Reactions of EDTA Complexes of Fe, Zn, Mn, and Cu with Soils[1]

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ABSTRACT

The Fe, Zn, Cu, and Mn complexes and the Na salt of EDTA (ethylenediaminetetraacetic acid) were reacted with suspensions of acid, neutral, and calcareous soils. The initial concentration of chelate was $1 \times 10^{-4}M$ or on a soil weight basis, 11.2, 13.1, 12.7, and 11.0 ppm of Fe, Zn, Cu, and Mn, respectively. Suspensions were aerated and shaken continuously for periods of 2 hours to 30 days. At the termination of each reaction period the pH of the suspensions was measured; following centrifugation, the supernatant solutions were analyzed for Fe, Zn, Cu, Mn, Ca, and Mg by atomic absorption spectrophotometry. The concentration of ^{14}C-labeled EDTA was determined by liquid scintillation.

FeEDTA was stable in soil suspensions of pH 5.7 and 6.1, moderately stable at pH 6.75, and unstable at pH 7.3 and 7.85. This behavior was satisfactorily predicted using formation constants to describe equilibria of EDTA with Fe^{3+}, Ca^{2+}, and H^+, with the assumption that the Fe^{3+} concentration was controlled by the solubility of amorphous iron(III) oxides. ZnEDTA and CuEDTA were most stable in suspensions near neutrality. In acid soils Cu and Zn were increasingly displaced by Fe as pH decreased while in calcareous soils these metals were displaced by Ca as pH increased. The loss of Mn from MnEDTA was very rapid in all soils and was essentially complete in less than one day from suspensions of pH 6.1 to 7.85.

Additional Key Words for Indexing: ethylenediaminetetraacetic acid, iron(III) oxides, metal chelates, micronutrient fertilizers, FeEDTA, ZnEDTA, CuEDTA, MnEDTA.

FOR MANY years EDTA (ethylenediaminetetraacetic acid) has been used as a chelating agent for supplying micronutrient cations to plants. The effectiveness of EDTA chelates as metal carriers in soils depends on their ability to keep these metals in soluble, mobile forms. To accomplish this, the EDTA ligand must remain in solution and continue to complex the applied metal ion.

The loss of EDTA from soil solutions results primarily from its adsorption by soil particles. The rate of adsorption or "fixation" is usually rapid during the first few days after application but decreases sharply after the 2nd or 3rd day. Hill-Cottingham and Lloyd-Jones (1957) found that about 30% of the EDTA from a FeEDTA addition to a calcareous soil was lost in 15 days, but more than 80% of this loss occurred during the first 2 days. Similar losses from FeEDTA in both acid and calcareous soils were found by Stewart and Leonard (1955) and by Wallace et al. (1955). The adsorption of EDTA onto soils from ZnEDTA appli-

cations is less serious than losses from FeEDTA (Anderson, 1964; Wallace and Lunt, 1956). Although a portion of the applied EDTA is probably always lost, these results indicate that in most soils the majority remains in solution for at least a few weeks and perhaps much longer. Separation of metal from the chelating agent appears to be a much more serious limitation of the effectiveness of EDTA as a micronutrient metal carrier.

In soil solutions, EDTA is involved in simultaneous equilibria with a variety of cations; each of these cations is concurrently involved in equilibria with one or more soil phases. In principle, the relative importance of each EDTA complex present can be calculated from formation constants, solubility products, and other appropriate equilibrium constants. In general, this is not possible because of the heterogeneous, poorly defined nature of participating soil phases. For this reason, most investigations of EDTA reactions in soils have primarily been empirical.

The major conclusions of studies on the stability of EDTA chelates in soils can be summarized briefly. In acid soils FeEDTA is usually stable, and Fe dissolved from the soil tends to displace Zn and Mn from ZnEDTA and MnEDTA, (Stewart and Leonard, 1955; Perkins and Purvis, 1954). FeEDTA is less stable in calcareous soils where Fe is probably displaced by Ca (Hill-Cottingham and Lloyd-Jones, 1957). The reduced stability of FeEDTA in alkaline soils is usually attributed to decreased solubility of "ferric hydroxide" (hydrous iron(III) oxides). Unlike FeEDTA, ZnEDTA tends to be more stable in alkaline soils than in strongly acid soils (Leonard and Stewart, 1958; Anderson, 1964).

