

Iron oxide solubilization by organic matter and its effect on iron availability

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Abstract

The solubility of Fe in soils is largely controlled by Fe oxides; ferrihydrite, amorphous ferric hydroxide, and soil-Fe are generally believed to exert the major control. Fe(III) hydrolysis species constitute the major Fe species in solution. Other inorganic Fe complexes are present, but their concentrations are much less than the hydrolysis species. Organic complexes of Fe including those of organic acids like citrate, oxalate, and malate contribute slightly to increased Fe solubility in acid soils, but not in alkaline soils.

The most important influence that organic matter has on the solubilization of Fe is through reduction. Respiration of organic matter creates reduction microsites in soil where Fe^{2+} concentrations increase above those of the Fe(III) hydrolysis species. Fluctuating redox conditions in these microsites are conducive to the formation of a mixed valency ferrosic hydroxide. This metastable precipitate maintains an elevated level of soluble inorganic Fe for prolonged periods and increases Fe availability to plants. The release of reducing agents and acids next to roots, as well as the production of siderophores by microorganisms within the rhizosphere, contribute to the solubilization and increased availability of Fe to plants.

Introduction

Organic matter is credited for having an important influence on the solubility and availability of Fe. Iron released during microbiological breakdown of organic residues contributes directly to supplying available Fe to plants. The released Fe soon re-precipitates as Fe(III) oxides and again becomes unavailable. Studies have shown that organic matter added to soils deficient in available Fe often corrects the deficiency, but if the same organic residues are ashed and the ash is applied to Fe deficient soils, the deficiencies still persist. Organic matter can undergo partial decomposition and give rise to organic acids and other breakdown products which combine to form soluble Fe-organic complexes.

To the extent that such complexes are present, they raise the concentration of total soluble Fe, making it more mobile and available to plants.

When organic matter undergoes biological degradation in soils, electrons or other reducing agents are released to the surrounding soil. This reduction process lowers redox and significantly increases the solubility of Fe^{2+} . The reduction process is especially important at the surface of roots and in the rhizosphere where root exudates are released.

The purpose of this paper is to examine important interactions of organic matter with soils in order to explain how organic matter aids in solubilizing Fe and making it more available to plants.

Iron oxide solubility controls in soils

Before we can understand the interaction of organic matter with Fe oxides in soils, we must first understand Fe oxides and the factors that control their solubilities (Lindsay, 1988; 1990). Iron present in most primary minerals is there as Fe(II). Weathering of these minerals in oxidizing environments releases Fe^{2+} which readily oxidizes and precipitates as Fe(III) oxides. These oxides primarily control Fe solubility in soils.

Lindsay (1979) graphically compared the solubilities of several commonly reported Fe(III) oxides. Freshly precipitated or amorphous Fe(III) oxide is the most soluble oxide. It readily precipitates whenever Fe^{3+} is added to soils, Fe^{2+} is oxidized to Fe^{3+} , pH is increased, or redox is raised. Norvell and Lindsay (1982a, 1982b) demonstrated that Fe solubility in soils tends to stabilize near an ion activity product of $(\text{Fe}^{3+})(\text{OH}^-)^3 = 10^{-39.3}$. This observed solubility relationship of Fe in soils (sometimes designated 'soil-Fe') can be expressed by the equilibrium equation:

$$(\text{Fe}^{3+}) = 10^{2.70}(\text{H}^+)^3 \quad (1)$$

This solubility corresponds to an Fe^{3+} activity that is 0.84 log units lower than that supported by amorphous Fe(III) oxide. The crystalline Fe(III) oxides commonly found in soils are listed below in the order of their decreasing solubilities: $\gamma\text{-Fe}_2\text{O}_3$ (maghemite), γFeOOH (lepidocrocite), $\alpha\text{-Fe}_2\text{O}_3$ (hematite), and $\alpha\text{-FeOOH}$ (goethite). The transformation of one of these oxides to another in soils occurs very slowly because of their extremely low solubilities. For this reason several Fe(III) oxide minerals may persist together in soils for long periods without transforming to the most insoluble mineral. For comparison, amorphous Fe(III) oxide is 3630 times more soluble than $\alpha\text{-FeOOH}$ (goethite).

