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Effect of Potassium Salts on Extractable Soil Manganese[1]

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ABSTRACT

Incubation experiments with an acid, poorly drained soil (Typic Albaqualf) showed that the level of extractable Mn was increased by salt treatments. The relative order of the salt effect was KBr > KCl > KNO_3 > K_2SO_4. Soil pH changes accounted for the majority of the KNO_3 and K_2SO_4 treatment effects, but the KCl and KBr effects could not be explained on this basis. In addition, ionic strength considerations and differential biological activities were not found to be factors influencing the K salt effects in the soil system. A hypothesis is presented to explain the KCl or KBr effect, in which the anion would function in an oxidation-reduction reaction. This hypothesis is supported by the fact that the soil treated with KBr contained more extractable Mn than that treated with KCl, in accordance with theory. Theoretical calculations also suggested the possibility that both Cl^- and Br^- could reduce the lower valency Mn oxides under the experimental soil conditions.

Additional Key Words for Indexing: **pH effect, redox reactions.**

RESEARCH emphasis regarding Mn availability has generally been placed on those materials that cause a pronounced change in soil pH, thereby changing soil Mn availability; however, some neutral salts, KCl, NaCl (York, Bradfield, and Peech, 1954), and $CaCl_2$ (Foy, 1964), have increased the Mn content of plants and the exchangeable Mn levels in acidic soils (Foy, 1964). Hamilton (1966) found a positive correlation between Cl^- concentration and Mn uptake by oats. The Cl salts also increased the Mn content of bush beans and sweet corn more than SO_4 and CO_3 salts in an acidic soil such that Mn toxicity symptoms were present in the Cl salt treatments (Jackson, Westermann, and Moore, 1966).

The earlier study by Hamilton and Lathwell (1965) showed that Cl salts were more effective than other salts in increasing the diffusion of soluble Mn^{2+} away from fertilizer bands of either $Ca(H_2PO_4)_2$ or $(NH_4)_2HPO_4$. These salts also diminished the pH in the layer of soil around the $Ca(H_2PO_4)_2$; however, no relationship was found between the salt-associated soil pH and the amount of soluble Mn.

These results indicate that the effect of Cl^- on soil Mn availability is different from the effect of other anions in certain agricultural soils. The following research was conducted to determine the magnitude and mechanism(s) of the Cl^- effect on the level of extractable Mn.

EXPERIMENTAL METHODS AND MATERIALS

These studies were conducted on the surface horizon (0–20 cm) of a Dayton silt loam (Typic Albaqualf, depositional planosol; Parsons and Balster, 1967). This soil is naturally acid, with pH values from 4.5 to 5.3, and is waterlogged from midfall to midspring. It also contains numerous Fe-Mn concretions. Chemical characterization (Alban and Kellogg, 1959) was made of the two bulk soil samples; the oxidized sample was taken in the fall of 1967, and the reduced sample in the winter of 1968 (Table 1). Extractable Mn in the oxidized sample is similar to that expected in these soils in late spring, whereas the extractable Mn level in the reduced sample is similar to that found under the reducing conditions of winter (Oregon Agr. Exp. Sta., 1967).

All bulk soil samples were air dried to 10 to 15% moisture, passed through a 0.64-cm screen, and stored in plastic-lined containers. Very little moisture was lost during storage, however, extractable Mn levels changed slightly.

Dry K salts, at concentrations of 0.9, 3.5, and 14.0 meq/100 g of soil, were mixed with 300 g of soil in 1-liter Erlenmeyer flasks. Soil moisture was adjusted to field capacity (24%); the flasks were plugged with cotton, shaken daily after the initial 24 hr to ensure aeration, and incubated in a 25C water bath. Distilled water was added as necessary to maintain soil moisture at field capacity. Soil samples were taken from duplicate flasks for analyses after 0, 5, 10, and 15 days of incubation.

All soil pH measurements were made on a 1:2 soil-water suspension one-half hour after thoroughly mixing. Manganese was extracted from 10 g of soil with three successive 30-ml portions of 1*N* $Mg(NO_3)_2$. The individual portions were filtered, combined, and diluted to 100 ml with the extractant. The Mn extracted by this method was determined directly by atomic absorption. A preliminary study indicated that a HNO_3-$HClO_4$ digestion of the extract was not necessary for complete Mn recovery by atomic absorption.

