

FINAL REPORT (1989)

- 1. Title of Project: Influence of Potassium Chloride and Polyphenols on the Dynamics of the Release of Manganese from Soils
- 2. Project Leader: P.M. Huang
- 3. Location of Research: Department of Soil Science
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4. Objectives of the Study:

- (1) To investigate the effect of KCl on the release of Mn from a series of Mn-bearing minerals and representative soils from temperate and tropical regions.
- (2) To study the release of Mn from a series of Mn-bearing minerals in relation to their ability to catalyze the polymerization of polyphenols and the subsequent formation of humic substances.

5. Specific results and conclusions for each objective:

The dynamics of soil manganese and its availability to plants are determined by many factors including pH, Eh, the nature and concentration of cations and anions, clay mineralogical composition, and microorganisms (Barber, 1984). Fertilizer carriers containing Ca, K, Na, CO₃, or OH reduced Mn toxicity, whereas carriers containing Cl, SO₄, H, or Br increased toxicity (Cheng, 1981). Therefore, K and Cl should theoretically counteract in the soil Mn dynamics when potash is applied to soils as a K-fertilizer. However, it was reported that KCl increased Mn availability while other K salts viz., K₂SO₄ and K₂CO₃ had essentially no effect on the Mn uptake by plants (Westermann *et al.*, 1971). Much of the potentially available Mn in typical aerobic agricultural soils is in the form of Mn oxide minerals and Mn adsorbed on/or coprecipitated with hydrous oxides of iron. Soils developed under different pedogenic environments are, thus, expected to show a wide variation in the Mn release characteristics which affects the Mn availability to plants. No systematic attempt has so far been made to explain and quantify the soil Mn dynamics as influenced by KCl, one of the most commonly used potash fertilizers.

Polyphenols such as hydroquinone, resorcinol, and catechol and their derivatives are widely distributed in soils (Harborne and Simmonds, 1964; Hayes and Swift, 1978). The existing literature indicates that the oxidative polymerization of polyphenols by

manganese-bearing minerals is an important process in the formation of humic substances (Shindo and Huang, 1982, 1984). During the process, manganese-bearing minerals act as Lewis acids which accept electrons from polyphenols leading to their oxidative polymerization. Therefore, the solubility of soil manganese may be in part related to the extent of the catalytic reaction of soil manganese-bearing minerals in promoting the formation of humic substances.

The research highlights of the project are summarized as follows:

Soils representing different taxonomic orders

Mn release from fourteen soils representing seven taxonomic orders and collected from six countries in temperate, subtropical, and tropical regions increased 10 to infinite times, after 24 h reaction period, as the concentration of KCl increased from 0 to 0.01, 0.1, and 1.0 M. The Mn released by KCl was significantly correlated with the ionic strength, temperature (4, 25, and 44°C), and time of reaction (logarithm). Mn release from calcareous Vertisols was the lowest, even though the total Mn content of these soils was the highest among the soils studied. This could be attributed to the high soil pH (7.8-8.7). The Mn release from the soils followed a multiple zero order kinetics with at least three distinct reaction stages, namely, fast (0-1 h), medium (1-24 h), and slow (24-216 h). The rate constants of Mn release by M KCl during the fast reaction stage were 10-71 times and 62-785 times larger than those during the medium and slow reaction stages, respectively. The activation energy of Mn release varied from 2.9 to 28.1 kJ.mole⁻¹ among the soils, suggesting that the release is controlled by diffusion process. The differences in the amounts and rate constants of Mn release by M KCl from the soils studied is attributable to the nature of Mn-bearing minerals (the specific surface, crystallinity and crystal structure) present in these soils and the associated soil properties.

Soils from Indonesia and Oregon, U.S.A.

The kinetics of Mn release by M KCl from seven samples of two soil profiles (one each from Sialong and Beijangkar) of Indonesia and three samples of one soil profile

(Dayton, Oregon) of Northwestern U.S.A., supplied by the Potash & Phosphate Institute of Canada, was studied. The soils were reported to be Mn toxic to plants when Potash was applied as a K-fertilizer to the crops. The amounts of Mn release from the Ap horizon of the soils were 1.43 to 2.02 times higher than those from the soil samples from the B horizon, and was 2.86 to 10.18 times higher than those from the soil sample from the subsurface C horizon, of Sialong, Beijangkar, and Dayton soils. The Mn release by KCl from the soils increased with increasing KCl concentration and time and followed a multiple zero order kinetics with four distinct reaction stages, namely, fast (0-0.15 h), medium fast (0.15-1.0 h), medium (1-24 h) and slow (24-312 h) processes. The rate constants of Mn release by M KCl from the soil samples were greatly different and presumably reflect the divergent Mn mineralogy of these soils.

Selected Mn-bearing minerals and their size fractions

The Mn release from three selected Mn oxide minerals (pyrolusite, cryptomelane, and hausmannite), and two selected Mn-bearing minerals (manganite, and tephroite) was studied as a function of pH (4, 6 and 8), time of reaction (0-216 h), particle size (2-50 μm , and 50-100 μm) fractions, and concentration of KCl (0, 0.01, 0.1, and 1.0 M). The Mn release increased consistently with time and the ionic strength of KCl, and decreased with the increase in particle size and in pH. The Mn release with time obeyed a multiple zero order kinetics with four distinct reaction stages, namely, fast (0-0.25 h), medium fast (0.25-1 h), medium (1-24 h) and slow (24-216 h) processes.