These results indicate some of the reactions that may limit the availability of Mn, Zn, and FeEDTA in certain soils and demonstrate a definite pH-dependent trend in the stability of the latter two chelates. However, additional work is needed to determine the pH ranges in which Fe, Cu, Zn, and Mn EDTA chelates are most stable and to identify reactions limiting the stability of each of these chelates in acid, neutral, and calcareous soils.

Despite the interest in chelates as micronutrient carriers, no general theoretical treatment of chelate-soil equilibria was attempted until Lindsay, Hodgson, and Norvell (1967) developed an expression for calculating the fraction of a chelating ligand associated with any cation. This development considered the competition of Fe^{3+}, Ca^{2+}, and H^+ for three chelating agents including EDTA. Published formation constants were used to describe equilibria between these cations and the chelating ligands as well as between Fe^{3+}, Ca^{2+}, and solid phases in the soil. The concentration of Fe^{3+} was assumed to be controlled by the pH-dependent solubility of amorphous iron(III) oxides. The Ca^{2+} concentration was assumed to be either constant or controlled by pH and the partial pressure of CO_2 in the presence of calcium carbonate. The calculated fraction of EDTA or other chelating agent present as Fe complexes

was plotted as a function of pH, and the resulting stability-pH diagrams clearly demonstrated the dependence of FeEDTA stability upon pH and CO_2 level. Satisfactory agreement between predicted FeEDTA stability and initial experimental results was reported. Further testing and development of the theoretical approach to metal chelate equilibria in soils is needed.

The objectives of the present study were: (i) to determine the stability of Fe, Zn, Cu, and MnEDTA in acid, neutral, and calcareous soils, (ii) to identify some of the reactions or soil phases controlling the stability of these chelates, and (iii) to test the validity of the previously developed stability-pH diagram for FeEDTA.

EXPERIMENTAL METHODS

Solutions of Fe, Zn, Cu, and Mn complexes and the Na salt of EDTA were reacted with five soils as suspensions for periods up to 30 days. Medium-textured agricultural soils, ranging in pH from 5.5 to 7.8, were chosen for these experiments. Some characteristics of these soils are presented in Table 1. The air-dry soils were passed through a 2-mm stainless steel screen and stored in polyethylene-lined containers.

Stock solutions of Fe, Zn, Cu, Mn, and NaEDTA were prepared from 99.7% pure Na_2H_2EDTA. The heavy metal chelates were obtained by mixing equimolar quantities of reagent grade $Fe_2(SO_4)_3$, $ZnSO_4$, $CuSO_4$, and $MnCl_2$, respectively, with Na_2H_2EDTA. Three aliquots of each stock solution were adjusted to approximately pH 6.0, 6.8, and 7.5 to provide EDTA solutions close to the pH of the five soil suspensions. Tracer quantities of EDTA tagged with ^{14}C-labeled carboxyl groups were added, and the solutions were diluted to a final concentration of $1.5 \times 10^{-3}M$ with an activity of 0.02 μc ^{14}C/ml.

The concentrations of micronutrient metals in the $1.5 \times 10^{-3}M$ stock solutions were verified by atomic absorption spectrophotometry. The concentration of EDTA in these solutions was checked by a procedure similar to that used by Tiffin, Brown, and Krauss (1960) for the determination of "iron chelating capacity." Excess Fe was added to one of the FeEDTA solutions in order to saturate completely any excess EDTA present. After a few hours the solution was adjusted to pH 8.5 and heated to approximately 90C for 1 hour. After standing 2 days, the precipitated iron oxides were removed by high speed centrifugation. The concentration of iron remaining in solution was measured and found to be the same as in the original FeEDTA solution, indicating that EDTA was present at a concentration of $1.5 \times 10^{-3}M$.