Schwertmann (1988) described ferrihydrite as a highly disordered Fe(III) oxide of very fine particle size. He reported its solubility to be in the range of $10^{-37.0}$ to $10^{-39.4}$ M (Schwertmann, 1977). This range of solubilities represents products that are much more soluble than amorphous Fe(III) oxide to products nearly equal in solubility to that of soil-Fe. Our best evidence to date

suggests that Fe solubility in well-aerated soils tends to lie very close to that represented by soil-Fe (Norvell and Lindsay, 1982a, b).

The solubility of inorganic Fe in soils is not determined by Fe^{3+} alone. The hydrolysis species and inorganic complexes are important as shown by Figure 1 (from Lindsay, 1981). The hydrolysis species of Fe(III) are the most abundant aqueous solution species in the pH range above 4.5. The remaining inorganic complexes of Fe contribute only slightly to total soluble Fe. Iron has a minimum solubility in the pH range of calcareous soils (7.5 to 8.5). When Fe reaches equilibrium with soil-Fe, total soluble Fe in this pH range is near $10^{-10.4}$ M. This concentration is considerably below the 10^{-8} M level shown by Schwab and Lindsay (1989) to be necessary for the normal growth of soybeans [*Glycine max* (L.) Merr.]. Other plants may require different critical levels for normal growth. Thus, Fe deficiencies are common in well-aerated soils where calcium carbonate buffers the pH in the region of minimum Fe solubility.

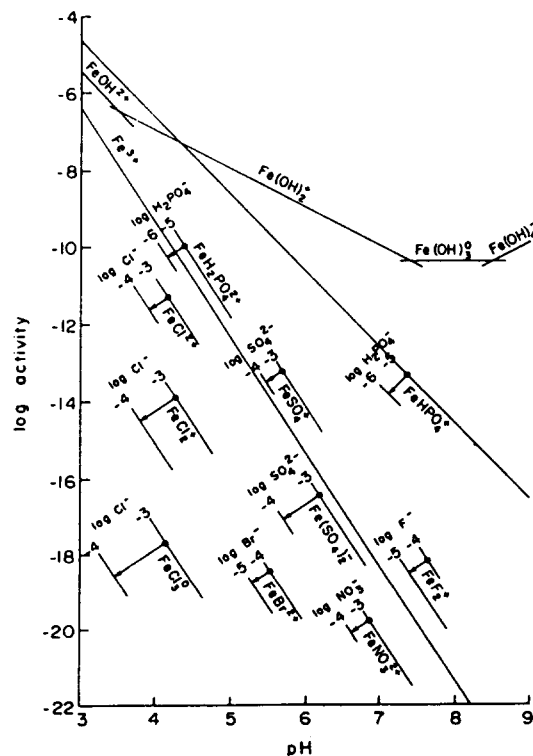
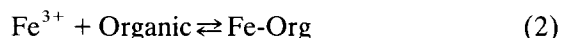


Fig. 1. Inorganic complexes of Fe(III) in equilibrium with soil-Fe compared to the hydrolysis species of Fe^{3+} (from Lindsay, 1981).

Addition of soluble Fe salts to soils can increase soluble Fe by 0.84 log units with the precipitation of amorphous Fe(III) oxides, but this 7-fold increase in soluble Fe soon drops back to that of soil-Fe within a few days (Norvell and Lindsay, 1982b).

Role of organics in iron solubilization

Soluble organic matter has the ability to form Fe(III) complexes with Fe^{3+} . These complexes may or may not contribute significantly to total soluble Fe in soil solution. There are several factors that determine if organic complexes of Fe will be significant. Let us consider the formation of a simple Fe(III) organic complex:



Utilizing the equilibrium constant (K°) of this reaction, we obtain:

$$K^\circ = \frac{(\text{Fe-Org})}{(\text{Fe}^{3+})(\text{Org})} \quad (3)$$

and rearranging gives:

$$\frac{(\text{Fe-Org})}{(\text{Fe}^{3+})} = K^\circ(\text{Org}) \quad (4)$$

Equation 4 shows that the activity ratio of $(\text{Fe-Org})/(\text{Fe}^{3+})$ is equal to the product of K° times the activity of the free organic ligand with which Fe^{3+} combines. The problem with this simple analysis is that other cations also react with the organic ligand to form additional metal-organic complexes. This competition lowers the free organic ligand activity. Each competing metal ion has its own activity in the soil which reflects its ability to compete. All of these factors must be considered to arrive at a quantitative solution to the Fe-organic matter complexing problem. Furthermore, there are many different organic compounds that combine with Fe to form organic-Fe complexes. The total solubility of Fe will be the summation of all organic and inorganic complexes of Fe.

