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The Adsorption of Lead and Other Heavy Metals on Oxides of Manganese and Iron

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Abstract

Measurements were made of the adsorption of cobalt, copper, manganese, nickel, lead, and zinc on nine synthetic manganese oxides and three synthetic iron oxides, to determine the mechanism by which lead accumulates in the manganese oxides in soils.

Adsorption of lead by the manganese oxides was up to 40 times greater than that by the iron oxides, and lead was adsorbed more strongly than any of the other ions studied by all of the oxides except goethite. This is considered to be the reason for the accumulation of lead in the manganese oxides in soils. No evidence was found for the oxidation of lead, nor for the formation of specific lead-manganese minerals.

Introduction

Lead has been shown to accumulate in the manganese oxides in soils (Taylor and McKenzie 1966; Norrish 1975), and the addition of manganese dioxide to soils contaminated with lead reduces the uptake of lead by plants (McKenzie 1978).

There are three possible mechanisms to account for the binding of lead by oxides of manganese, viz.

(*a*) strong specific adsorption;

(*b*) a special affinity for oxides of manganese, as found for cobalt (McKenzie 1970, 1975), with the possibility of oxidation of the lead; or

(*c*) the formation of some specific lead–manganese mineral such as coronadite.

Results in the literature do not resolve these possibilities. Van der Weijden and Kruissink (1977) found that lead was sorbed more strongly than barium on birnessite, but the reverse was the case with a poorly crystalline cryptomelane. Gadde and Laitinen (1974) found adsorption in the order lead > zinc > cadmium on amorphous hydrous oxides of iron and manganese, and Forbes *et al.* (1976) found that adsorption on goethite decreased in the order copper > lead > zinc > cobalt > cadmium.

In view of the current concern over lead in the environment, it is of considerable interest to determine the relative importance of these three mechanisms. The present work attempts to do this by comparison of the adsorption of lead with that of cobalt, copper, manganese, nickel and zinc on nine synthetic manganese oxides and three synthetic iron oxides.

Materials

The synthetic oxides were prepared by the following methods.

B9. Birnessite. Bubble oxygen through a suspension of manganese hydroxide in a large excess of potassium hydroxide. Then add nitric acid to pH 7·5. Surface area 75 m^2/g, zero point of charge (ZPC) 2·4.

B36. Birnessite. As for *B9*, adding nitric acid to pH 6·5. Surface area 100^2 m/g. This sample contained some hausmannite.

B14. Birnessite. Add hydrochloric acid to a hot solution of potassium permanganate. Surface area 32 m^2/g, ZPC 2·0.

B38. Birnessite. As for B14. This sample was washed with 0·05 M perchloric acid, and then with water. Surface area 98 m^2/g, ZPC 1·8. This oxide was stored as a suspension in water.

C17. Cryptomelane. Ignite a preparation similar to B14 for 4 h at 400°C. Surface area 58 m^2/g, ZPC 2·0.

C15. Fine-grained cryptomelane. Pour a hot solution of potassium permanganate into a hot solution of manganese sulfate in 2 N acetic acid. Surface area 220 m^2/g, ZPC 2·2.

C37. Fine-grained poorly crystalline cryptomelane. As for C15. Surface area 206 m^2/g.

ρ-MnO_2. Dissolve a birnessite containing potassium in cold concentrated hydrochloric acid. Filter into a large volume of water. Surface area 178 m^2/g, ZPC 3·5.

γ-MnO_2. Disproportionation of hausmannite at pH 1·5. Surface area 122 m^2/g.

Goethite. Add ammonium hydroxide to a solution of ferric chloride to pH 8. Filter and wash the precipitate, add potassium oxide to pH 12 and age at room temperature. Surface area 75 m^2/g, ZPC 7·6.

Hematite. Add ammonium hydroxide to a solution of ferric chloride to pH 7·5. Filter and wash precipitate, add hydrochloric acid to pH 4 and age at 60°C. Surface area 20 m^2/g, ZPC 7·0.

Magnetite. Precipitate with ammonium hydroxide from a solution containing 84·5 g of $FeSO_4.7H_2O$ and 293 g of $NH_4Fe(SO_4)_2.12H_2O$ in 4 l. of water. This preparation contained a small amount of goethite. Surface area 85 m^2/g, ZPC 6·2.

Further details of the preparation of the first eight manganese oxides, and of the hausmannite used for the preparation of γ-MnO_2 were given by McKenzie (1971). All of the oxides were thoroughly washed with water and dried at 45°C, with the exception of B38, which was stored as a suspension in water. The oxides were identified by X-ray diffraction using iron Kα radiation for the manganese oxides, and surface areas were determined by adsorption of nitrogen gas at the temperature of liquid nitrogen. Zero points of charge were measured by a salt titration method.

Methods

Adsorption experiments were carried out in air in 50 ml Polythene centrifuge tubes, with a final suspension of 0·1 g of oxide in 20 ml of 0·1 M potassium nitrate containing the desired concentration of adsorbate ion. The tubes were stoppered and shaken for 24 h. It was found to be necessary to make periodic adjustments to the pH throughout this period to maintain the desired value. Because desorption is slow and incomplete, pH adjustments were made only in an upward direction, using small volumes of potassium hydroxide that did not significantly alter the total volume.