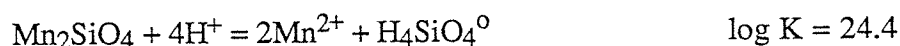
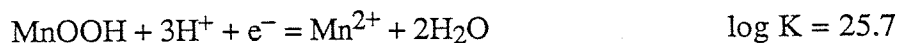
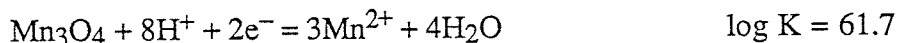
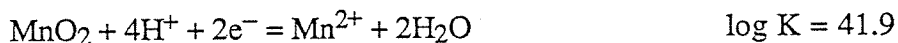
The differences in Mn release characteristics of the minerals were explained based on the surface properties, crystal structure, and atomic bonding of the minerals.

Mechanism of increase of Mn release by M KCl

The Mn-bearing minerals are unstable at the pH and Eh values of the systems studied. In aqueous solution, both Mn^{4+} and Mn^{3+} are unstable and rapidly disproportionate to the stable Mn^{2+} species. The increase in the dissolution of Mn-bearing minerals by KCl may proceed through complexation and ionic strength effects. The

reduction of Mn^{4+} to Mn^{2+} by Cl^- , as hypothesized by earlier workers, is not thermodynamically feasible under the experimental conditions.

Disproportionation in aqueous systems



Complexation:



Complexation of Mn^{2+} , which is released in aqueous system due to disproportionation, with Cl^- of KCl depletes the level of Mn^{2+} , resulting in an increased dissolution of Mn-bearing minerals.

Ionic strength of KCl

Theoretical calculations showed that the concentration of Mn(II) increased on an average 1.4 times as the ionic strength increased ten-fold in the KCl concentration range of 0.01M to 1.0 M.

The Mn release and soil Mn availability to plants can, thus, vary depending on the amount and nature of Mn-bearing minerals present in different mechanical size separates of soils. Further work on characterizing the Mn-mineralogy of the soils is in the progress.

Release of Mn by Polyphenols

The data obtained show that the release of Mn from birnessite ($\delta\text{-MnO}_2$) was enhanced by pyrogallol which is a common polyphenol in soils. Furthermore, the Mn release was related to the catalytic power of birnessite in the polymerization of pyrogallol. The humic polymers derived from pyrogallol resembled soil humic substances in IR and ^{13}C NMR CPMAS spectra.

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- Shindo, H. and P.M. Huang. 1982. Role of Mn(IV) oxides in abiotic formation of humic substances in the environment. *Nature* 298: 363-365.
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- Westermann, D.T., T.L. Jackson, and D.P. Moore. 1971. Effect of potassium salts on extractable soil manganese. *Soil Sci. Soc. Am. Proc.* 35: 43-46.

Publications arising from this project

Papers published

- G.S.R. Krishnamurti and P.M. Huang. 1988. Kinetics of manganese released from selected manganese oxide minerals as influenced by potassium chloride. *Soil Sci.* 146: 326-334.

Papers presented

- G.S.R. Krishnamurti and P.M. Huang. 1986. Kinetics of the release of manganese from selected manganese-bearing minerals as influenced by potassium chloride. Abstract p. 17. The 1986 Annual Meeting of the Canadian Society of Soil Science, Saskatoon, SK.
- M.C. Wang and P.M. Huang. 1986. Polyphenol transformations as catalyzed by oxides of Mn, Fe, Al and Si. The 1986 Annual Meeting of the Soil Science Society of America, Agronomy Abstracts. p. 173, New Orleans, LA.
- G.S.R. Krishnamurti and P.M. Huang. 1987. Influence of potassium chloride on the kinetics of Manganese release from soils representing different taxonomic orders. The 1987 Annual Meeting of the Soil Science Society of America, Agronomy Abstracts p.170, Atlanta, GA.
- G.S.R. Krishnamurti and P.M. Huang. 1988. Influence of pH and particle size on Mn release from selected crystalline Mn-bearing minerals by KCl. The 1988 Annual Meetings of the Soil Science Society of America, Agronomy Abstracts p.200, Anaheim, CA.

Ph.D. thesis

- M.C. Wang. 1987. Catalytic role of selected soil minerals in the abiotic formation of humic substances and the associated reactions. Ph.D. thesis, University of Saskatchewan, Saskatoon, SK.

6. Planned changes for next year: No
7. Can PPI/FAR cite data? Yes
8. Give a brief economic analysis of any observed response: Not applicable.
9. Please give a brief interpretive statement:

Potash applied to certain temperate and tropical soils enhances release of Mn which should make this essential micronutrient more available to plants. The response of soils to potash application in releasing Mn should vary with the nature and amounts of Mn-bearing minerals and associated soil properties which govern the dynamics of soil Mn. In addition, polyphenols are common in soils. Their role in releasing Mn from soils should not be overlooked.

KINETICS OF MANGANESE RELEASED FROM SELECTED MANGANESE OXIDE MINERALS AS INFLUENCED BY POTASSIUM CHLORIDE¹

G. S. R. KRISHNAMURTI² AND P. M. HUANG²

We studied the influence of KCl on the dynamics of Mn release from selected manganese oxide minerals. The release of Mn increased consistently with increasing concentration of KCl (0, 0.01, 0.1, and 1 M). As the concentration was increased from 0 to 1 M, the release in a 20-h reaction period at 297K increased 7.2, 2.9, and 1.6 times at pH 5.0 and 7.0, 2.0 and 1.4 times at pH 7.0 for pyrolusite, hausmannite, and cryptomelane, respectively. The release of Mn was attributed to the reduction and disproportionation of Mn(IV) and Mn(III) of the Mn oxides to Mn(II) in aqueous system, as confirmed by ESR spectroscopy, and to the subsequent formation of $MnCl^+$ complex in the KCl system. The Mn release was rapid initially (0 to 0.25 h) and then decreased subsequently (1 to 20 h), following a multiple zero-order kinetics. The rate constants of the Mn release are in the same order as the specific surface of the minerals, i.e., cryptomelane > hausmannite > pyrolusite. The kinetic data indicate that more than one factor controlled the Mn release from the three Mn oxide minerals. The dependence of Mn release on KCl concentration, temperature, and time was evaluated and an empirical equation was derived relating these variables. The results indicate that the Mn release varies with the nature of Mn-bearing minerals studied.

