Ecological Soil Screening Level
for
Iron

Interim Final

OSWER Directive 9285.7-69

U. S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460

November 2003

TABLE OF CONTENTS

This Page Intentionally Left Blank

SUMMARY OF ECO-SSLs FOR IRON

Iron is a commonly occurring metallic element, comprising 4.6% of igneous rocks and 4.4% of sedimentary rocks (Morel and Hering, 1993). The typical iron concentrations in soils range from 0.2% to 55% (20,000 to 550,000 mg/kg) (Bodek et al., 1988), and concentrations can vary significantly, even within localized areas, due to soil types and the presence of other sources. Iron can occur in either the divalent (ferrous or Fe^{+2}) or trivalent (ferric or Fe^{+3}) states under typical environmental conditions. The valence state is determined by the pH and Eh (redox potential) of the system, and the iron compound is dependent upon the availability of other chemicals (e.g., sulfur is required to produce FeS_2 or pyrite).

Iron is essential for plant growth and is generally considered to be a micronutrient (Thompson and Troeh, 1973). Iron is considered the key metal in energy transformations needed for syntheses and other life processes of the cells. Consequently, plants regulate iron uptake.

Ferrous iron is more soluble and bioavailable to plants than ferric iron. Iron occurs predominantly as Fe^{+3} oxides in soils (Bodek et al., 1988). Goethite (α-FeOOH) is the predominant mineral form (Kabata-Pendias and Pendias, 1984). The divalent state (or ferrous state) can be oxidized to the trivalent state (or ferric state), where it may form oxide or hydroxide precipitates, and become unavailable to plants as a micronutrient (Thompson and Troeh, 1973).

The general rule governing the mobilization and fixation of iron are that oxidizing and alkaline conditions promote the precipitation of insoluble iron Fe^{+3} oxides, whereas acidic and reducing conditions promote the solution of ferrous (Fe^{+2}) compounds. The availability of ferrous vs. ferric iron is also dependent on the soil-water status of a particular environment. For example, reduced environments (which include lowland or waterlogged soils) promote the availability of ferrous iron to plants, while oxidized environments (upland or well-aerated soils) promote the precipitation of ferric-oxide compounds, which are not available to plants for uptake. If excess ferrous iron occurs, iron toxicity may occur in plants, but this is highly dependent upon plant species. Likewise, if ferrous iron is not available in soils due to precipitation of ferric iron compounds, iron deficiency or chlorosis may occur. Proper soil management can help control the pH and soil-water status and allow optimal concentrations of bioavailable ferrous iron to plants.

Currently, identifying a specific benchmark for iron in soils is difficult since iron's bioavailability to plants and resulting toxicity are dependent upon site-specific soil conditions (pH, Eh, soil-water conditions). To evaluate site-specific conditions and potential toxicity of iron to plants, it is recommended that the site-specific measured pH and Eh (collected concurrently in the field) be used to determine the expected valence state of the iron and associated chemical compound and resulting bioavailability and toxicity in the environmental setting. In well-aerated soils between pH 5 and 8, the iron demand of plants is higher than the amount available (Römheld and Marschner, 1986). Because of this limitation, plants have evolved various mechanisms to enhance iron uptake (Marschner, 1986). Under these soil conditions, iron is not expected to be toxic to plants.

1.0 INTRODUCTION

Iron, like aluminum, is a commonly occurring metallic element, comprising 4.6% of the igneous rocks and 4.4% of sedimentary rocks (Morel and Hering, 1993). The typical range of iron concentrations in soils is from 0.2% to 55% (20,000 to 550,000 mg/kg) according to Bodek et al. (1988). Native iron concentrations are region-specific, and can vary significantly even within localized areas due to soil types and presence of other sources. Sandy soils have the lowest overall iron content, and clayey soils have the highest iron content (McGovern, 1987); however, there is significant overlap in these ranges and, therefore, this should only be used as a general guide.