After equilibration, the suspensions were centrifuged and the supernatant solution was analysed by atomic absorption spectroscopy.

The amounts of H^+ released during adsorption were measured by titrating suspensions with 0·1 M potassium hydroxide to maintain constant pH during addition of the sorbate. The suspensions were prepared and allowed to stand for several days to stabilize the pH and rehydrate the surface before the addition of the sorbate. Suspensions of 0·2 g of oxide in 20 ml of 0·25 M potassium nitrate at pH 4 were used for the manganese oxides, using additions of 0·5 and 1·0 mmol/g of lead, copper or manganese, and 0·5 mmol/g of zinc. For the iron oxides, 1 g of oxide in 50 ml of 0·2 M potassium nitrate was used, and triplicate measurements were made at pH 5, with additions of 0·05 mmol/g of lead or copper. Manganese released during the adsorption of lead, copper or zinc was determined in the same experiments by measurement of the amount of manganese appearing in solution (McKenzie 1979).

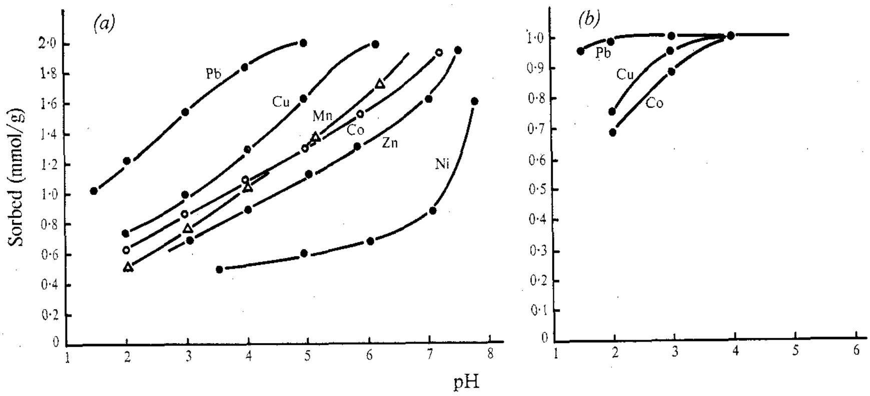

Fig. 1. Adsorption *v.* pH on birnessite B38. (*a*) 2 mmol/g added; (*b*) 1 mmol/g added.

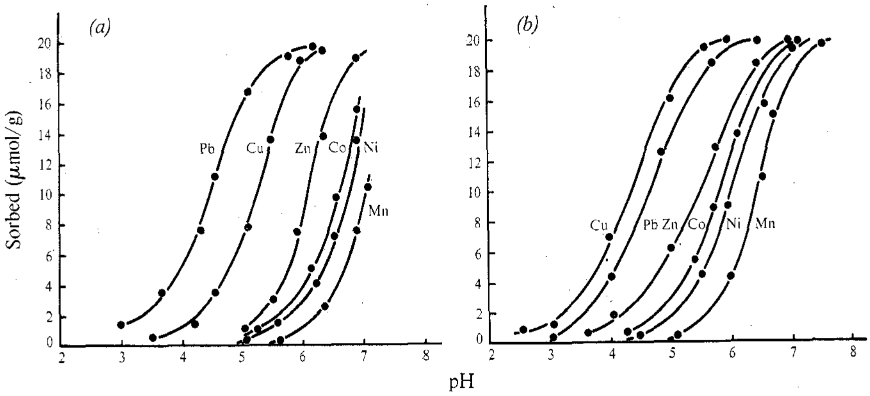

Fig. 2. Adsorption *v.* pH on iron oxides, 20 μmol/g added. (*a*) Hematite. (*b*) Goethite.

The amounts of adsorbed lead and copper extractable by 2·5% acetic acid, and the effect of aging on the extractability were also measured. Similar amounts of copper or lead were allowed to adsorb on 0·1 g aliquots of various oxides at pH 5·5, and the oxides were then washed with water, and stored wet for various periods.

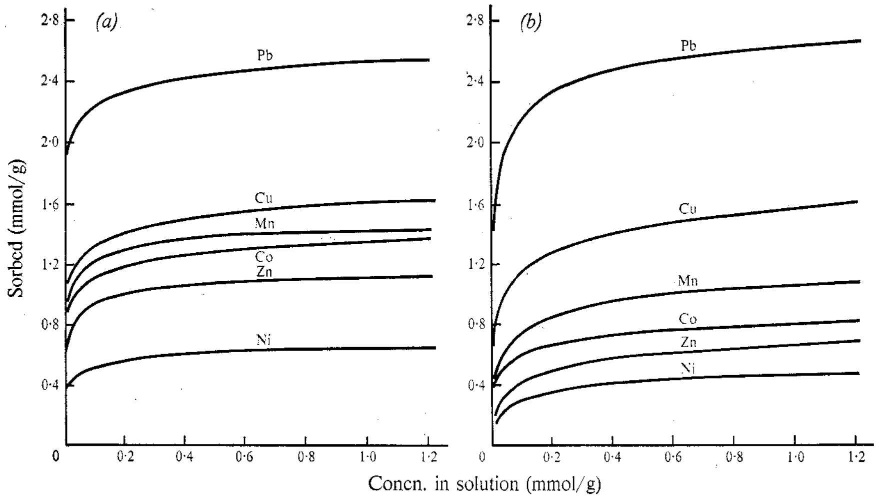

Fig. 3. Adsorption isotherms for manganese oxides. (*a*) Birnessite B38. (*b*) Cryptomelane C37.