The dynamics of soil manganese and its availability to plants are determined by many factors including pH, Eh, the nature and concentration

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of cations and anions, clay mineralogical composition and microorganisms (Jackson et al. 1966; Dalal and Chatterjee 1970, 1971; Barea et al. 1971; Cheng 1972, 1982; Barber 1984). Some neutral salts, KCl, NaCl (York et al. 1954), and $CaCl_2$ (Foy 1964) have also increased the Mn availability and exchangeable Mn levels in soils. Fertilizer carriers containing Ca, K, Na, CO_3 , or OH reduced Mn toxicity; while carriers containing Cl, SO_4 , H, or Br increased toxicity (Cheng 1982). Further, KCl increased Mn availability while other K salts, viz., K_2SO_4 and K_2CO_3 , had essentially no effect on the Mn uptake by plants (Jackson et al. 1966; Westermann et al. 1971).

Much of the potentially available Mn in typical aerobic agricultural soils is in the form of Mn-oxide minerals and Mn adsorbed on or coprecipitated with hydrous oxides of iron (Hem 1963; Taylor et al. 1964, McKenzie 1977). Manganese-bearing minerals are fine grained and enriched in the 75- to 150- μm size fraction of the soils (Taylor et al. 1964). The influence of KCl on the release of Mn from soils could vary with the structure and chemical composition of manganese-bearing minerals as well as soil parent materials and pedogenic processes. Little is known of the influence of KCl on Mn release from Mn-bearing minerals. This paper reports the influence of KCl on the dynamics of Mn released from selected Mn-oxide minerals.

MATERIALS AND METHODS

Preparation and characterization of Mn-oxide minerals

Pyrolusite, hausmannite, and cryptomelane were prepared following the methods outlined by McKenzie (1971). The 50- to 100- μm particle size fraction of the minerals was obtained by wet-sieving (Jackson 1979). The x-ray powder diffraction patterns of the three Mn-oxide minerals were obtained using $Fe-K\alpha$ radiation (Phillips x-ray diffractometer Model PW 1310). The Mn-oxides were also characterized for surface area by the EGME method (Eltantawy and Arnold 1973) and cation exchange capacity by weighing-in the excess salts (Jackson 1979).

The infrared spectra of the minerals synthesized were taken (1 mg mineral/300 mg KBr) on a Perkin-Elmer infrared spectrophotometer Model 983.

Mn release

Fifty milligrams of each mineral, in duplicate, was suspended in 25 ml of deionized distilled water or KCl solution (concentration 0.01, 0.1, and 1 M), preadjusted to pH 5.0 or 7.0 (with 0.01 M HNO₃ or 0.01 M NH₄OH), in a 50-ml Pyrex tube. The suspension was shaken for a predetermined period (0.25, 0.5, 1.0, 5, 16, and 20 h) at different temperatures (277, 297, and 317 ± 1K) in a constant-temperature water bath. Air had free access to the suspension. At the end of each reaction period, the suspension was filtered under vacuum, using 0.45-μm nitrocellulose membrane. Manganese in the filtrate was measured by atomic absorption spectrophotometry. The pH and Eh of the suspension, before and after the reaction, were measured on a Fisher Acumet pH meter, Model 825 MP, using a pH combination electrode and a platinum combination electrode, respectively. The ESR spectra of the filtrates after the reaction were taken on a Bruker-Physik B-ER 418S EPR spectrometer in X band.

RESULTS AND DISCUSSION

Characterization of Mn-oxides

Cryptomelane (α-MnO₂). The x-ray diffraction pattern of the mineral showed a low degree of crystallinity with reflections at approximately 7.0, 4.9, 3.1, 2.4, 2.2, and 1.8 Å, which match well with the data for cryptomelane (ASTM 4-778; 20-908). The infrared spectrum of the mineral is characterized by absorption bands at 3419, 1621, 705, 530, and 480 cm⁻¹, which compare well with the data of Gadsden (1975) and Potter and Rossman (1979).

Pyrolusite (β-MnO₂). The x-ray diffraction pattern of the mineral showed a high degree of crystallinity with well-defined reflections at 3.12, 2.41, 2.12, 1.97, 1.63, 1.56, and 1.43 Å; these spacings match well with the data of pyrolusite (ASTM 24-735). The infrared spectrum of the mineral is characterized by absorption bands at 3441, 622, and 404 cm⁻¹, which compare well with the data of Gadsden (1975) and Potter and Rossman (1979).