All chelate-soil reactions were carried out in suspensions containing 15 g soil and 30 ml solution. Small additions of dilute HCl, $CaCl_2$, KOH, or Na_2CO_3 were included, as needed, to adjust the pH and Ca concentration to the values given in Table 1. Soil suspensions were aerated and shaken continuously in 125 ml Pyrex flasks with polyethylene fittings at a temperature of 25 ± 1C. Flasks were covered with aluminum foil so that all reactions occurred in the dark. Two or three times daily the flasks were shaken vigorously to resuspend adhering or settled soil particles. All suspensions were shaken 7 days before the EDTA chelates were added. On the eighth day 2 ml of the ^{14}C-labeled EDTA solutions were added, bringing the final volume of the solution phase to 30 ml. The initial concentration of all EDTA chelates in the solution phase was thus $1 \times 10^{-4}M$, or 11.2, 13.1, 12.7, and 11.0 ppm of Fe, Zn, Cu, and Mn, respectively, expressed on a soil weight basis. EDTA chelates were not added to freshly prepared suspensions because preliminary experiments showed that appreciable quantities of Mn temporarily entered solution for 2 or 3 days when the air-dry soils were first wetted.

Reaction periods, following EDTA chelate additions, were

Table 1—Description of soils and soil suspensions

Soil type	Location	pH in water, 1:1	CaCO₃ equivalent	Ca²⁺	pH
			%	mM	
Paxton silt loam	New Hampshire	5.5	–	2.5	5.70±.05
Keith loam	Colorado	6.2	–	1.5	6.10±.05
Monticello loam	Colorado	7.2	<0.5	2.4	6.75±.05
Platner loam	Colorado	7.4	<0.5	1.5	7.30±.05
Colombo-like silt loam	Colorado	7.8	5.6	0.8	7.85±.05

varied from 2 hours to 30 days. At the end of each reaction period, a set of flasks was removed, and the pH of the suspensions was measured immediately. The suspensions were centrifuged at 37,000 × gravity for 30 min and the supernatent solutions were filtered to remove floating organic material. In order to prevent the loss of metals from solution during storage, sufficient DTPA (diethylenetriaminepentaacetic acid) was added to chelate all of the micronutrient metals present and a majority of the Ca as well. Solutions were refrigerated until all analyses were completed.

The concentration of ^{14}C-tagged EDTA in each solution was measured by liquid scintillation using aqueous standards of ^{14}C-EDTA with a similar pH and salt content. Solutions were analyzed regularly for Fe, Zn, Cu, Mn, Ca, and Mg, and occasionally for Cr, Co, Cd, and Pb by means of atomic absorption spectrophotometry. In the presence of the relatively high concentrations of Ca, Mg, and Na contained in these solutions, practical detection limits for the micronutrient metals were about 0.5 μM for Fe and Mn, and 0.1 μM for Cu and Zn. The micronutrient metals measured in solution were assumed to be present as EDTA complexes because these metals could not be detected when EDTA was not added to suspensions. Furthermore, when $1 \times 10^{-4}M$ solutions of inorganic salts of these metals were reacted with suspensions, the concentrations of the added metals in solution fell below detectable levels within a few hours.

RESULTS AND DISCUSSION

In all experiments a portion of the added EDTA was lost from solution. The total loss ranged from 5 to 25% and the majority of this occurred during the first few days, as is typical of the adsorption of chelates by soils (Hill-Cottingham and Lloyd-Jones, 1957, 1958). The greatest losses occurred in acid soil suspensions containing FeEDTA and the least in alkaline suspensions containing CuEDTA or ZnEDTA. Although these losses were not serious, the factors influencing the stability of EDTA chelates in soils are more easily evaluated if the effect of the continually changing concentration of the chelating ligand is eliminated. For this reason the results of this study are expressed as the percentage of EDTA remaining in solution that was complexed with each of the micronutrient metals. This percentage was calculated by dividing the experimentally measured molar concentration of each metal by the measured molar concentration of EDTA and multiplying by 100.