Iron can occur in either the divalent (Fe^{+2}) or trivalent (Fe^{+3}) states. Iron occurs predominantly as Fe^{+3} oxides in soils (Bodek et al., 1988). Goethite (α-FeOOH) is the predominant mineral form (Kabata-Pendias and Pendias, 1984). The divalent state (or ferrous state) can be oxidized to the trivalent state (or ferric state), where it may form oxide or hydroxide precipitates, and become unavailable to plants as a micronutrient (Thompson and Troeh, 1973). Roots of some plants are able to reduce iron from the ferric to the ferrous state, and allow iron uptake into the plant (Grussak, 1996).

Significant amounts of iron are released into the environment as a result of coal mining. During these operations, pyrite (FeS_2), which is found in coal seams, is exposed to air and water and is oxidized to sulfate by bacterial and chemical reactions. This process releases dissolved ferrous iron (Fe^{+2}) into mine drainage. The ferrous iron then reacts with oxygen to form ferric iron (Fe^{+3}), which hydrolyzes to form insoluble ferric hydroxide ($FeOH_3$). The ferric hydroxide precipitates out in mines and streams where it acts as a reservoir for insoluble ferric iron, which then reacts with pyrite to generate soluble ferrous iron (Bodek et al., 1988).

2.0 IRON GEOCHEMISTRY

The iron in most primary minerals (ferromagnesian and oxide phases) occurs in the ferrous (Fe^{+2}) oxidation state, which is more soluble than ferric iron (Fe^{+3}). There are several different kinds of iron oxides, each with a different solubility (Schwertmann, 1988). Figure 2.1, taken from Lindsay (1979), compares the solubility of several of the commonly reported iron oxides.

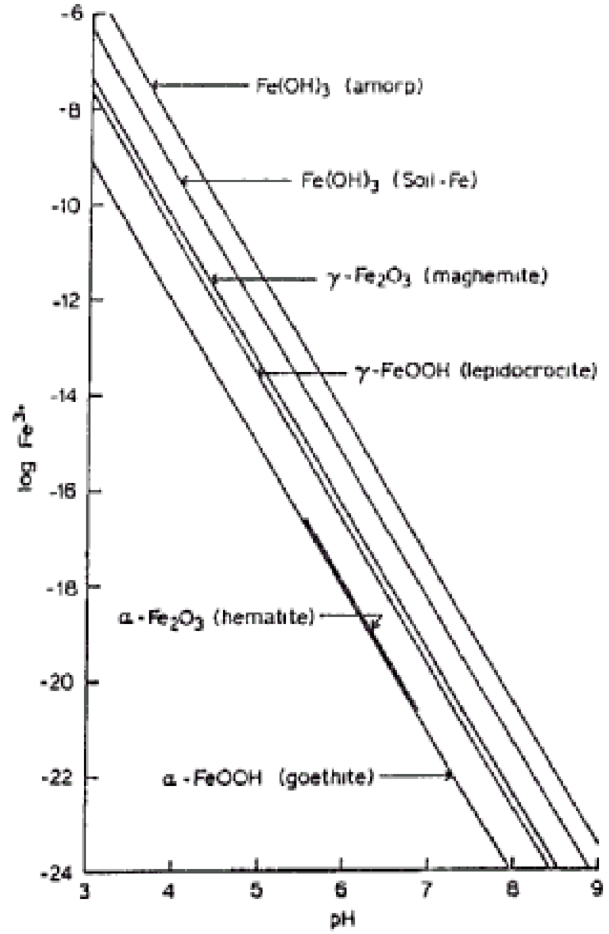

Figure 2.1 The Activity of Fe^{+3} in Equilibrium with Various Fe (III) Oxides (Lindsay, 1979 as cited in Bodek et al., 1988 and SSSA, 1991).

Free iron minerals that occur in soil are used as a key characterization for soils and for soil horizons. Iron minerals that are known to also form pedogenically are included in Table 2.1 (Kabata-Pendias and Pendias, 1992) (Dragun, 1988).