Successful attempts have been made to develop the theoretical basis for predicting metal chelate equilibria in soils where equilibrium constants are known (Lindsay *et al.*, 1967; Lindsay, 1979; Norvell, 1972). The major competing cations in soils considered by Norvell (1972) and the calculated fraction of total chelate that remains saturated with Fe are shown together in Figure 2. In this development Fe, Al, Ca, Mg, and H were considered to be the major competing ions. These cations were controlled in soil as shown on the left side of the diagram. The fraction of each chelate that retains Fe is shown

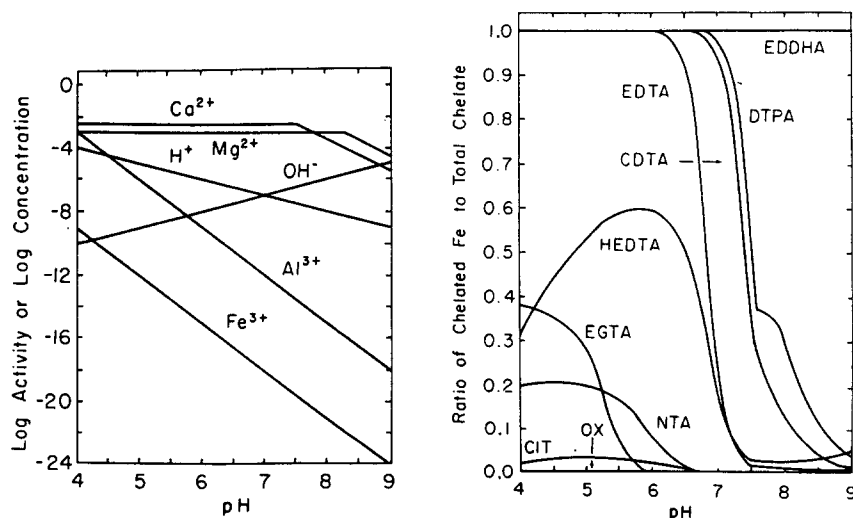


Fig. 2. Comparison of Fe-chelate stabilities in soils (right) in equilibrium with metal activities commonly found in soils (left) (from Norvell, 1972).

on the right side of the diagram. There are vast differences in ability of the various organic chelates to maintain soluble Fe in soil solution. The order of decreasing ability to chelate Fe in soils is: EDDHA > DTPA > CDTA > EDTA > HEDTA > EGTA > NTA > CIT > OX. The technical names of the first five chelates are given by Lindsay (1979). The remaining chelates include NTA (nitrilotriamine), OX (oxalate), and CIT (citrate). Only EDDHA, DTPA, and CDTA have the ability to chelate significant amounts of Fe in the pH range above 7.0. The chelates EDTA and HEDTA are slightly stable near pH 7, while EGTA, NTA, CIT, and OX are not effective above pH 7. The equilibrium relationships depicted here are typical of those generally observed when these chelates are used as Fe fertilizers in soils of different pH.

Similar studies were reported by Cline *et al.* (1982) for nutrient solutions when amorphous Fe(III) oxide was present and various organic acids or DFOB (a natural hydroxamic siderophore: desferrioxamine B from ectomycorrhizal fungus *Boletus edulis*) was added. They found that α -keto glutarate, oxalate, pyruvate, malonate, malate, and succinate maintained less than 1% of their initial Fe above pH 6 (Fig. 3). Citrate was slightly more effective, but lost

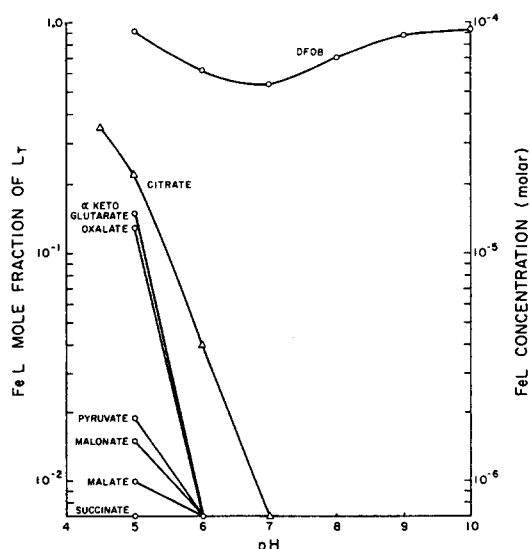


Fig. 3. Comparison of 8 organic acids to maintain Fe in nutrient solution over the pH range of 5 to 10 (from Cline *et al.*, 1982).