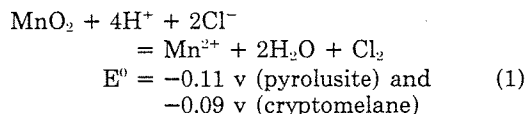
Hausmannite (Mn₃O₄). The x-ray diffraction pattern of the mineral gave well-defined sharp diffraction peaks at 4.93, 3.09, 2.89, 2.77, 2.50, 2.38, 2.04, 1.80, 1.58, and 1.54 Å, which match well with the data on synthetic hausmannite (ASTM 24-734). The infrared spectrum of the mineral showed strong absorption bands at 354, 418, 527, and 631 cm⁻¹, in addition to weak bands at 975, 1440, and 1660 cm⁻¹; these data are in agreement with Gadsden (1975).

Effect of KCl concentration and pH on Mn release

Appreciable amounts of Mn were also released from the minerals with deionized distilled water (Table 1). In a 20-h reaction period, Mn release was increased by 7.2, 2.9, and 1.6 times in pyrolusite, hausmannite, and cryptomelane, respectively, when the molarity of the KCl solution was increased from 0 to 1.0 M and the initial pH of the solution was adjusted to 5.0. The increase was 7.0, 2.0, and 1.4 times when the initial pH was adjusted to 7.0 (Table 1).

Stability relations of some Mn-oxide minerals as a function of Eh and pH, at a dissolved Mn²⁺ activity of 10⁻⁶ M are shown in Fig. 1 (after Bricker 1965). MnO₂ and Mn₃O₄ are unstable at the pH and Eh values of the Mn oxide-H₂O-KCl system studied. In aqueous solution, both Mn(IV) and Mn(III) are quite unstable, being easily reduced to Mn(II) (Baes and Mesmer 1976). These oxidation states rapidly disproportionate. In the measured Eh-pH range (Table 1), Mn(IV) and Mn(III) solution species can be neglected, since the Mn(II) species are the only stable Mn species. The dissolution of Mn from Mn oxides was evidently enhanced by KCl as shown in Table 1. This enhancement in the Mn release could proceed through oxidation-reduction, complexation, and ionic strength effects.

In the case of pyrolusite and cryptomelane, the reduction of Mn(IV) to Mn(II) by Cl⁻ is not thermodynamically feasible at standard conditions



On the other hand, the reduction of Mn(III) to Mn(II) by Cl⁻ is thermodynamically feasible in

TABLE 1

The amount of Mn released from selected Mn-oxide minerals as influenced by initial pH and KCl concentration after a 20-h reaction period at 297K

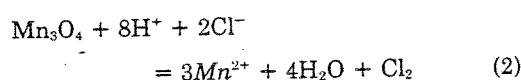
Mn-oxide mineral	Concentration of KCl, M	pH ^a		Final Eh, mv ^b	Mn released, mmol·kg ^{-1c}
		Initial	Final		
Pyrolusite	0	5.0	5.0	+725	0.7 ± 0.2
		7.0	6.4	+600	0.6 ± 0.2
	0.01	5.0	5.0	+740	1.8 ± 0.2
	0.1	5.0	5.0	+760	2.6 ± 0.3
	1.0	5.0	5.0	+850	5.3 ± 0.4
Hausmannite	0	7.0	6.0	+620	4.2 ± 0.4
		5.0	6.6	+450	6.0 ± 0.2
	0.01	5.0	6.6	+450	4.2 ± 0.2
	0.1	5.0	6.6	+450	6.8 ± 0.4
	1.0	5.0	6.7	+460	9.1 ± 0.9
Cryptomelane	0	7.0	6.7	+540	17.4 ± 0.9
		5.0	3.6	+940	8.3 ± 0.6
	0.01	5.0	3.4	+945	77.3 ± 2.5
	0.1	5.0	3.4	+950	94.6 ± 1.9
	1.0	5.0	3.4	+990	85.5 ± 1.6
		7.0	3.4	+975	103.7 ± 1.4
					121.0 ± 1.9
					134.7 ± 2.1

^a The precision of the pH measurements was ±0.1.

^b Initial E_h = +540 mv; the precision of E_h measurements was ±15 mv.

^c Average of duplicates.

the hausmannite system at standard conditions Eh = +0.50



$$E^0 = +0.50 \text{ v}$$

The E⁰ values for the reduction of pyrolusite and hausmannite were calculated using the free energy values of the oxides as given by Lindsay (1979), and the E⁰ value for cryptomelane used the free energy value provided by McKenzie (1972); the E⁰ value for the oxidation of Cl⁻ was obtained from Weast (1981).

To apply the above reactions to the systems studied, the Nernst equation was used and written for pyrolusite, cryptomelane, and hausmannite in Eqs. (3), (4), and (5), respectively.

$$\text{Eh} = -0.11$$

$$-0.0295 \log \frac{(\text{Mn}^{2+})(\text{H}_2\text{O})^2(\text{Cl}_2)}{(\text{MnO}_2)(\text{H}^+)^4(\text{Cl}^-)^2} \quad (3)$$

$$\text{Eh} = -0.09$$

$$-0.0295 \log \frac{(\text{Mn}^{2+})(\text{H}_2\text{O})^2(\text{Cl}_2)}{(\text{MnO}_2)(\text{H}^+)^4(\text{Cl}^-)^2} \quad (4)$$

$$-0.0295 \log \frac{(\text{Mn}^{2+})^3(\text{H}_2\text{O})^4(\text{Cl}_2)}{(\text{Mn}_3\text{O}_4)(\text{H}^+)^8(\text{Cl}^-)^2} \quad (5)$$

In calculating the Eh values, the following assumptions are made: (1) the activity of the Mn oxides is unity, (2) the activity of water in M KCl is 0.93 (Garrels and Christ 1965), (3) the activity of Cl₂ is 0.0061 (Westermann et al. 1971), (4) the activity of Cl⁻ in M KCl is 0.604 (Weast 1981), (5) the pH is 5.0, and (6) the activity of solution Mn²⁺ approximates the initial concentration of Mn at the 0.25-h reaction period (1.19 × 10⁻⁶, 3.44 × 10⁻⁵, and 4.57 × 10⁻⁶ M for pyrolusite, cryptomelane, and hausmannite, respectively). The Eh values calculated were -0.48, -0.50, and -0.17 v for pyrolusite, cryptomelane, and hausmannite, respectively. This would indicate that it is not feasible for Cl⁻ to reduce these oxides under the experimental conditions. Calculations also show that Cl⁻-induced reduction of the Mn oxides is not feasible at the initial pH of 7.