It is impossible to interpret the reactions of EDTA chelates in soils without considering Ca^{2+} competition for the EDTA ligand. The importance of Ca^{2+} competition would be obvious if the concentration of CaEDTA in soil solutions could be measured directly. Unfortunately, it is difficult to determine the concentration of this chelate in the presence of excess Ca^{2+} and various other EDTA complexes. However, any EDTA in solution which is not present as chelates of transition metals can be safely assumed to complex Ca^{2+} because Ca^{2+} forms a more stable com-

100
80
60
40
20
0

% EDTA Complexed with Fe

pH 5.7
pH 6.1
pH 6.75
pH 7.3, 7.85

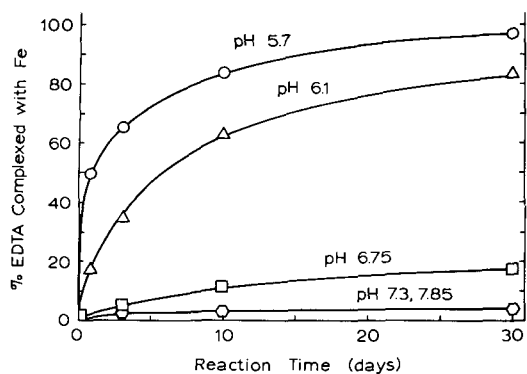0   10   20   30

Reaction Time (days)

Fig. 1—Dissolution of Fe from five soils of different pH by NaEDTA.

plex with EDTA than do any of the other relatively abundant cations in soil solutions. In this study, Ca was assumed to occupy essentially all of the EDTA in solution that was not present as Fe, Zn, Cu, Mn, Cd, Pb, Co, and Cr chelates.

When NaEDTA is reacted with soils, the EDTA ligand quickly forms complexes with various cations in the soil solution. CaEDTA is undoubtedly the dominant species formed initially, but many other complexes are also formed and may become increasingly important with time. The dissolution of Fe resulting from the reaction of NaEDTA with the five soil suspensions of this study is summarized in Fig. 1. The rate at which Fe entered solution and became complexed varied markedly with soil pH. In the soil suspension at pH 5.7, Fe entered solution rapidly, occupying more than 75% of the EDTA at 1 week and nearly 97% at 30 days. At pH 6.1, the fraction of EDTA complexed with Fe increased less rapidly, but reached 83% at 30 days. In the three more alkaline suspensions, the rate of Fe dissolution continued to decrease as the pH increased.

Small amounts of other metals were also released from the soil as a result of reaction with NaEDTA. In the pH 5.7 suspension, Cu and Zn entered solution rapidly during the first day, occupying a maximum of approximately 8 and 18% of the EDTA, respectively. During the remainder of the experiment these metals were slowly displaced from the EDTA by Fe. At pH 6.1, complexation of Cu and Zn showed a similar rise and decline, but the maxima, which occurred at 3 days, were only 4 and 3%, respectively. In
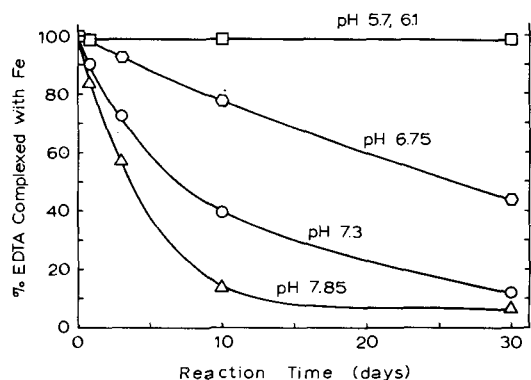
the other soils, the percentages of CuEDTA and ZnEDTA increased slowly throughout the experiment. After 30 days reaction, Cu occupied approximately 1, 1, 1.5, 1, and 0.5% of the EDTA in solution in the five soils in order of increasing pH, while ZnEDTA represented 2, 2, 7, 4, and 3% in these same soils. The presence of Mn, Co, Cd, Pb, and Cr were not detected in any of the suspensions; therefore, these metals could not have occupied more than 1% of the EDTA in solution.