A sterile soil system was prepared by adding 2 ml of propylene oxide to 25 g of soil (oven-dried basis) at 10 to 15% moisture in a 125-ml Erlenmeyer flask. The flasks were stoppered with cotton plugs, covered with Gladwrap, and placed in a 27C water bath for 48 hr, after which the Gladwrap was removed. The residual propylene oxide vapors were then removed by increasing the water bath temperature to 45C for 48 hr, after which the incubation experiments began. (The use of specific brand names is for the information of the reader. No endorsement by USDA of the named product is intended or implied.)

The salt materials were dry sterilized at 180C for 3 hr and added to the soil system after completion of the soil sterilization procedure to avoid possible propylene oxide-salt interactions. Sterilized distilled water was added as needed to maintain soil moisture.

Two flasks of each treatment were removed at each sampling and were tested for sterility before the chemical measurements were made. Sterility was evaluated by inoculating duplicate nutrient-broth tubes with 0.3 to 0.5 g of soil from each flask and incubating the tubes for 10 days at 25C.

RESULTS

Effect of K Salts on Extractable Mn

Levels of extractable Mn were increased by all salts in both the oxidized and reduced soil samples (Fig. 1 and 2). The levels continued to increase in the soils treated with KCl, KNO_3, or KBr up to at least 15 days; whereas the

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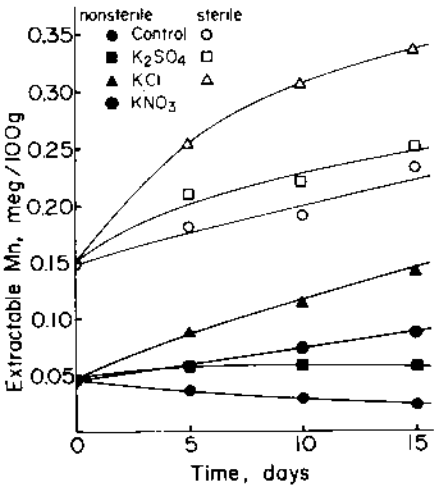

Fig. 1—The effect of selected K salts on 1*N* $Mg(NO_3)_2$ extractable Mn in a sterile and nonsterile oxidized soil. Salt concentration was 14.0 meq K/100 g. LSD (5%) = 0.01, 0.02, 0.02 and 0.07, 0.03, 0.02 meq Mn/100 g for comparisons of treatment effects at 5, 10, and 15 days for the nonsterile and sterile soil systems, respectively.

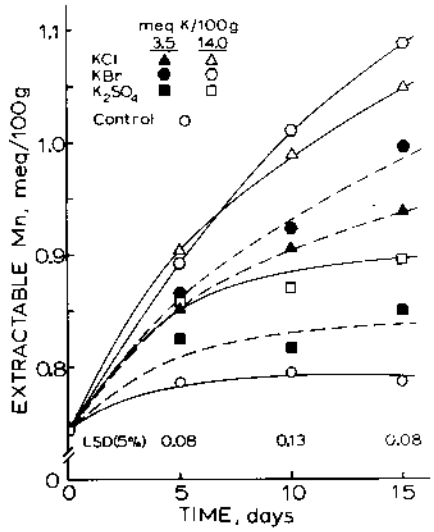

Fig. 2—The effect of KCl, KBr, and K_2SO_4 on 1*N* $Mg(NO_3)_2$ extractable Mn at two salt concentrations in the reduced soil sample.

majority of the K_2SO_4 effect occurred within the first 5-day incubation period. Increasing the salt concentrations from 3.5 to 14.0 meq/100 g also increased the level of extractable Mn (Fig. 2). Even at the lower salt concentration, 0.9 meq/100 g of soil, all salt treatments contained more extractable Mn than the control treatment at all sampling intervals (data not shown). Measurements of extractable Mn after 20 days' incubation in the nonsterile oxidized soil showed that all the treatment effects continued for that period.

It was initially postulated that the salt effects found in the oxidized soil sample would not be present in the reduced sample. However, it appears that the relative effects of the salt treatments were similar in both nonsterile soils (Fig. 1 and 2), even though the initial level of extractable Mn was nearly 16 times greater in the reduced sample (Table 1).