The ESR spectra of the supernatants after the reaction of the Mn oxides with water and

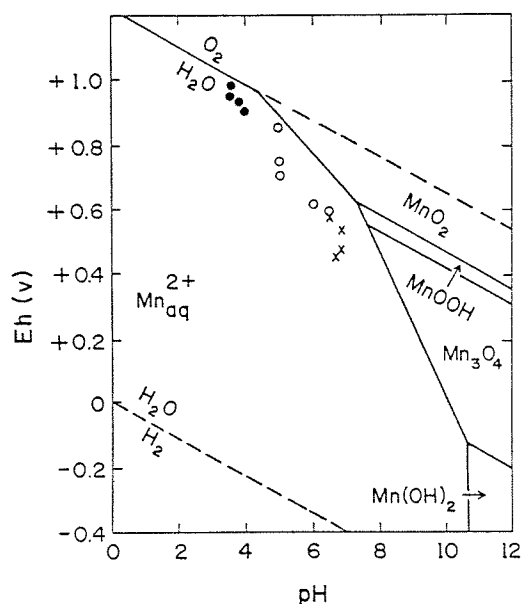
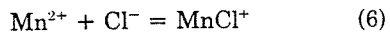


FIG. 1. Stability relations of MnO_2 , Mn_3O_4 , and Mn_{aq}^{2+} at 298K, 0.101 MPa, and $\alpha_{Mn^{2+}} = 10^{-6}$ (after Bricker 1965). The Eh-pH values of the respective Mn oxide-KCl suspensions of the present study are plotted: ● cryptomelane, × hausmannite, ○ pyrolusite. In some cases one plotting may represent more than one observation, because some of the Eh and pH values observed in the systems were identical or very similar (Table 1).

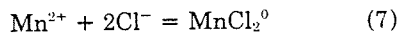
KCl solutions show the presence of Mn^{2+} species in solution as illustrated in Fig. 2 (the spectra for the cryptomelane system are given as an example). The g and hyperfine G values for Mn(II) in the supernatants compare well with the standard data of 2.007 and 95.2 G, respectively (Bielski and Gebicke 1967). The formation of Mn^{2+} species apparently proceeds through the reduction and disproportionation of Mn(IV) and Mn(III) of these oxides in aqueous systems (Baes and Mesmer 1976; Cotton and Wilkinson 1980). The release of Mn through the dissolution of these oxides was enhanced in the KCl system through complexation and ionic strength effects as discussed below.

The formation of the $MnCl^+$ and $MnCl_2^0$ complexes through the reaction of Mn^{2+} with Cl^- is thermodynamically feasible, as shown in Eqs. (6) and (7)



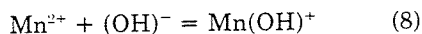
$\log K_{MnCl^+} = 1.10$ (Bixler and Larson 1974), 0.61 (Lindsay 1979), and 1.03 (calculated from

crystal radii, Mittigod and Sposito 1977)



$\log K_{MnCl_2^0} = 0.04$ (Lindsay 1979)

These complexation reactions would compete with the formation of $Mn(OH)^+$ which is also thermodynamically feasible, as shown in Eq. (8)



$\log K_{MnOH^+}$

$= 3.4$ (Mattigod and Sposito 1977)

The computer program GEOCHEM (Sposito and Mattigod 1979), as modified by Parker et al. (1987), was used to calculate the proportion of different Mn species present in solution in the MnO_2 -KCl systems. The program incorporates the effect of the ionic strength, complexation, and the equilibrium pH. The data calculated at pH 5.0 and the pe + pH value of 14 are shown in Table 2 as an example. Based on $\log K_{MnCl^+} = 0.61$, the % Mn bound with Cl^- increased 22.8 times as the KCl concentration increased from 0.01 M to 1.0 M. This increase would deplete the level of Mn^{2+} , resulting in an increased dissolution of the Mn oxides.

The sole effect of ionic strength on the dissolution of Mn oxides through the reduction of Mn(IV) and Mn(III) to Mn(II) in the aqueous system was significant. The concentration of Mn(II) at different ionic strengths in the aqueous system was calculated for the three oxides using the activity coefficients of Mn^{2+} (Sposito and Traina 1987) and water (Garrels and Christ 1965) and the free energy values of the oxides (Lindsay 1979; McKenzie 1972). The calculations show that the concentration of Mn(II) increased on an average 1.4 times as the ionic strength increased 10-fold, in the concentration range of 0.01 to 1.0 M, at both the pH values of 5 and 7 (the effect of complexation was not considered in the calculations).