Table 2.1 Summary of Iron Minerals		
Mineral	**Chemical Formula**	**Characteristics**
Hematite	αFe_2O_3	Hematite, which has a pint to bright red color, occurs mainly in highly weathered soils of arid, semiarid, and tropical regions and is most often inherited from parent material. It is only slightly less common than goethite. Like goethite, hematite is a stable mineral in an oxidizing environment. However, because Fe^{+3} can be reduced to Fe^{+2} under reducing conditions that can occur in saturated soils, hematite is unstable under reducing conditions.
Maghemite	γFe_2O_3	Maghemite is formed in highly weathered soils of tropical zones and most often occurs in concentrations accompanied by hematite, magnetite, or goethite.
Magnetite	Fe_3O_4	Magnetite is a magnetic iron oxide that usually occurs as a sand-sized mineral and is mostly inherited from parent material. Oxidation of magnetite yields maghemite (Fe_2O_3), which is also magnetic.
Ferrihydrite	Fe_2O_3 x n H_2O	Ferrihydrite is a common, but unstable, soil mineral and is easily transformed to hematite in warm regions and to goethite in humid temperature zones.
Goethite	$\alpha FeOOH$	Goethite is the most common iron mineral in soils over broad climatic regions, from temperate to tropical. It is responsible for the brownish to yellowish color of many soils, even though it may be present in small quantities. Goethite is stable in an oxidizing environment. However, ferric iron (Fe^{+3}) can be reduced to ferrous (Fe^{+2}) under the reducing conditions that can occur in saturated soils; as a result, goethite is unstable under reducing conditions.
Lepidocrocite	γ-FeOOH	Lepidocrocite is common to poorly drained (e.g., paddy soils) soils of humid temperate regions. The formation of this mineral in soils is favored by lower pH, lower temperature, and the absence of Fe^{+3}.
Ilmenite	$FeTiO_3$	Ilmenite is not common in soils. As a mineral resistant to weathering, it is usually inherited from igneous parent rocks.
Pyrite	FeS_2	Pyrite is widely distributed in submerged soils containing sulfur (e.g., acid sulfate soils).
Ferrous sulfide	FeS	Ferrous sulfide is widely distributed in submerged soils containing sulfur (e.g., acid sulfate soils).
Jarosite	$KFe_3(SO_4)_2(OH)_6$	Jarosite is widely distributed in submerged soils containing sulfur (e.g., acid sulfate soils).

The solubility of Fe^{+3} is usually controlled by the most soluble oxide present; thus, freshly precipitated amorphous magnetite or siderite (Soil-$Fe(OH)_3$) is the most soluble Fe^{+3} oxide and generally controls the activity of Fe^{+3} and the solubility of Fe^{+2} in soils, depending on redox and CO_2 (Bodek et al., 1988). Under oxidizing conditions (pe + pH > 11.5), soil-$Fe(OH)_3$ (which is intermediate in solubility to amorphous hydroxide and crystalline oxide) controls the solubility;

below 11.5, magnetite (Fe_3O_4) is the stable phase until siderite ($FeCO_3$) forms, as determined by the partial pressure of CO_2(g) (Lindsay, 1979).

Other Fe^{+3} oxides are listed in order of decreasing solubilities:

- $Fe(OH)_3$ (soil-Fe);
- γ-Fe_2O_3 (maghemite);
- γ-FeOOH (lepidocrocite)
- αFe_2O_3 (hematite); and
- αFeOOH (goethite).

The solubility of $Fe(OH)_3$ (amorp) is 3,630 times more soluble than that of goethite (Lindsay, 1979).

2.1 Weathering Processes Affect on Iron

The reactions of iron in the processes of weathering are dependent largely on the Eh-pH system of the environment and on the stage of oxidation of the iron compounds involved. The electron potential for the Fe(II)/Fe(III) couple is -0.771 V (Bodek et al., 1988). The general rule governing the mobilization and fixation of iron are that oxidizing and alkaline conditions promote the precipitation of insoluble iron Fe^{+3} oxides, whereas acidic and reducing conditions promote the solution of ferrous (Fe^{+2}) compounds. The released iron readily precipitates as oxides and hydroxides, but it substitutes for Mg and Al in other minerals and often complexes with organic ligands (Kabata-Pendias and Pendias, 1992).