Biological Effects

The addition of the salt materials could have had at least two beneficial effects on the Mn-reducing organisms. First, the salt materials could have influenced the relative distribution of the Mn-reducing and oxidizing organisms as suggested by Timonin (1950, 1965). Secondly, Mn oxidation may have been reduced by the salts since the intensity of Mn oxidation by organisms increases with pH in the range of 4.8 to 8.9 (Dhawan, Singh, and Bhatnagan, 1950).

Table 1—Chemical characteristics of the bulk laboratory soil samples at the time of field sampling

Soil sample*	pH	P†	Exchangeable cations K	Mg	Ca	Mn	CEC
		ppm	meq/100 g				
Oxidized	5.8	22.5	0.53	2.3	6.8	0.05	12.0
Reduced	4.8	10.0	0.20	1.3	3.0	0.79	11.5

* Soil samples taken in the fall and winter months, respectively. The oxidized sample had been previously limed and fertilized. (Both soil samples contained 0.120% total Mn.)

† $NaHCO_3$ extractable.

Soil sterilization caused an increase in the extractable Mn levels in all treatments (Fig. 1); however, the relative differences between treatments in the sterile soil system were similar to those in the nonsterile soil system. The extractable Mn levels continued to increase in the KCl treatments; however, the relative differences between the K_2SO_4 and control treatments remained nearly constant after 5 days in either system. The authors are not aware of a suitable explanation for the increase in extractable Mn with time in the sterilized K_2SO_4 and control treatments, except for continued solubilization of Mn oxides by residual propylene oxide and/or enzymatic release of Mn from organic bound forms. Biological recontamination was not detected in any of the sterilized treatments and thus a chemical mechanism(s) must be responsible for the salt effects in this well-aerated soil system.

Chemical Effects

Soil pH's were decreased immediately upon the addition of the salts and changed very little during incubation (Table 2). The pH's of the KCl-, KBr-, and KNO_3-treated soils were very similar and were generally 0.3 pH unit lower than the K_2SO_4-treated soil at equivalent salt concentrations. Similar pH differences between K salts have been observed by Chao, Harward, and Fang (1965). Since extractable Mn was inversely related to soil pH

Table 2—The effect of K salts and salt concentration on soil pH

Soil	Treatment	Added K salt concentration	Elapsed incubation time, days 0	5	10	15
		meq/100 g	pH			
Oxidized	Control	--	5.56	5.42	5.36	5.29
	KCl	14.0	--	4.65	4.74	4.65
	KNO_3	14.0	--	4.66	4.58	4.66
	K_2SO_4	14.0	--	4.90	4.98	4.89
Reduced	Control	--	5.12	5.08	5.14	5.05
	KBr	3.5	--	4.30	4.29	4.26
		14.0	--	4.08	4.10	4.04
	KCl	0.9	--	4.63	4.70	4.58
		3.5	--	4.34	4.34	4.32
		14.0	--	4.06	4.12	4.08
	K_2SO_4	0.9	--	4.66	4.66	4.72
		3.5	--	4.54	4.56	4.56
		14.0	--	4.34	4.38	4.41

(Fig. 1 and 2, and Table 2) and since the solubilities of the Mn oxides are pH dependent, experiments were conducted where the initial treatment pH was adjusted to determine if the salt-associated pH differences were responsible for the extractable Mn differences.

Acidifying the K_2SO_4-treated soil with 0.1*N* H_2SO_4 to the same soil pH as in the KCl or KNO_3 treatment increased its extractable Mn level to that of the KNO_3 treatment but not to that of the KCl treatment (Fig. 1, nonsterile soil). The extractable Mn level in the pH-adjusted K_2SO_4 treatment was significantly greater than that found in the unadjusted treatment after 10 and 15 days of incubation.

The salt-associated pH differences then appear to be responsible for the majority of the extractable Mn differences between K_2SO_4 and KNO_3. This salt-associated pH difference did not, however, entirely account for the greater extractable Mn levels found in the KCl- or KBr-treated soils, since the pH's of the KCl, KNO_3, and KBr treatments were equivalent within a given soil and salt concentration (Table 2). It was also found that there were no significant differences in the extractable Mn levels between the KNO_3, K_2SO_4, and control treatments up to 15 days of incubation when their soil pH's were equivalent (Westermann, 1969).