Murray reported (1975) that the sorptive capacity of hydrous Mn-dioxide for the Mn^{2+} ion is considerably greater than for any other divalent ions studied. The sorption of Mn^{2+} ion by the hydrous Mn-oxide surface results in the release of protons to solution, which would further promote the reduction of Mn(IV) in the Mn oxides to Mn(II) through the consumption of protons. The release of protons to solution in the case of cryptomelane, with high specific

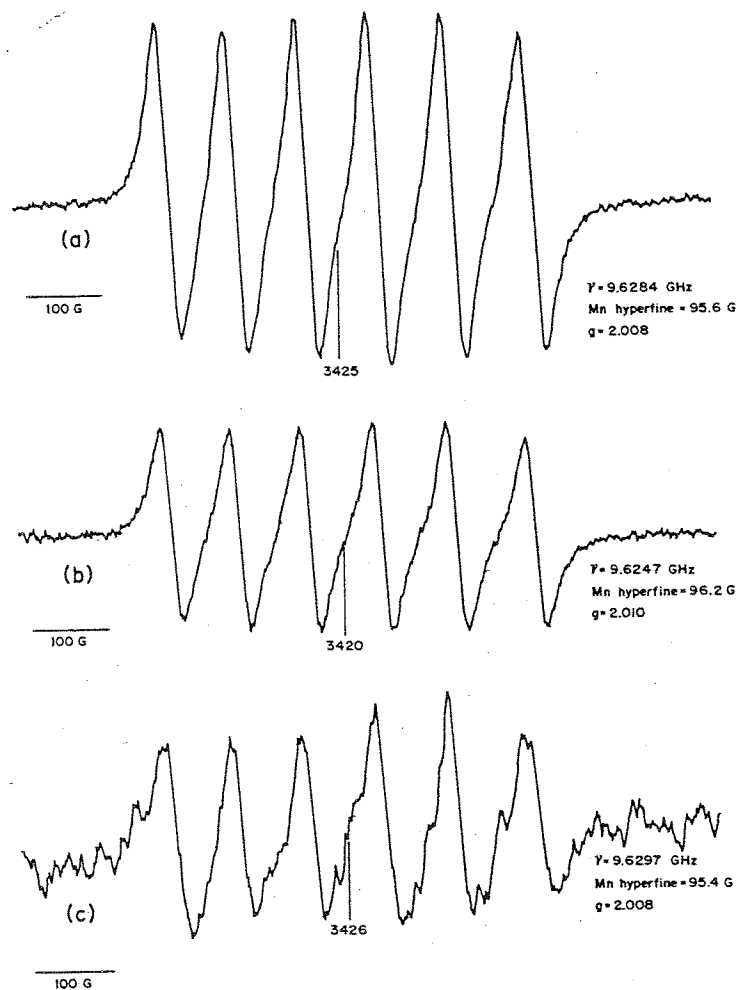


FIG. 2. ESR spectra of Mn(II) in solution: (a) MnCl_2 solution, (b) cryptomelane-water and (c) cryptomelane-*M* KCl solution (pH 5.0; reaction time 20 h). (The Mn released from cryptomelane is shown as an example.) The precision of g values is ± 0.002 .

surface ($475 \text{ m}^2/\text{g}$, Table 5), was substantial, resulting in a considerable decrease of pH (Table 1), whereas the increased consumption of the protons by hausmannite during the reduction of Mn(IV)/Mn(III) in the Mn-oxide to Mn(II) (Eq. (2)) offset the release of protons upon the adsorption of Mn^{2+} , resulting in an increase in pH from the initial pH of 5.0 (Table 1). In the case of pyrolusite, with low specific surface ($39 \text{ m}^2/\text{g}$, Table 5), a slight decrease or no change in pH was observed (Table 1). These changes in the final pH of the reaction also would influence the Mn release from the oxides.

The variation of the release of Mn from the Mn-oxides to the solution with different kinds of chloride salts at the same level of Cl^- (Table 3) may be due to the influence of ion exchange or the differences in the ionic strengths of the

solutions used. The Mn release by Ca and Mg chlorides was substantially higher than that released by Na, NH_4 , or K chloride. The Mn release by chlorides was in the order $\text{Na} \approx \text{NH}_4 \approx \text{K} < \text{Ca} \approx \text{Mg}$.

Effect of time and temperature on Mn release

Manganese was released to solution, in increasing quantities, with time both in water and in *M* KCl solution (Table 4). The kinetics of Mn release by KCl followed a multiple zero-order reaction

$$(\text{Mn}) = C - kt$$

where (Mn) and C are the concentration (mmol/kg) of Mn remaining in the Mn-oxides at time = t and time = 0, respectively, and k is

TABLE 2

Proportion of different species of Mn formed in the MnO₂-KCl system at pH 5.0 and $pe + pH = 14$ and different KCl concentrations (final concentration of total Mn in solution = 1×10^{-6} M)^a

KCl	Concentration, M			Mn ²⁺ % distribution	Mn bound with Cl % distribution
	Mn ²⁺	MnCl ⁺	MnCl ₂ ⁰		
0.01	9.74 ± 10^{-7}	2.61×10^{-8}	5.69×10^{-11}	97.4	2.6
0.10	8.70×10^{-7}	1.28×10^{-7}	1.97×10^{-9}	87.0	13.0
1.0	4.07×10^{-7}	5.34×10^{-7}	5.96×10^{-8}	40.7	59.3

^a GEOCHEM (Sposito and Mattigod 1979) as modified by Parker et al (1987) was used in the computation; the Mn(OH)⁺ species are negligibly small ($<10^{-12}$ M) and thus are not shown. The redox reaction illustrated is $MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$ ($\log K = 42.0$). The stability constants used: $\log K_{MnCl^+} = 0.61$ and $\log K_{MnCl_2^0} = 0.04$ (Lindsay 1979). The values of % distribution of Mn bound with Cl, which were calculated based on $\log K_{MnCl^+} = 1.10$ (Bixler and Larson 1974), are 7.7, 31.3, and 80.7, respectively, at 0.01, 0.10, and 1.0 M KCl.