Results from the reaction of FeEDTA with the five soils are summarized in Fig. 2. Both the rate and extent of Fe loss from the chelate increased markedly with increase of pH. In the suspensions of pH 5.7 and 6.1, FeEDTA was very stable. After 30 days Fe continued to occupy more than 98% of the EDTA in solution. At pH 6.75, Fe was lost continually during the reaction period, but even after 30 days FeEDTA represented 44% of the EDTA in solution. In the two alkaline suspensions, most of the Fe was lost from the chelate in 30 days. At pH 7.85 the percentage of FeEDTA fell rapidly to less than 14% in 10 days.

Small quantities of Cu and Zn were brought into solution as a result of the FeEDTA addition. After 30 days reaction, Cu occupied approximately 0.5, 0.5, 1, 1, and 1% of the EDTA in the five soil suspensions in order of increasing pH, while ZnEDTA represented 1, 0.5, 5, 3, and 3% of EDTA in solution in these same soils.

The trend in FeEDTA stability reported above may be understood in terms of Fe-Ca competition for the EDTA ligand as proposed by Lindsay et al. (1967) in their development of stability-pH diagrams for soils. These diagrams were derived assuming a formation constant of 10^{39}, selected from Sillén and Martell (1964), for amorphous, hydrous iron(III) oxides. The recent study by Bohn (1967) of the $(Fe)(OH)^3$ ion product in acid soils provides additional support for this value. Current work in our laboratory suggests a value of 10^{39} to 10^{40} for nearly neutral soils. A formation constant of $10^{39.5}$ was selected by Lindsay and Norvell (1969) in their extension of metal chelate stability calculations to include competition of Fe, Ca, H, and Zn for EDTA and DTPA. For comparison with the results of the present study, stability-pH diagrams for FeEDTA were derived assuming a Ca^{2+} concentration of $2.5 \times 10^{-3}M$ and
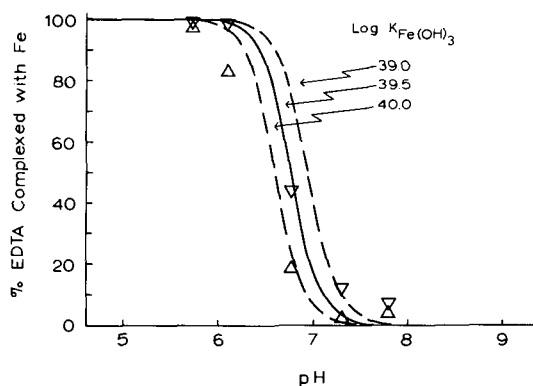
100
80
60
40
20
0

% EDTA Complexed with Fe

pH 5.7, 6.1
pH 6.75
pH 7.3
pH 7.85

0   10   20   30

Reaction Time (days)

Fig. 2—Loss of Fe from FeEDTA in five soils of different pH.

100
80
60
40
20
0

% EDTA Complexed with Fe

Log $K_{Fe(OH)_3}$
39.0
39.5
40.0

5   6   7   8   9

pH

Fig. 3—Comparison of calculated and measured FeEDTA stability after 30 days reaction of NaEDTA (△) and FeEDTA (▽) with five soils.
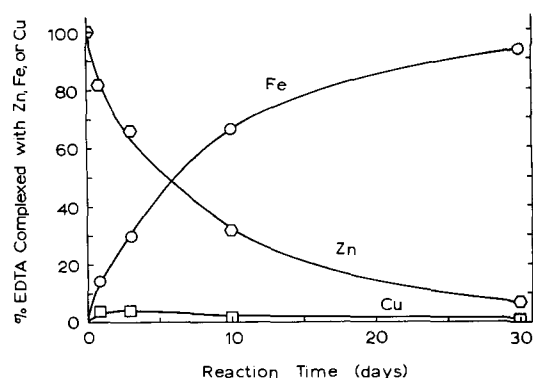
Fig. 4—Reaction of ZnEDTA with soil of pH 5.7.

Fig. 5—Reaction of CuEDTA with soil of pH 5.7.

formation constants of $10^{39.0}$, $10^{39.5}$, and $10^{40.0}$, for amorphous iron(III) oxides. (The extended Debye-Hückel equation was used to correct all equilibrium constants to an ionic strength of 0.01, a value appropriate to the suspensions of this study as well as to many soil solutions.) In Fig. 3, the three curves represent the calculated stability of FeEDTA in equilibrium with iron(III) oxides having the indicated formation constants.