The general behavior of iron in the weathering zone can be summarized under four headings.

- In an oxidizing environment, with atmospheric O_2 dominant, iron forms goethite (α-FeOOH) as the stable mineral (or other hydroxy phases metastably) as the normal trend. For high S_2, low CO_3 (the acid sulfate environment), jarosite [$KFe_3(SO_4)_2(OH)_6$] may form. In organic-rich conditions, iron is transported as chelates in solution.

- In a reducing environment, with bacteria using C to reduce Fe^{+3} to Fe^{+2}, and SO_4 to S, high S_2 yields pyrite FeS_2, low S_2 and high CO_3 yields siderite ($FeCO_3$), and Fe^{+3} remains in solution if both S_2 and CO_3 are low.

- Glauconite is the only authigenic iron silicate forming in modern sediments, although iron smectites occur in the weathering zone, transilently, as alteration products of ferromagnesian phyllosilicates.

- Iron is transported principally as fine, particulate hydroxides, or as coatings on detrital grains. Sorting is accomplished by different settling rates (SSSA, 1991).

Iron's natural equilibrium state exists as an oxidized ion (Fe_2O_3, FeO, Fe_3O_4), but when processed into iron or steel, it loses the oxygen and becomes elemental iron (Fe^0). In the presence of water and oxygen, nature reverts elemental iron into an oxide compound. The corrosion processes of iron involve three steps:

1. Some of the elemental iron (Fe^0) is lost to the water solution and becomes the oxidized Fe^{+2} ion. This part of the metal is called the anode.

$$\textit{Anodic reaction: } Fe^0 >> Fe^{+2} + 2e-$$

2. When the Fe^{+2} ion is formed, two electrons are released to flow through the steel of the cathode area.

3. Oxygen (O_2) in the water solution near the surface of the metal uses the electrons to form hydroxyl ions (OH^-). This part of the metal is called the cathode. The loss of O_2 into(OH^-) causes a movement of O_2 towards the cathode. The electrical circuit is now complete.

$$\textit{Cathodic reaction: } \tfrac{1}{2}\, O_2 + H_2O + 2e- >> 2(OH^-)$$

If oxygen is not present for the reaction, the hydrogen ion (H^+) replaces oxygen at the cathode (Dragun, 1988).

There are other mechanisms which can influence the valence state of the iron in the environment. Photoreduction of Fe^{+3}, can also occur in low pH waters, where reoxidation is slow, as evidenced by diel variations of Fe^{+3} especially in acidic waters (Morel and Hering, 1993). Although a preliminary search of the literature did not confirm or deny that this phenomenon would occur in soils, it is not likely to be significant due to attenuation of light at the soil surface and at depth within the soil column.

2.2 Soil Conditions Affect on Iron

The iron oxide that is present in soil is dependent upon the moisture content, pH, and oxygen content of the soil. In wet, but oxic soil conditions, the iron oxide typically would exist in the hydrated ferric oxide state. In wet and hypoxic soil conditions, the typical iron oxide is in the ferrous state. The conversion to the ferrous state is used to identify the boundaries of hydric soils typical of wetlands (NSCSS, 1999).

The solubility of inorganic Fe in well-aerated soils is controlled by the dissolution and precipitation of Fe^{+3} oxides. As previously stated, the concentration of Fe^{+3} is related to pH, increasing from 10^{-8} to10^{-20} M as pH increases from 4 to 8 (Römheld and Marschner, 1986). High HCO_3 concentrations decrease the availability of Fe in calcareous soils (Bloom and Inskeep, 1988).

Except under special conditions, the transformation of one Fe^{+3} oxide to another in soils occurs slowly due to the low solubilities of these minerals. Thus, several Fe^{+3} oxide minerals may persist together in soils for long periods of time without being transformed in their entirety to the most insoluble mineral form (SSSA, 1991).

In various soils and especially at low pH, iron oxides can precipitate on clay surfaces. These coatings, once formed, are stable at higher pHs. The coatings are gel-like in appearance, may flow when wet, shrink and become porous when heated, and cement primary particles into aggregates. These amorphous coatings transform to crystalline forms when aged (Dragun, 1988).