Increasing the relative ionic strength of the soil-salt system to 0.633 or 0.942 with K_2SO_4 failed to significantly increase the extractable Mn levels up to 15 days of incubation when the treatment pH's were equivalent to that of the control (data not shown). The lack of difference between the KNO_3 and pH-adjusted K_2SO_4 treatments is also additional evidence that the ionic strength effect was not significant in these soil-salt systems. The apparent lack of an ionic strength effect may have been related to nonequilibrium conditions in the soil-salt system since the effect of K salts on the equilibrium solubility of some selected Mn oxides in solution was partially related to ionic strength and to the ability of the anion to complex Mn^{2+} (Westermann, 1969).

DISCUSSION AND CONCLUSIONS

The KNO_3 and K_2SO_4 salt effects are primarily related to salt-associated pH changes. This pH effect did not, however, account for the extractable Mn differences between the KCl and KNO_3 treatments. Neither ionic stength nor biological activity was found to have a significant influence. This would indicate that another mechanism was responsible for the Cl^- effect.

One possible mechanism by which a Cl salt might influence soil Mn availability would be through oxidation-reduction reactions. Halide influence on Mn^{2+} oxidation in soils has been studied by Sherman, McHargue, and Hageman (1943). They added Mn^{2+} to both an alkaline (pH 7.4) and a high Mn-acidic soil (pH 4.1). The oxidation of the added Mn^{2+} was increased by F^- in both soils and by Br^- and I^- in the alkaline soil, while Cl^- had no influence on Mn^{2+} oxidation in either soil.

Direct evidence supporting a Cl-Mn oxide redox hypothesis in soil systems is difficult to obtain because of the physical problems involved and because of the mixed chemical state of Mn in the soil. The redox potentials (Table 3) show that there is an increasing thermodynamic tendency for the halide electrode to give up electrons going from F^- to I^-. If the higher extractable Mn level in the presence of the Cl salt resulted from a redox mechanism, then the application of a Br or I salt should release more extractable Mn than the Cl salt.

Table 3—Standard oxidation potential of selected reactions*

Reaction			E*, volts
γ-MnO_2 (Nautite)			
$2\ MnO_2 + 4\ H^+$	$\rightarrow$	$2\ Mn^{2+} + 2\ H_2O + O_2$	0.043
$MnO_2 + 4\ H^+ + 2\ Cl^-$	$\rightarrow$	$Mn^{2+} + 2\ H_2O + Cl_2$	-0.086
$MnO_2 + 4\ H^+ + 2\ Br^-$	$\rightarrow$	$Mn^{2+} + 2\ H_2O + Br_2$	0.207
γ-Mn_2O_3			
$4\ MnOOH + 8\ H^+$	$\leftrightarrow$	$4\ Mn^{2+} + 6\ H_2O + O_2$	0.215
$2\ MnOOH + 2\ H^+$	$\leftrightarrow$	$MnO_2 + Mn^{2+} + 2\ H_2O$	0.314
$2\ MnOOH + 6\ H^+ + 2\ Cl^-$	$\rightarrow$	$2\ Mn^{2+} + 4\ H_2O + Cl_2$	0.184
Bixbyite			
$Mn_2O_3 + 6\ H^+ + 2\ Cl^-$	$\leftrightarrow$	$2\ Mn^{2+} + 3\ H_2O + Cl_2$	0.085
$Mn_2O_3 + 2\ H^+$	$\rightarrow$	$MnO_2 + Mn^{2+} + H_2O$	0.225
γ-Manganite			
$2\ MnOOH + 6\ H^+ + 2\ Cl^-$	$\rightarrow$	$2\ Mn^{2+} + 4\ H_2O + Cl_2$	0.135
Mn_3O_4 (Hausmannite)			
$Mn_3O_4 + 8\ H^+ + 2\ Cl^-$	$\rightarrow$	$3\ Mn^{2+} + 4\ H_2O + Cl_2$	0.456
$Mn_3O_4 + 4\ H^+$	$\leftrightarrow$	$MnO_2 + 2\ Mn^{2+} + 2\ H_2O$	0.526
Halides			
$2\ F^-$	$\leftrightarrow$	$F_2 + 2\ e^-$	-2.87
$2\ Cl^-$	$\rightarrow$	$Cl_2 + 2\ e^-$	-1.36
$2\ Br^-$	$\leftrightarrow$	$Br_2 + 2\ e^-$	-1.06
$2\ I^-$	$\leftrightarrow$	$I_2 + 2\ e^-$	-0.54

* The half-cell potentials for the Mn oxides were calculated from the free energy values given by Bricker (1965). All other half-cell potentials and free energy values were taken from Handbook of Chemistry and Physics, 40th Edition. 1959.