The adsorbed ions were then extracted by shaking overnight with 20 ml of 2·5% acetic acid, followed by a second extraction for 2 h with a further 20 ml of acetic acid.

Results

Adsorption v. pH

The effects of pH on adsorption are shown in Fig. 1 for birnessite B38, and in Fig. 2 for hematite and goethite. The amounts of the metal ions added were 2 mmol/g (Fig. 1*a*) and 1 mmol/g (Fig. 1*b*) for the birnessite, and 20 μmol/g for the iron oxides (Fig. 2). The curves for the iron oxides show that an increase of 2 pH units resulted in an increase in adsorption from a low value to 100% of the amount added. The

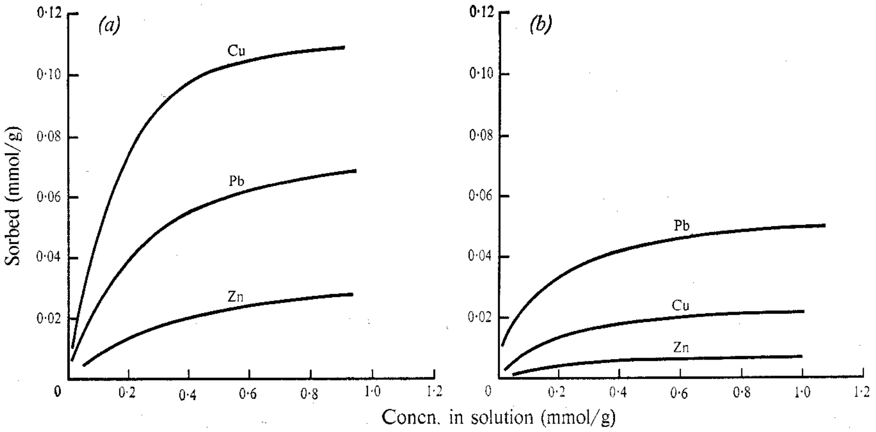

Fig. 4. Adsorption isotherms for iron oxides. (*a*) Goethite. (*b*) Hematite.

curves were of similar shape to hydrolysis curves, but were displaced towards lower pH. The slope of the curves for birnessite (Fig. 1*a*) were much lower, and considerable adsorption occurred at the ZPC (pH 1·8).

Copper was adsorbed by goethite more strongly than lead, in agreement with Forbes *et al.* (1976), but the other oxides adsorbed lead more strongly. Over the pH range of Fig. 2, the amount of lead adsorbed by hematite was greater than that by goethite, whereas all of the other ions were more strongly adsorbed by goethite.

Lead was very strongly adsorbed by the birnessite B38, and when a smaller amount of lead was added (Fig. 1*b*), 95% was adsorbed at pH 1·5.

The curves for manganese and cobalt on birnessite (Fig. 1*a*) cross at pH 4·5, so that at low pH, the adsorption of cobalt exceeds that of manganese.

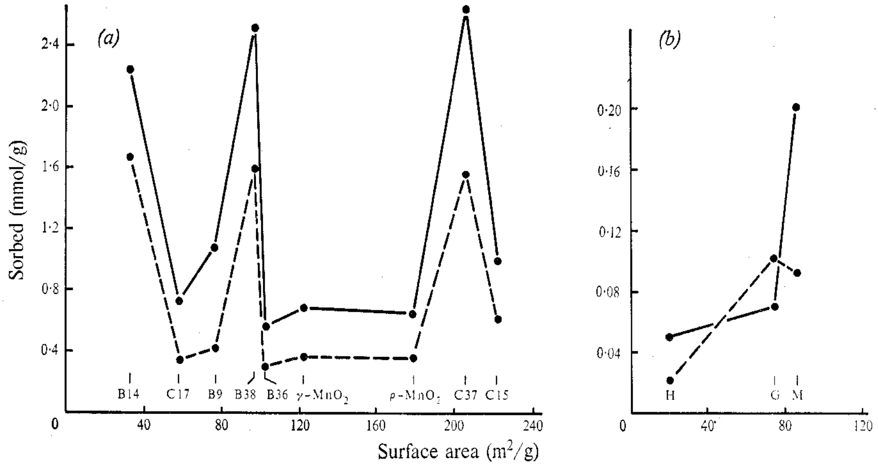

Fig. 5. Adsorption of lead and copper *v*. surface area. ——— lead; - - - - copper. (*a*) Manganese oxides. (*b*) Iron oxides. H, hematite; G, goethite; M, magnetite.