>99% of its Fe above pH 6.8. DFOB, on the other hand, retained from 50–90% of its Fe over the pH range of 5–10. The effectiveness of these chelates to retain Fe in solution in soils may be even less than in nutrient solutions because of the greater competition from soil cations.

The conclusion is drawn that DFOB and EDDHA are strong chelators of Fe and have the ability to increase its solubility in the pH range between 7.0 to 9.0 where Fe deficiencies are commonly found. DTPA, CDTA, and EDTA are somewhat effective in the lower end of this pH range. Except for citric acid which showed some effectiveness above pH 6, the other organic oxides were of little value. The persistence of high levels of organic acids in soils is unlikely due to their rapid decomposition by microorganisms.

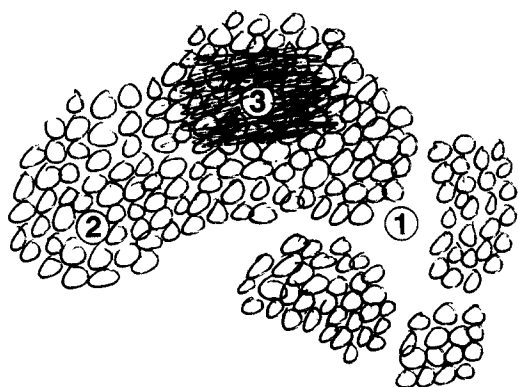
Siderophore solubilization of iron oxides

Considerable attention has been directed toward siderophores which are secreted by certain organisms in the rhizosphere of plant roots. These complex sequestering agents can solubilize Fe and aid its transport to plant roots. As mentioned in the previous section, DFOB has been shown to be a strong chelator of Fe in soils and to be effective in correcting Fe chlorosis in alkaline environments (Cline *et al.*, 1982). Stability constants of siderophores for many of the competing metals are not known with great accuracy. For this reason, it is difficult to make a detailed quantitative examination of the equilibrium relationships that are necessary to predict their importance. There are a number of different kinds of siderophores having different chemical, physical, and absorptive characteristics. More and more is being learned about these fascinating chelating agents and how they are able to solubilize Fe from soils, transport it across depletion zones near absorbing roots, and release it again either near or inside absorbing cells.

Organic matter and redox solubilization of Fe

The solubility of Fe in soils is greatly influenced by the redox of soils. Most soils are well-aerated

REDOX MICROSITES IN SOILS



1. Aerobic Gas Phase
2. Aerobic/Anaerobic with water films
3. Anaerobic - Spaces filled with water

Fig. 4. Diagrammatical representation of redox microsites caused by decomposing organic matter in soils subjected to different degrees of aeration.

and Fe(III) oxides control the solubility of Fe. Reduction occurs in soils near respiring roots, in microsites where organic matter is actively being degraded, and generally throughout submerged soils. Reduced microsites in soils (Fig. 4) are affected by texture, pore size distribution, organic matter content, and moisture. Water-filled pores greatly restrict the movement of oxygen into these regions. Organic matter is the carbon source utilized by many organisms in soils. If oxygen is present, it is utilized as the electron acceptor. Thus, organic matter and microorganisms are responsible for the reduction and increased solubilization of Fe.

Figure 5, adapted from Lindsay (1979), depicts, in a general way, how changes in redox affect the activity of Fe^{2+} in equilibrium with various Fe minerals. The redox parameter ($pe + pH$) used here was described previously (Lindsay, 1979; Lindsay and Sadiq, 1983). A value of 0 corresponds to the redox imposed by one atmosphere of $H_2(g)$ and a $pe + pH$ value of