The standard oxidation potentials for the reactions of Cl^- with γ-Mn_2O_3, bixbyite, γ -manganite, and hausmannite indicate that Cl^- can reduce these oxides under standard state conditions (Table 3). Since standard state conditions are not directly applicable to soil systems, it would be informative to apply these reactions to a soil system by the use of the Nernst equation. The following reaction:

$$Mn_3O_4 + 8\ H^+ + 2\ Cl^- \leftrightarrow 3\ Mn^{2+} + 4\ H_2O + Cl_2$$

was chosen for this illustration since the reduction of this oxide by Cl^- has the greatest feasibility (Table 3) and it is one of the first Mn oxides to form in an oxygenated chemical system (Bricker, 1965). The Nernst equation would then appear as

$$E = 0.456 - 0.0295 \log \frac{(\alpha_{Mn^{2+}})^3\ (\alpha_{H_2O})^4\ (\alpha_{Cl_2})}{(\alpha_{Mn_3O_4})\ (\alpha_{H^+})^8\ (\alpha_{Cl^-})^2}$$

where E is the calculated oxidation potential in volts.

Making the assumptions that (i) the activity of the solid Mn oxide is unity; (ii) the water-soluble Mn^{2+} in the soil

approximates the initial activity of Mn^{2+} (6.34×10^{-7}); (iii) an activity of 0.0061 for Cl_2 (saturated aqueous solutions at 25C contain 0.061 moles per liter of Cl_2, the actual activity of Cl_2 may be very much smaller in the soil system); (iv) adjustment of the activity of water for the dissolved salts; (v) activity of Cl^- as 0.633 (initial molar concentration); and (vi) a soil pH of 4.0, results in a calculated E value of 0.113 volts. This would indicate that it is feasible for Cl^- to reduce this oxide under these soil conditions. A similar treatment shows that Br^- could also reduce this oxide and γ-Mn_2O_3 under the same assumed conditions. It should be emphasized that these calculations only give the thermodynamic tendency and do not give any information on the kinetics of the reaction.

An additional factor to consider is that pure Mn oxides or hydroxides have rarely been found as secondary minerals in soils (Taylor, McKenzie, and Norrish, 1964). Nodules of MnO_2 admixed with Fe oxides have frequently been found on the floors of ocean basins and as coatings on clays and other minerals (Hem, 1963). The existence of Mn oxides as amorphous coatings on other minerals may facilitate their reduction by Cl^- or Br^-. Westermann (1969) reported that air drying the soil to less than 5% moisture before the salt treatment removed the differential effect of the salts. Drying may be considered as a process which speeds up the rate of aging of the hydrous oxides by removing adsorbed water and by disproportionation of the lower Mn oxides to MnO_2 and Mn^{2+} (Table 3). This would suggest that the form of Mn sensitive to Cl^- is a poorly crystalline hydrous oxide.

The majority of the experimental observations indicate that the Cl^- effect is observed in acidic soils (Foy, 1964; Hamilton, 1966; Cheng and Ouellette, 1968), and since liming has been shown to reduce the differential effects of the anions on Mn uptake by plants (Jackson, Westermann, and Moore, 1966), it would appear that the Cl^- effect is dependent upon the initial soil pH. In weakly acidic and neutral soils, the salt-associated pH decrease may not be great enough to facilitate the Mn oxide reduction by Cl^-. Under the previously assumed soil conditions, a Cl^- reduction of Mn_3O_4 would not be feasible at pH 5.0. The effect of salt concentration would be primarily through its effect on soil pH. Increasing the salt concentration results in a lower soil pH, increasing the probability of a Cl^- effect. The salt concentrations that were used in this study would closely approximate that concentration around a fertilizer band. The Cl^- effect on Mn uptake by plants has not been observed where the Cl salt was broadcast on an acidic soil. (Unpublished data, 1966. T. L. Jackson, Soils Dept., Oregon State Univ., Corvallis, Ore. 97331.)

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