Adsorption Isotherms

Adsorption isotherms at pH 5·0 for birnessite B38 and cryptomelane C37 are shown in Fig. 3, and for hematite and goethite in Fig. 4. Isotherms for magnetite were similar to those for hematite, and those for the other seven manganese oxides were similar to those in Fig. 3, differing only in the amount adsorbed. These isotherms also show that goethite was the only oxide in which the adsorption of lead was less than that of copper. Comparison of the isotherms for lead on goethite and hematite shows that lead is adsorbed more strongly by goethite above a concentration of 10^{-4} M lead in solution, and more strongly by hematite below this concentration. This supports the similar conclusion drawn from the curves of adsorption *v*. pH in Fig. 2.

Although cobalt was sorbed by the manganese oxides less strongly than manganese (Fig. 3), this order was reversed when the concentration of adsorbing ions was less than about 10^{-6} M.

Adsorption v. Surface Area

The amounts of lead and copper adsorbed by all of the oxides at a solution concentration of adsorbing ions of 10^{-3} M (at which adsorption is near the maximum) are plotted against surface area in Fig. 5. The results for the iron oxides, in conjunction with those in Figs 2 and 4, suggest that the reversal of the usual order of adsorption of copper and lead on goethite was due to depression of the lead adsorption on goethite.

Adsorption by the manganese oxides (Fig. 5*a*) showed no tendency to increase with surface area, and the adsorption of copper remained roughly proportional to that of lead. Three of the oxides showed outstandingly high adsorption. Samples C37 and C15 are both fine-grained cryptomelane of similar surface areas, prepared by the same method, yet adsorption on C37 was more than double that on C15. Similarly, the birnessites B14 and B38, prepared by reduction of potassium permanganate with hydrochloric acid, sorbed more than twice as much as the birnessites B9 and B36, prepared by oxidation of manganese hydroxide. The adsorption density is equivalent to one Pb^{2+} ion to 13 $Å^2$ in C37, to 6·3 $Å^2$ in B38, and to 2·4 $Å^2$ in B14. This is close to monolayer cover of the unhydrated Pb^{2+} ion (ionic radius 1·20 Å) in B38, but is a considerable excess over monolayer cover in B14. Adsorption of the Pb^{2+} ion with its first hydration sphere [$r(Pb^{2+})+2r(H_2O) = 3{\cdot}96$ Å], as was suggested by James and Healy (1972), would give an excess over monolayer cover in all of the manganese oxides used here. This excess would range from slight in β-MnO_2 to very large in B14.

Table 1. Fractions of adsorbed metals not extractable by $2\frac{1}{2}$% acetic acid

Oxide	Metal adsorbed	Amount adsorbed (mmol/g)	Non-extractable after 1 day (%)	Non-extractable after 28 weeks (%)
B36	Pb	0·20	93·0	99·6
B36	Cu	0·21	19·6	37·7
B38	Pb	1·0	91·8	98·7
B38	Cu	0·91	47·9	62·1
C17	Pb	0·20	89·8	95·3
C17	Cu	0·20	18·6	28·9
C37	Pb	1·0	90·8	98·5
C37	Cu	0·96	45·8	61·0
Hematite	Pb	0·054	43·6	62·0
Goethite	Pb	0·051	9·7	18·5

Extractability of Adsorbed Ions

Table 1 shows that a very high proportion of the lead adsorbed on the manganese oxides was not extractable by 2·5% acetic acid, and this proportion increased further on aging. On the other hand, a large part of the adsorbed copper remained in an extractable form, even after aging. Compared with goethite, a higher proportion of the lead sorbed on hematite was fixed in a non-extractable form, and this further emphasizes the differences between these two oxides.

Release of Protons during Adsorption

The ratios of moles of H^+ released per mole of metal ion adsorbed are shown in Table 2. The concurrent release of Mn^{2+} from the manganese oxides was less than 0·05% of the amount of metal ion adsorbed. Table 2 shows that the ratio H^+ released/M^{2+} adsorbed was close to 1 for the birnessites, but higher than that for the cryptomelanes. To confirm that the difference between these two oxides was due to their different crystal structure, some of the birnessite B38 was boiled in water for 4 h, when its recrystallization to cryptomelane was confirmed by X-ray diffraction. Measurements of H^+ released were then repeated, and the results in the bottom row of Table 2 show that the ratios then agreed with those for cryptomelane. The values for birnessite are in agreement with those given by Murray (1975*a*). The ratios for the iron oxides ranged from 1·3 to 2, somewhat lower than those of 1·8–2 reported by Forbes *et al.* (1976) for goethite.

Table 2. Ratio moles H^+ released/moles metal ion adsorbed
(SD of determination 0·05)

Sample	Moles H^+ released/moles M^{2+} adsorbed Lead	Copper	Manganese	Zinc
Birnessite (B38)	1·00	1·07	1·14	1·02
Birnessite (B36)	1·11	0·99	1·23	1·19
Cryptomelane (C15)	1·34	1·60	1·71	1·63
Cryptomelane (C37)	1·31	1·48	1·46	1·36
Cryptomelane (B38 boiled)	1·27	1·50	1·62	1·61

X-ray Diffraction

Some of the manganese oxides were examined by X-ray diffraction before and after various treatments with 0·01 M lead nitrate or copper chloride solutions.