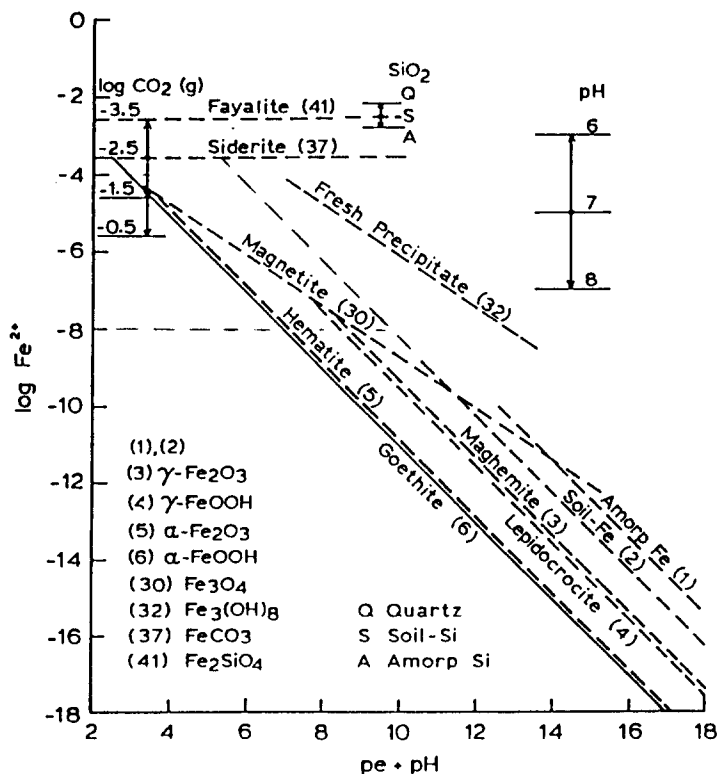


Fig. 5. The effect of $pe + pH$, $CO_2(g)$, and silica on the solubility of Fe minerals at pH 7 showing shifts with pH; the horizontal line at 10^{-8} is typical of the Fe level needed by plants (adapted from Lindsay, 1979 and Schwab and Lindsay, 1989).

20.6 corresponds to atmospheric $O_2(g)$. This diagram was drawn for pH 7.0, but it can easily be interpreted for any pH by using the pH-arrow sketch at the upper-right corner of the diagram. A unit decrease in pH shifts all lines up by 2 log units and corresponding increases in pH shift the lines down 2 log units.

The redox of most well-aerated soils lies in the $pe + pH$ range of 12–16. Figure 5 shows that if soil-Fe controls Fe solubility, $pe + pH$ would have to be, <10.0 (at pH 7) or <8.0 (at pH 8) for Fe^{2+} activity to exceed the minimal $10^{-8} M$ which Schwab and Lindsay (1989) found to be necessary for soybeans [*Glycine max* (L.) Merr.]. Soils that lie in the well-aerated range of $pe + pH > 12$ cannot supply adequate Fe for plants. Calcareous soils having $pe + pH$ values <8.0 should have no problem maintaining adequate available Fe. Submerged soils used for growing rice usually have $pe + pH$ values near 4 and are able to supply more than ample available Fe (Hanif *et al.*, 1986).

Schwab and Lindsay (1989) demonstrated that soybeans could lower the redox in a hydroponic media $pe + pH$ values <7 during absorption of Fe over a 24-hour period. Based on this observation, they concluded that the release of electrons near actively absorbing roots is a major mechan-

ism by which iron-stressed plants are able to obtain adequate Fe.

Organic matter and ferrosic hydroxide

Solubility relationships of Fe in many natural environments suggests that Fe may attain equilibrium with the mixed valency $Fe_3(OH)_8$ (ferrosic hydroxide). There is some controversy about the nature and exact composition of this solid described by Arden (1950) as ferrosic hydroxide. Schwab and Lindsay (1983) reviewed the literature on Fe solubility in natural environments and found that Fe solubility did not conform to a single mineral control (Fig. 6). Several studies showed elevated levels of soluble Fe that fell on or near the ferrosic hydroxide solubility line. This mixed valency mineral apparently persists in soils for extended periods of time (Schwab and Lindsay, 1983) and maintains Fe at a higher solubility than any of the Fe(III) oxides. The presence of ferrosic hydroxide extends the redox range at which adequate Fe ($10^{-8} M$) remains in solution to $pe + pH$ 14 (Fig. 6). The formation and persistence of this mixed valence Fe oxide is believed to be possible under conditions of alternating redox where Fe is solubilized

