03044	117.10
	Interaction	15	0.00058	2.23
	Error	24	0.00026	
1-66	Treatment	3	91.30	1660.00
(Appendix 9)	Time	9	8.38	152.36
	Interaction	27	1.89	34.36
	Error	39	0.055	