Birnessite B36 contained birnessite and hausmannite. After soaking in lead nitrate for 4 months, the intensities of all of the lines were reduced, but the basal spacings at 7·30 and 3·57 Å were reduced in intensity more than the weaker lines at 2·45 and 1·43 Å. Boiling the product after soaking in lead nitrate caused the appearance of some amorphous material.

Birnessite B38 had broader lines in the X-ray pattern, showing it to be finer-grained than B36. After soaking for 3 days in lead nitrate solution, the basal spacings disappeared completely, but the other two weaker lines were only slightly reduced in intensity. After a similar treatment in cupric chloride solution, the basal spacings were slightly reduced in intensity, but the other lines were unchanged from the original material.

Cryptomelane C15. The crystallinity of this sample was unchanged by 3 days' soaking in solutions of lead nitrate or cupric chloride.

Cryptomelane C37 was a very poorly crystallized cryptomelane with some amorphous material. After soaking for 3 days in lead nitrate, the diffraction lines almost completely disappeared, and the background due to amorphous material was also reduced. This was unchanged after soaking for 4 months, or by boiling the material after prolonged soaking. Treatment with cupric chloride for 3 days produced no changes in the diffraction pattern.

None of these treatments produced diffraction lines which were not present in the original materials.

Discussion

Figs 1 and 2 show that all of the metal ions were more strongly adsorbed on the manganese oxides than on the iron oxides, but the adsorption of manganese and cobalt increased more than that of the other ions, so that these two ions occupied a higher position in the series on the manganese oxides. Also, a colour change from brown to black was observed in the manganese oxides after adsorption of cobalt or manganese, which was not evident with the other ions studied. These observations show that there is a special affinity between these ions and the manganese oxides. The special features of the adsorption of cobalt by the manganese oxides have been discussed by McKenzie (1970), Loganathan and Burau (1973), Murray (1975*b*) and Burns (1976). Posselt *et al.* (1968) suggested that the greater affinity of the hydrous manganese oxides for the manganous ion was due to its oxidation according to the reaction

$$Mn^{2+}+MnO_2+2H_2O \rightarrow 2MnOOH+2H^+ \qquad \Delta G = 9 \cdot 58 \text{ kcal/mole}, \qquad (1)$$

from which it is calculated that

$$\log[Mn^{2+}] = 7 \cdot 02 - 2\text{pH}.$$

(Free energy data used in calculations for this and subsequent equations were those tabulated by Hem (1978). The birnessite value was used for manganese dioxide.) This reaction could reduce the activity of Mn^{2+} to 57 ppm at pH 5. However, two moles of H^+ should appear in solution for each mole of Mn^{2+} reacted. The results in Table 2 show that, although the adsorption of manganese may release a little more H^+ than does that of the other ions, this reaction could occur to only a very limited extent, and does not account for the relatively high amount of adsorption that occurred.

In contrast to the adsorption of cobalt and manganese, there does not appear to be a special affinity between lead and the manganese oxides beyond strong specific adsorption. With the exception of goethite, the adsorption of lead was about double that of copper for all of the oxides studied. Furthermore, the parallel between lead and copper adsorption by the manganese oxides in Fig. 5 shows that there is no special affinity between lead and any particular oxide of manganese.

Gadde and Laitinen (1974) considered that some oxidation of lead could occur by the reaction

$$MnO_2+Pb^{2+} \rightarrow Mn^{2+}+PbO_2 \qquad \Delta G = 7 \cdot 68 \text{ kcal/mole} \qquad (2)$$

in spite of the unfavourable free energy change. A further possibility for oxidation is by the reaction

$$2MnO_2+Pb^{2+}+2H_2O \rightarrow 2MnOOH+PbO_2+2H^+ \qquad \Delta G = 17 \cdot 3 \text{ kcal/mole}. \qquad (3)$$

The unfavourable free energy changes for these reactions as written do not necessarily mean that the lead could not be oxidized, since the oxidized lead is unlikely to be in the form of solid lead oxide, but in some form of adsorbed lead(IV), for which the free energy is unknown. However, the first reaction requires the dissolution of one mole of Mn^{2+}, and the second requires 2 moles of H^+ to appear in solution, for each mole of lead adsorbed. Since only a very small amount of Mn^{2+} was dissolved and only one mole of H^+ appeared in solution per mole of lead adsorbed on birnessite (Table 2), oxidation of the lead could not have occurred to any extent.

No diffraction spacings belonging to coronadite or any other lead–manganese mineral were observed during these experiments, although this does not preclude the possibility of the formation of such minerals after prolonged aging in the soil. However, the results of the present experiments and the fact that lead is fixed rapidly by manganese dioxides in soils (McKenzie 1978) suggest that fixation is due to strong specific adsorption over a wide range of pH, rather than to any special reaction such as oxidation of the lead or the formation of specific minerals.

At low concentrations, lead was adsorbed more strongly by hematite than by goethite, and the results in Table 1 show that the lead adsorbed on hematite was much less extractable by acetic acid than that on goethite. This suggests that hematite in soils is likely to act as an important sink for lead. Although the capacity of some of the manganese oxides was about 40 times that of hematite, the latter occurs in soils in much higher concentrations, and is generally more dispersed.