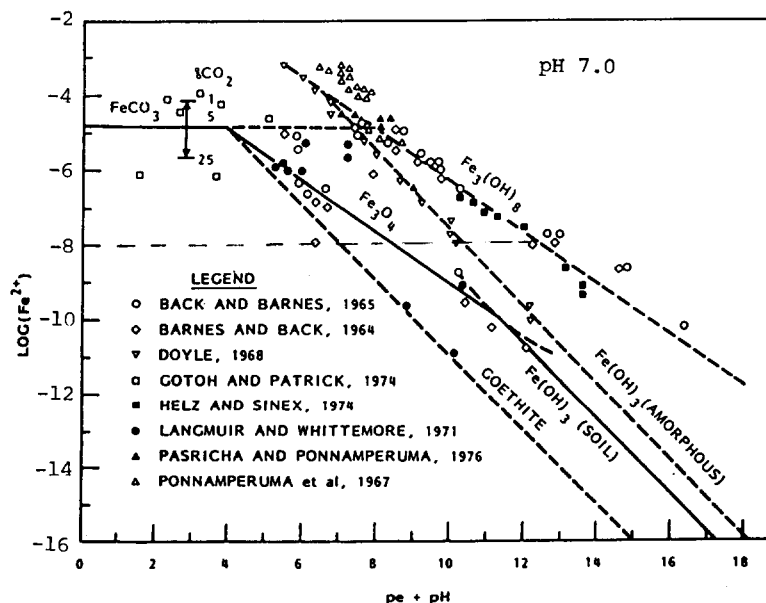


Fig. 6. Comparisons of measured and theoretical solubility relationships of Fe recalculated from the literature (from Schwab and Lindsay, 1983).

within reduced microsites and precipitated at more oxidized sites (Lindsay and Schwab, 1982). Several studies in our laboratory have demonstrated elevated solubilities of Fe that correspond to ferrosic hydroxide. The presence of this metastable precipitate may help to explain why some soils show Fe deficiencies while similar soils do not. Unless detailed redox relationships are examined on a micro-scale, the factors responsible for such subtle differences would not be detected.

Summary

Iron solubility in many soils (soil-Fe) reflects an ion activity product near $10^{-39.3}$. This solubility is slightly less than that of amorphous Fe(III) oxide, but more soluble than the common crystalline Fe(III) oxides. Addition of Fe salts to soils has little lasting effect on increasing Fe solubility because the amorphous precipitate soon reverts to soil-Fe.

The hydrolysis species of Fe^{3+} are the major solution species of Fe in aqueous environments and raise soluble Fe far above that of Fe^{3+} . These species reach a minimum solubility near $10^{-10.4}$ in the pH range of 7.5–8.5. Plants, on the other hand, require $>10^{-8}$ M Fe in solution to meet their needs. Calcium carbonate buffers soil pH in this range and explains the frequent occurrence of Fe deficiencies on calcareous soils.

Inorganic Fe(III) complexes form in soils and some of them are more plentiful than Fe^{3+} , but these complexes are usually insignificant compared to the hydrolysis species. Thus, inorganic complexes of Fe(III) normally do not increase Fe solubility significantly.

Iron also forms soluble organic complexes with organic acid anions and other organic functional groups. To assess the importance of organic complexes, one must consider competing metals, the activities of those metals in soils, and the concentration of free organic ligands. Again, the general conclusion is that most commonly found Fe-organic complexes are present at lower levels than the Fe hydrolysis species in the pH range above 7.

Siderophores or naturally occurring chelating agents are secreted by various organisms. Many

of these siderophores have sufficient affinity for Fe that they are stable in soil environments and are effective in keeping Fe in solution. In this way, Fe can be solubilized in the root zone and transported across diffusion gradients to active uptake sites of roots. To the extent that plants and associated organisms have the ability to produce effective siderophores, those plants are able to obtain adequate Fe.

Organic matter performs another significant function in increasing Fe availability to plants. Most soils contain microsites where organic matter is actively metabolized. When these sites become water-saturated, oxygen entry is restricted, and the sites become partially anaerobic. Iron oxides dissolve releasing Fe^{3+} and Fe^{2+} which precipitate a mixed-valent, metastable ferrosic hydroxide. Fluctuating redox conditions are conducive to the dissolution and precipitation of Fe. This precipitate temporarily maintains elevated levels of soluble Fe.

Respiration processes near plant roots create reduced microenvironments where elevated levels of Fe^{2+} occur. The level of soluble Fe^{2+} in the reduced microsites soon exceeds that of the hydrolysis species and the critical level of Fe required by plants. Organic matter decomposition provides the release of electrons and other reducing agents responsible for the increased solubility and availability of Fe.

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