TABLE 3

Effect of chloride salts on the Mn release from selected Mn-oxides at 297K and a reaction time of 20 h

Salt solution ^a	Ionic strength	Mn released, mmol kg ⁻¹			LSD $p = 0.05$
		Pyrolusite	Hausmannite	Cryptomelane	
M NaCl	1.0	4.2	9.9	109.2	4.3
M NH ₄ Cl	1.0	4.4	10.2	113.7	3.9
M KCl	1.0	5.3	17.4	121.0	5.0
0.5 M CaCl ₂	1.5	7.6	25.2	169.2	10.2
0.5 M MgCl ₂	1.5	9.2	26.8	187.2	13.0
LSD $p = 0.05$		1.0	2.0	6.0	

^a pH of salt solution was adjusted to 5.0 initially.

TABLE 4

Time function of Mn release from selected Mn-oxide minerals as influenced by M KCl (pH was adjusted to 5.0) at 297K

Time, h	Mn released, mmol kg ⁻¹			LSD $p = 0.05$
	Pyrolusite	Hausmannite	Cryptomelane	
0.25	2.9 (0.27) ^a	11.1 (3.2)	83.7 (68.2)	3.1 (2.0)
0.50	3.5 (0.30)	12.7 (3.4)	90.1 (69.2)	2.8 (2.5)
1.0	3.8 (0.36)	13.7 (3.7)	96.5 (70.1)	2.9 (2.5)
5.0	4.2 (0.46)	14.6 (4.5)	103.7 (71.9)	2.8 (2.6)
16.0	4.9 (0.63)	16.7 (5.5)	111.9 (75.5)	3.8 (3.2)
20.0	5.3 (0.73)	17.4 (6.0)	121.0 (77.3)	5.1 (4.0)
LSD $p = 0.05$	0.1 (0.01)	0.3 (0.1)	6.3 (2.0)	

^a The values inside the parentheses refer to the Mn released by deionized distilled water (pH 5.0).

the rate constant (mmol kg⁻¹ h⁻¹). The rate curves for the release of Mn from the Mn-oxides exhibited two distinct reaction rates; namely, the rapid (0 to 0.25 h) and slow (1 to 20 h) release reactions (Fig. 3). Many investigators have reported multiple rates in kinetic studies involving heterogeneous systems (Mortland 1958; Jurinak and Griffin 1972; Oscarson et al. 1983). The rate constants of the Mn release were calculated (Table 5) from the slopes of the

straight lines obtained by linear least-squares analysis of the data; the r^2 values vary between 0.86 and 0.99, significant at $p < 0.001$.

The rate constant for the zero-order reaction is numerically equal to the amount of Mn released per unit time; k , therefore, is a measure of the relative rate of the release of Mn from the mineral surface. During the rapid reaction, the rate constants of Mn release for pyrolusite are 3.7 and 27.8 times (with M KCl) and 12.6 and

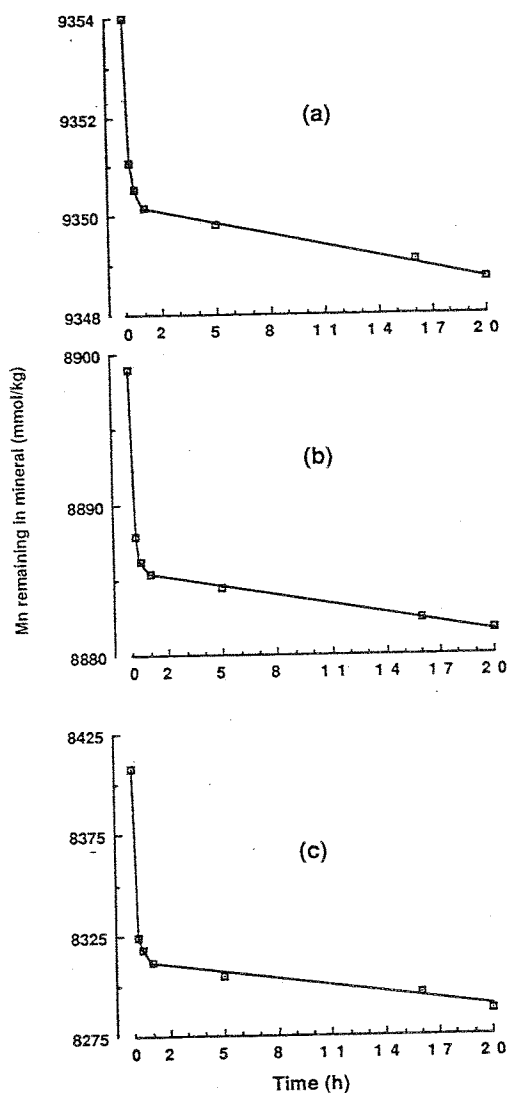


FIG. 3. Rate curves of Mn release from Mn oxides by M KCl (pH 5.0) at 297K. (a) pyrolusite, (b) hausmannite, and (c) cryptomelane (the LSD is given in Table 4).

273.0 times (with water) less than those from hausmannite and cryptomelane, respectively. During the slow reaction, the corresponding values are 2.6 and 16.4 times (with M KCl) and 5.5 and 18.5 times (with water). This is attributed to the relatively low specific surface (Table 5) and high crystallinity of pyrolusite. In the rapid reaction, the KCl solution increased the rate constants of Mn release by 12.0, 3.5, and 1.2 times, respectively, for pyrolusite, cryptomelane, and hausmannite, whereas in the slow reaction the rate constants were increased by 3.5, 1.6, and 3.1 times, respectively.