Three of the manganese oxides showed exceptionally high adsorption capacities for all of the ions. The birnessites B14 and B38, prepared by reduction of potassium permanganate had capacities of two to four times those of the birnessites B9 and B36, prepared by oxidation of manganese hydroxide. Previous work (McKenzie 1971, 1977) has shown that birnessite prepared by oxidation of manganese hydroxide consisted of thin platelets about 3–4 μm in size, whereas those prepared by reduction of potassium permanganate consisted of aggregates of much smaller platelets. The present X-ray diffraction results also show that the particle size of B38 is smaller than that of B36. Such differences in particle size have little effect on the surface area of thin platelets, and these two oxides had similar surface areas. Adsorption of lead would be expected to reduce the intensity of the X-ray diffraction patterns due to the increased mass absorption coefficient, but after making allowance for this it is seen that the basal spacings were completely destroyed in B38, but only partly destroyed in B36, whereas the weaker lines at 2·45 and 1·43 Å were virtually unchanged. These latter two lines are characteristic of δ-MnO_2, a cryptocrystalline, structurally disordered form of birnessite. Birnessite has a layer structure, and it is evident that lead was able to penetrate completely into the interlayer regions in B38, degrading it to δ-MnO_2, but was only able to penetrate to a limited extent into the much larger platelets of B36. This explains the higher adsorption capacities of samples B14 and B38, and also explains the fact that the adsorption capacity of B14 was greater than that required for monolayer cover of the surface. Penetration of the basal spacings of B38 by copper was less pronounced, in accordance with the smaller amount of copper adsorbed.

The cryptomelanes C37 and C15 were prepared by the same method, and had similar surface areas, but C37 adsorbed more than twice as much copper and lead as C15. Adsorption of lead had no effect on the diffraction pattern of C15, but in C37, which adsorbed much more lead, the diffraction lines almost completely disappeared. This sample was very poorly crystalline, and the diffraction lines were weak. Since the background due to amorphous material also disappeared, the effect was probably due to absorption of the diffracted beam by the high lead content of the sample (54% lead, based on the original weight of sample). The reason for the higher adsorption by C37 is not clear. Cryptomelane has a framework structure, so that penetration of interlayer regions is not possible, while entry of lead into the potassium sites would be expected to give the pattern of coronadite. Furthermore, sample C37 also has a high capacity for all of the other ions, which are much too small to fit into the potassium sites. Davis and Leckie (1978) presented some evidence to suggest that the BET method underestimated the surface area of amorphous iron oxyhydroxide, and it is possible that in the present case, the surface area of the poorly crystalline C37 has been underestimated, in contrast to the well crystallized C15, Forbes *et al.* (1976) calculated an order of affinity, at zero sorption, of heavy metal cations for the goethite surface which decreased in the order lead > copper > zinc > cobalt > cadmium. At finite values of adsorption, however, the order of lead and copper were reversed. They postulated that this was due to the higher interaction energy of the larger Pb^{2+} ion. Their calculated order is in agreement with the order lead > copper > zinc > cobalt > nickel > manganese found for hematite in the present study, where once again the order of lead and copper were reversed on goethite. The order of affinity found here for the hematite surface was similar to that of the respective hydrolysis constants of the metal ions. p^*K_1 values are lead 8·0, copper 8·0, zinc 9·0, cobalt 9·5, nickel 9·6 and manganese 10·6 (average values from Perrin 1969).

Several models have been proposed to represent the adsorption of hydrolysable metal ions by oxide surfaces. These models define adsorption as due to:

(1) ion exchange of free metal and hydroxo complexes with surface protons, or
(2) aquo hydroxo complexes, or
(3) surface hydrolysis of metal ions.

James *et al.* (1975) compared these three models, and found that, in spite of the conceptual differences, all three reduced to similar mathematical forms, and all gave good agreement with experimental results.

James and Healy (1972*b*) proposed a model in which adsorption is the result of the competition between the free energy changes favourable to adsorption, i.e. coulombic and chemical energy changes, and the unfavourable change in solvation energy. This model predicts that the adsorption of hydroxo complexes is favoured because of their lower hydration energies. The authors postulated that the sudden increase in adsorption over a narrow pH range, which coincides with a sudden reversal of the zeta potential, was due to the interfacial precipitation of the hydroxide of the adsorbing ion. This precipitation occurred at a pH below that at which it would occur in the bulk solution, because the solubility product at the interface was lowered by the electrostatic field. At higher pH, another charge reversal occurred, which corresponded to the ZPC of the adsorbed metal hydroxide. This model is supported by the adsorption of cobalt(II), lanthanum(III) and thorium(IV) on silica (James and Healy 1972*a*), cobalt(II) on manganese dioxide (Murray 1975*b*) and zinc(II) on manganese dioxide (Loganathan *et al.* 1977).

More recently, Davis *et al.* (1978) developed the site-binding model, in which the ion exchange model is modified to include the effects of the electrostatic field at the interface. This model also predicts that the hydroxo complexes are more strongly bonded to the surface than the free aquo ions (Davis and Leckie 1978). Both of these models, and also that of Bowden *et al.* (1973), included a specific adsorption term which was used to improve the fit to experimental data.