When NaEDTA was reacted with the five soil suspensions, the EDTA ligand was initially undersaturated with respect to Fe, and Fe was dissolved from the soil. Conversely, when FeEDTA was reacted with the suspensions, the chelate was initially oversaturated with Fe and a portion of the associated Fe was lost to the soil. The percentage of EDTA complexed with Fe after 30 days reaction is plotted in Fig. 3 for comparison with the calculated curves. The upward and downward pointing triangles represent values attained from undersaturation and supersaturation, respectively. At pH 5.7, 6.1, 6.75, and 7.3, the measured percentages of FeEDTA were obviously approaching equilibrium values in excellent agreement with the predicted curves. At pH 7.85 the concentration of Ca, in equilibrium with calcium carbonate, was only one-third the concentration assumed in the derivation of the predicted curves. In this suspension, the calculated curves overestimated the effectiveness of Ca competition for EDTA and resulted in the apparent discrepancy between predicted and experimental percentages of FeEDTA. Thus the stability of FeEDTA in all five soils corresponded very closely to
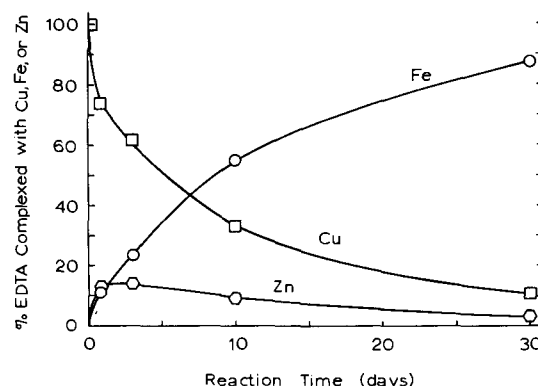
predictions based on the assumption that Fe^{3+} activity was controlled by the solubility of amorphous iron(III) oxides.

The agreement between experimental and predicted FeEDTA stability was reduced only slightly by the presence of ZnEDTA and CuEDTA because these chelates represented only 2 to 8.5% of total EDTA in each suspension. It is possible that in some soils Zn, Cu, or other transition metals might compete more successfully with Fe and Ca. In this case, a stability-pH diagram based on Fe-Ca competition would fail to predict FeEDTA stability satisfactorily; but the diagram would still indicate the expected ratio of FeEDTA/(FeEDTA + CaEDTA).

Results from the reaction of ZnEDTA with the pH 5.7 suspension are shown in Fig. 4. Zn was rapidly displaced by soil Fe, and after 30 days ZnEDTA represented only 8% of total EDTA in solution. When CuEDTA was reacted with this soil (Fig. 5), more Cu was initially displaced by soil Zn than by Fe. However, Fe saturation of the chelate increased rapidly and Fe soon displaced the great majority of both Zn and Cu.

The loss of Zn from ZnEDTA at pH 6.1 was less serious (Fig. 6). During the first day, the chelate equilibrated rapidly with the soil suspension and approximately 15% of the Zn was displaced by Ca. Thereafter, the loss of Zn continued more slowly as complexation of Fe increased steadily with time. After 30 days Zn still occupied 45% of EDTA in solution but replacement by Fe was continuing. The results for CuEDTA in this soil were essentially identical as shown in Fig. 7.
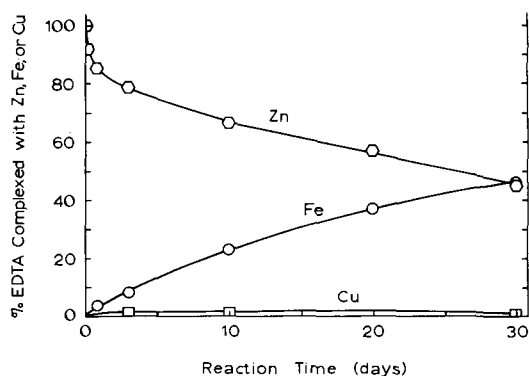