The effect of temperature on Mn release from the Mn-oxide minerals was studied at 277, 297, and 317K and at the end of a 20-h reaction period (Table 6). The data show the trend that the Mn release from the Mn-oxides both in the absence and presence of KCl (in the concentration range studied) increased with increasing temperature. Therefore the data indicate that the kinetics of Mn release in soils may vary with seasonal temperature fluctuations.

Multiple regression analysis

Manganese release from the individual Mn oxide minerals as influenced by KCl in the systems studied is a function of a number of independent variables, i.e., molarity of KCl, pH (Table 1), time (Table 4), and temperature (Table 6). Manganese release from each Mn-oxide mineral at the same initial pH of the KCl solution can be represented as

$$R = f(M, T, t)$$

where R is the mmol of Mn released per kg of mineral, M the molar concentration of KCl solution, T temperature in K, and t time in h.

The simple regression analysis of the experimental data on the Mn release from the Mn-oxide minerals indicated that, at the same initial

TABLE 5
Specific surface and CEC (at pH 7.0) of the Mn-oxide minerals and rate constants of the Mn release from the Mn-oxides by M KCl (pH was adjusted to 5.0)

Mn-oxide mineral	Mn content, mmol kg ⁻¹	Specific surface, m ² /g	CEC, cmol kg ⁻¹	Rate constants			
				M KCl		Water	
				Rapid reaction	Slow reaction	Rapid reaction	Slow reaction
				mmol kg ⁻¹ h ⁻¹			
Pyrolusite	9354 ± 16	39 ± 2	2.0 ± 0.1	12 ± 2	0.07 ± 0.01	1.0 ± 0.1	0.02 ± 0.01
Hausmannite	8899 ± 15	143 ± 10	4.0 ± 0.1	44 ± 5	0.18 ± 0.02	12.6 ± 1.5	0.11 ± 0.02
Cryptomelane	8408 ± 15	475 ± 15	11.9 ± 0.3	333 ± 10	1.15 ± 0.04	273 ± 10	0.37 ± 0.04

pH of the KCl solution, Mn release correlated significantly with the square root of molarity of KCl solution, temperature in K and logarithm of time in h. A multiple regression analysis of the data show that 89 to 97% of the Mn release by KCl from the three Mn-oxide minerals studied can be explained by considering the effect of concentration of KCl, temperature, and time of reaction (Table 7). However, the relative importance of the factors in affecting the release of Mn from cryptomelane is different from pyrolusite and hausmannite. The beta coefficients (standard regression coefficients, Snedecor and Cochran 1980), which are given in parentheses under the respective factors in the equations (Table 7), show that the concentration of KCl solution is 3.30, 3.29, and 1.01 times more important than temperature and 3.02, 2.90, and

1.29 times more important than time in pyrolusite, hausmannite, and cryptomelane, respectively.

CONCLUSIONS

The data reported in this study clearly show the relative importance of molarity of KCl solution, temperature, and time in influencing the release of Mn from individual Mn-oxide minerals. Furthermore, the influence of KCl on the kinetics of Mn release varied with the kind of the Mn-oxide minerals. A detailed study of the nature and amounts of Mn-bearing minerals present in soil environments and the response of these minerals to KCl application with respect to the Mn release is essential to quantify the amount and rate of Mn release from soils and their availability to plants.

TABLE 6

Effect of KCl on Mn release from selected Mn-oxide minerals at different temperatures and at the end of a 20-h reaction period

Temperature, K	Concentration of KCl, M ^a	Mn released, mmol kg ⁻¹			LSD p = 0.05
		Pyrolusite	Hausmannite	Cryptomelane	
277	0	0.4	4.9	61.9	2.8
	0.10	1.8	7.5	81.9	2.9
	1.0	3.6	13.1	101.9	5.2
297	0	0.7	6.0	77.3	3.2
	0.01	1.8	6.8	85.5	4.2
	0.10	2.6	9.1	103.7	4.7
317	1.0	5.3	17.4	121.0	5.2
	0	1.5	7.8	106.8	3.5
	0.10	4.1	12.2	142.1	5.7
	1.0	5.7	21.1	156.5	7.0
LSD p = 0.05		1.1	2.1	6.1	

^a KCl solution (0, 0.01, 0.1, and 1.0 M), which was adjusted to pH 5.0 with 0.01 M HNO₃, was added to the Mn-oxides.

TABLE 7

Multiple regression analysis on the Mn release from selected Mn-oxide minerals as a function of KCl concentration (at pH 5.0), temperature, and reaction time

Mn-oxide	Regression equation ^a	Multiple correlation coefficient
Pyrolusite	$R = -13.282 + 3.585 M^{1/2} + 0.045 T + 0.756 \log t$ (0.912) (0.276) (0.302)	0.977 ^b
Hausmannite	$R = -35.399 + 10.223 M^{1/2} + 0.130 T + 2.242 \log t$ (0.918) (0.279) (0.317)	0.987 ^b
Cryptomelane	$R = -328.031 + 32.148 M^{1/2} + 1.332 T + 15.965 \log t$ (0.602) (0.595) (0.470)	0.945 ^b

^a R stands for the Mn release (mmol kg⁻¹), M for KCl concentration (M), T for temperature (K), and t for time of reaction (h). Beta coefficients are presented inside the parentheses.

^b Significant at p < 0.001.

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