In accordance with these models, the ion exchange reactions may be written

$$SOH^\circ + M^{2+} \rightarrow [SO^- - M^{2+}] + H^+ \tag{4}$$

$$SOH^\circ + M^{2+} + H_2O \rightarrow [SO^- - MOH^+] + 2H^+ \tag{5}$$

$$2SOH^\circ + M^{2+} \rightarrow [2SO^- - M^{2+}] + 2H^+, \tag{6}$$

where SOH° is an uncharged surface site, and the term in square brackets is the adsorbed form of the cation M^{2+}. For the adsorption of hydroxo species the equations are

$$\mathrm{S+M^{2+}+H_2O\rightarrow[S\text{–}MOH^{+}]+H^{+}} \tag{7}$$

$$\mathrm{S+M^{2+}+2H_2O\rightarrow[S\text{–}M(OH)_2]+2H^{+}}. \tag{8}$$

Equations (7) and (8) are two step reactions, which may be regarded as adsorption of the unhydrolysed ion followed by surface hydrolysis, or hydrolysis in solution followed by adsorption. Equation (6) represents the formation of a bidentate bond with the surface, with the release of $2H^+$ ions into solution. Davis and Leckie (1978) found that adsorption of the mono-hydroxo complex (equation 5) gave a better fit to the predictions of the site-binding model than the bidentate bond, although with different assumptions in their model, the bidentate form could be made to fit. Several workers have shown that the number of moles of H^+ released per mole of metal ion adsorbed varies between 1 and 2, and increases with pH (Morgan and Stumm 1964; Murray 1975*a*; Hohl and Stumm 1976). Even without evidence to the contrary, it seems more logical to change from adsorption of the unhydrolysed ion at low pH ($1H^+$ released, equation (4)) to the adsorption of the mono-hydroxo complex ($2H^+$ released, equation (5)) at higher pH, than to postulate a change to the quite different bidentate form of equation (6).

The results of the present work show that there was considerable adsorption by birnessite at the ZPC (pH 1·8). Since the pH at the ZPC is far below the first hydrolysis constant (p^*K_1 for lead = 8), the concentration of the unhydrolysed ion in solution will exceed that of the first hydrolysis product by a factor of 10^6. The most likely adsorbed form is then the Pb^{2+} ion (equation (4)). At pH 4, one mole of H^+ was released per mole of metal ion adsorbed, so that equation (4) is still the most probable reaction. With increasing pH, increasing adsorption of the mono-hydroxo complex would be expected (equation (5)), until eventually surface-induced interfacial precipitation of the metal hydroxide, or surface-induced hydrolysis of the adsorbed ions, occurs (equation (8)).

For the iron oxides, there is a sharp increase in adsorption over a narrow range of pH, and this is consistent with the attainment of a pH value at which the adsorption of MOH^+ becomes possible (equation (5)). Since 1·3–2 moles of H^+ were released per mole of metal ions adsorbed, the most likely forms of the adsorbed ions are M^{2+} and MOH^+, as was found by Davis and Leckie (1978).

The similarity of the order of the adsorption series to that of the hydrolysis constants is explained by the adsorption of hydroxo complexes. In the present work, a number of deviations from this order were found. Some of these, e.g. the enhanced adsorption of manganese and cobalt on the manganese oxides, the reversal of the usual order of lead and copper on goethite, and the high adsorption on B14, B38 and C37 relative to the other manganese oxides, may be allowed for in the mathematical treatment by measurement or estimation of the specific adsorption term for each individual system. Other deviations from the order, e.g. the reversal of the order of manganese and cobalt on manganese oxides at low pH and also at low concentrations of adsorbing ions; and the reversal of the order of hematite and goethite with respect to lead adsorption at low concentrations of lead, indicate that the specific adsorption term is not completely independent of pH and concentration of the adsorbing ion. These adjustments to the models may be made without postulating any mechanism for the differences, and at the present stage of development of the models, these differences are largely unpredictable.

Conclusions

The accumulation of lead in the manganese oxides in soils, and the resulting reduction of lead uptake by plants is due to the high specific adsorption of lead by the manganese oxides over a wide range of pH values, and the difficulty of removing the adsorbed lead. No evidence was found to suggest that oxidation of the lead, or the formation of specific lead–manganese minerals, are involved.

A significant amount of lead entered the interlayer spaces of fine-grained birnessites, resulting in an uptake of lead in excess of the amount required for a monolayer on the surface. Smaller amounts of lead were able to enter the interlayer spaces of birnessites with larger particle sizes.

At low concentrations, the affinity of lead for the hematite surface was greater than that for the goethite surface, although the surface area of the hematite was much smaller than that of the goethite. Coupled with the greater difficulty in extracting adsorbed lead from hematite, this suggests that hematite is also likely to be an important sink for lead in soils.

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References

Bowden, J. W., Bolland, M. D. A., Posner, A. M., and **Quirk, J. P.** (1973). Generalized model for anion and cation adsorption at oxide surfaces. *Nature Phys. Sci.* **245**, 81–3.