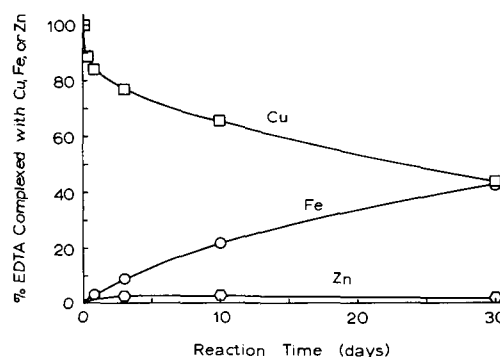Fig. 6—Reaction of ZnEDTA with soil of pH 6.1.
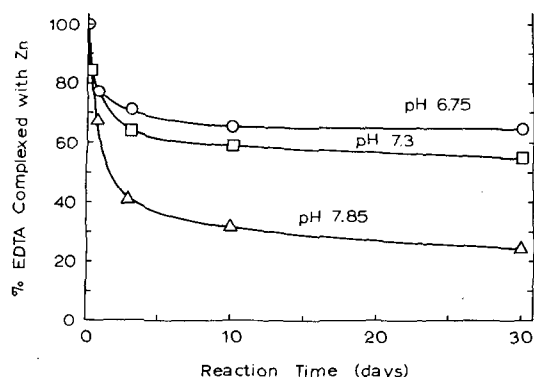

Fig. 7—Reaction of CuEDTA with soil of pH 6.1.

Fig. 8—Loss of Zn from ZnEDTA in three soils of different pH.

Fig. 9—Loss of Cu from CuEDTA in three soils of different pH.

The reactions of ZnEDTA and CuEDTA in the pH 6.75, 7.3, and 7.85 suspensions are summarized in Fig. 8 and 9. In these suspensions, the loss of Zn and Cu from solution was very rapid initially. Further loss occurred quite slowly and in most cases the percentage of ZnEDTA or CuEDTA became nearly constant with time. The stability of both chelates decreased in a similar manner with increasing pH, but CuEDTA was less stable than ZnEDTA in each case. The great majority of Zn and Cu lost from their respective chelates in these soils was displaced by Ca. Less than 3 to 15% of metal chelates other than the applied chelate and CaEDTA were ever present. Competition from Ca was also suggested by the very rapid initial displacement of Zn and Cu which indicated that the displacing cation was present in abundance.

In all suspensions, with the possible exception of that at pH 6.1, the major reaction between applied ZnEDTA or CuEDTA and the soil occurred within the 30-day reaction period. The relationship between pH and the 30-day stability of these chelates is shown in Fig. 10. The increase in stability between pH 5.7 and pH 6.75 resulted primarily from decreased competition by Fe for the EDTA ligand. This occurred because the concentration of Fe^{3+} decreased more rapidly with increasing pH than did the concentrations of Zn^{2+} and Cu^{2+}. The reduction in stability from pH 6.75 to pH 7.85 was caused by a more rapid decrease in the concentrations of Zn^{2+} and Cu^{2+} than in that of Ca^{2+}, the major competing cation in these more alkaline suspen-
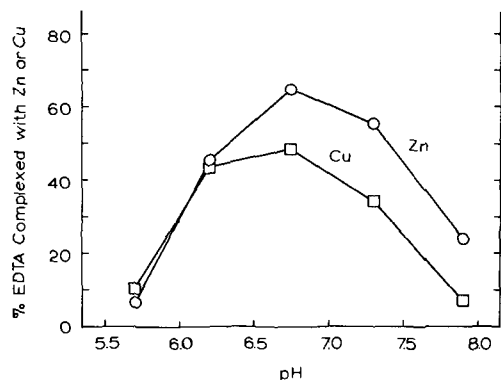
sions. The maximum stability, occurring in the pH 6.75 suspension, represented a balance between the two opposing trends.