Burns, R. G. (1976). The uptake of cobalt into ferromanganese nodules, soil and synthetic manganese (IV) oxides. *Geochim. Cosmochim. Acta* **40**, 95–102.

Davis, J. A., James, R. O., and **Leckie, J. O.** (1978). Surface ionization and complexation at the oxide/water interface. I. Computation of electrical double layer properties in simple electrolytes. *J. Colloid Interface Sci.* **63**, 480–99.

Davis, J. A., and **Leckie, J. O.** (1978). Surface ionization and complexation at the oxide/water interface. II. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *J. Colloid Interface Sci.* **67**, 90–107.

Forbes, E. A., Posner, A. M., and **Quirk, J. P.** (1976). The specific adsorption of divalent Cd, Co, Cu, Pb and Zn on goethite. *J. Soil Sci.* **27**, 154–66.

Gadde, R. R., and **Laitinen, H. A.** (1974). Studies of heavy metal adsorption by hydrous iron and manganese oxides. *Anal. Chem.* **46**, 2022–6.

Hem, J. D. (1978). Redox processes at surfaces of manganese oxides and their effects on aqueous metal ions. *Chem. Geol.* **21**, 199–218.

Hohl, H., and **Stumm, W.** (1976). Interaction of Pb^{2+} with hydrous γ-Al_2O_3. *J. Colloid Interface Sci.* **55**, 281–8.

James, R. O., and **Healy, T. W.** (1972*a*). Adsorption of hydrolysable metal ions at the oxide-water interface. II. Charge reversal of SiO_2 and TiO_2 colloids by adsorbed Co(II), La(III) and Th(IV) as model systems. *J. Colloid Interface Sci.* **40**, 53–64.

James, R. O., and **Healy, T. W.** (1972*b*). Adsorption of hydrolysable metal ions at the oxide-water interface. III. A thermodynamic model of adsorption. *J. Colloid Interface Sci.* **40**, 65–81.

James, R. O., Stiglich, P. J., and **Healy, T. W.** (1975). Analysis of models of adsorption of metal ions at oxide/water interfaces. *Faraday Discuss. Chem. Soc.* **59**, 142–56.

Loganathan, P., and **Burau, R. G.** (1973). Sorption of heavy metal ions by a hydrous manganese dioxide. *Geochim. Cosmochim. Acta* **37**, 1277–93.

Loganathan, P., Burau, R. G., and **Fuerstenau, D. W.** (1977). Influence of pH on the sorption of Co^{2+}, Zn^{2+} and Ca^{2+} by a hydrous manganese oxide. *Soil Sci. Soc. Am. J.* **41**, 57–62.

McKenzie, R. M. (1970). The reaction of cobalt with manganese dioxide minerals. *Aust. J. Soil Res.* **8**, 97–106.

McKenzie, R. M. (1971). The synthesis of birnessite, cryptomelane and some other oxides and hydroxides of manganese. *Min. Mag.* **38**, 493–502.

McKenzie, R. M. (1975). An electron microprobe study of the relationships between heavy metals and manganese and iron in soils and ocean floor nodules. *Aust. J. Soil Res.* **13**, 177–88.

McKenzie, R. M. (1977). Manganese oxides and hydroxides. *In* 'Minerals in Soil Environments', ed. J. B. Dixon, pp. 181–93. (Soil Sci. Soc. Am.: Madison, Wis.)

McKenzie, R. M. (1978). The effect of two manganese dioxides on the uptake of lead, cobalt, nickel, copper and zinc by subterranean clover. *Aust. J. Soil Res.* **16**, 209–14.

McKenzie, R. M. (1979). Proton release during adsorption of heavy metal ions by hydrous manganese dioxide. *Geochim. Cosmochim. Acta* **43**, 1855–7.

Morgan, J. J., and **Stumm, W.** (1964). Colloid chemical properties of manganese dioxide. *J. Colloid Sci.* **19**, 347–59.

Murray, J. W. (1975*a*). The interaction of metal ions at the manganese dioxide–solution interface *Geochim. Cosmochim. Acta* **39**, 505–19.

Murray, J. W. (1975*b*). The interaction of cobalt with hydrous manganese dioxide. *Geochim. Cosmochim. Acta* **39**, 635–47.

Norrish, K. (1975). Geochemistry and mineralogy of trace elements. *In* 'Trace Elements in Soil–Plant–Animal Systems.' ed. D. J. D. Nicholas and A. R. Egan, pp. 55–81. (Academic Press: New York.)

Perrin D. D. (1969). Dissociation constants of inorganic acids and bases in aqueous solution. *Pure Appl. Chem.* **20**, 133–236.

Posselt, H. S., **Anderson, F. J.**, and **Weber, W. J. Jnr** (1968). Cation sorption on colloidal hydrous manganese dioxide. *Environ. Sci. Technol.* **2**, 1087–93.

Taylor, R. M., and **McKenzie, R. M.** (1966). The association of trace elements with manganese minerals in Australian soils. *Aust. J. Soil Res.* **4**, 29–39.

Van der Weijden, C. H., and **Kruissink, E. C.** (1977). Some geochemical controls on lead and barium concentrations in ferromanganese deposits. *Mar. Geochem.* **5**, 93–112.

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