The tendency for the fraction of EDTA occupied by Zn and Cu to approach a limiting value with time indicates that the concentrations of Zn^{2+} and Cu^{2+} were similarly approaching a constant level. At least a temporary equilibrium was apparently established between these metals in solution and compounds or other phases in the soil. The concentrations of Zn^{2+} or Cu^{2+} present in the pH 6.75, 7.3, and 7.85 suspensions were calculated from the Ca^{2+} concentration and the ratio of ZnEDTA/CaEDTA or CuEDTA/CaEDTA. After 30 days reaction the calculated concentrations of Zn^{2+} were $10^{-7.9}$, $10^{-8.4}$, and $10^{-9.2}M$ in these three soils in order of increasing pH. The concentrations of Cu^{2+} were $10^{-10.7}$, $10^{-11.3}$, and $10^{-12.3}M$ in the same soils. These values agree satisfactorily with the solution concentrations of Zn^{2+} and Cu^{2+} in various Colorado soils reported by Hodgson, Lindsay, and Trierweiler (1966). The possibility that $ZnSiO_3$ was the solid phase controlling Zn^{2+} activity in the five soils used in this study is pursued in another paper (Lindsay and Norvell, 1969).

Results for the reaction of MnEDTA with the five soils are summarized in Fig. 11. Mn was lost very rapidly at pH 5.7; less than 3% remained in solution after 20 hours and only traces could be detected after 70 hours. At pH 6.1, the loss of Mn was essentially complete in 20 hours, and nearly 90% was lost in 6 hours. In the other three

Fig. 10—Stability of ZnEDTA and CuEDTA in five soils after 30 days reaction.
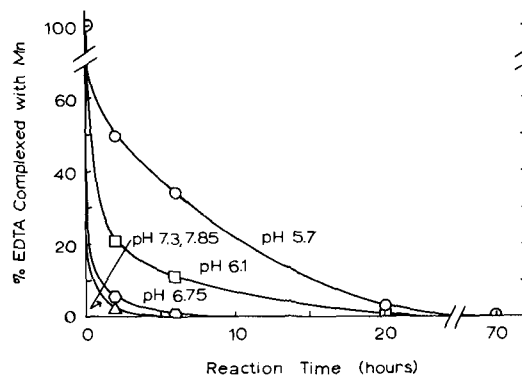

Fig. 11—Loss of Mn from MnEDTA in five soils of different pH.

suspensions, Mn was lost as rapidly from additions of MnEDTA as from additions of soluble inorganic Mn salts; and it is doubtful that even the few percent of MnEDTA plotted in Fig. 11 actually represent chelated Mn. These results strongly suggest that MnEDTA should have little advantage over soluble inorganic sources for application to soils. (To insure that all Mn losses occurred during reactions with soils and not during solution storage, some solutions were adjusted to approximately pH 1 following analysis for Mn and then were reanalyzed a week later. The Mn concentrations were not changed by this treatment indicating that the original analyses were correct.)

CONCLUSIONS

1) The stability of FeEDTA in five acid and calcareous soils was predicted very satisfactorily by assuming that the Fe^{3+} activity was controlled by the solubility of amorphous, hydrous iron(III) oxides. FeEDTA was stable in soil suspensions of pH 5.7 and 6.1, moderately stable at pH 6.75, and unstable at pH 7.3 and 7.85. These results confirm other studies indicating that the availability of Fe from FeEDTA is markedly reduced above pH 7, because Fe is lost quite rapidly from the chelate.

2) ZnEDTA and CuEDTA were most stable in the soils of pH 6.1, 6.75, and 7.3. In the most acid soil of pH 5.7, the great majority of both Zn and Cu was displaced by Fe, while in the most alkaline soil at pH 7.85, the metals were displaced by Ca. These results suggest that in moderately acid to slightly alkaline soils, the availability of Zn and Cu would not be limited by the instability of ZnEDTA and CuEDTA.

3) The tendency for the percentage of EDTA associated with Zn and Cu to approach a constant level with time, indicates that at least temporary equilibrium was established between Zn and Cu in solution and compounds or exchangeable sources of these metals in each soil.

4) MnEDTA was highly unstable in all soils, and this instability should seriously limit the usefulness of this chelate as an Mn fertilizer.

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