Amorphous and crystalline iron oxides play major roles in stabilizing soil structures. Iron oxides stabilize clay minerals by decreasing critical coagulation concentration, clay dispersion, water uptake, and clay swelling and by increasing microaggregation. They can increase aggregate stability, permeability, friability, porosity, and hydraulic conductivity. Also, these amorphous oxides can reduce swelling, clay dispersion, bulk density, and modules of rupture (Dragun, 1988).

The formation of iron oxides is also affected by organic matter and bacteria. Bacteria may mediate the conversion between the principal iron valence states. Iron bacteria oxidize Fe^{+2} to Fe^{+3}, incorporating the released energy as part of their metabolism. The mechanism is shown below:

$$4\ FeCO_3\ (s) + O_2\ (g) + 6\ H20 \rightarrow 4\ Fe(OH)_3\ (s) + 4\ CO_2\ (g)$$

Some of the common iron bacteria include *Ferrobacillus*, *Crenothrix*, *Lepthrix* and *Gallionella* (Bodek et al., 1988;WQA, 1997) and are observed as bacterial slimes in water systems. In addition, some bacteria species (e.g., *Metallogenium* sp.) are involved in iron cycling and are known to accumulate iron on the surfaces of living cells (Kabata-Pendias and Pendias, 1992). A preliminary review of the literature did not identify any studies that confirmed the presence of iron bacteria in soils stained with iron floc.

The distribution of extractable iron in soil depends on the presence of organic matter. Iron forms metal chelates with organic matter. Soil humic acid strongly adsorbs or complexes with iron at $pH > 3$ (Bodek et al., 1988). Other soil constituents that adsorb Fe^{+3} are crystalline oxides, clay minerals, and hydrous oxides of iron and manganese. Table 2.2 gives some adsorption constants for iron on clay minerals, silica, and organic matter. The solubility or iron depends primarily on the solubility of the hydrous Fe^{+3} oxides. Hydrolysis, complexation and redox processes are also important. In addition, iron solubilities may be significantly affected by the formation of other iron compounds, such as phosphates, sulfides, and carbonates (Bodek et al., 1988).

Variations in soil redox levels provide another means of increasing the solubility of iron in soils. Normally, soils are considered well-aerated with Fe(III) oxides controlling the solubility of iron.

However, reduction occurs in soils, near respiring roots, in microsites where organic matter is actively being degraded, and generally throughout submerged soils (SSSA, 1991).

Changes in soil properties, such as pH or redox status, can bring more insoluble iron into these fractions, making it less available to plants. In organic soils, 50% of the iron was found in the organic plus sulfide fraction (NaOCl), but little was found in this form in mineral soil horizons (Hoffman and Fletcher, 1978). Most of the iron resides in the amorphous and crystalline iron-oxide and residual fractions (Shuman, 1979, 1985; Hoffman and Fletcher, 1978).

Table 2.2 Adsorption Constants for Iron
(Electric Power Research Institute, 1984 as cited in Bodek et al., 1988)

Adsorbent	Analyte Conc. (M)	pH	A_m	K_L	A
Clay Minerals					
Kaolinite	$10^{-5.5}$ - 10^{-5}	3	4.3	5.5	-
Ca-saturated	$10^{-5.5}$ - 10^{-5}	4	14.9	6.0	-
Na form	0 - 0.015	3	1430	2.6	-
Bentonite, *Na form*	0 - 0.015	3	6180	2.8	-
Illite, *Na form*	0 - 0.015	3	4920	2.9	-
Montmorillonite	$10^{-2.5}$	>0.5	-	-	220
Na form	$10^{-2.5}$	>1.0	-	-	260
		>1.6			280
H form	$10^{-2.5}$ - $10^{-2.2}$	-	460	4.2	-
Silica					
SiO_2	$10^{-3.9}$	2.7	-	-	4.0
SiO_2	0 - $10^{-3.4}$	2.5	0.5	6.4	-
		3.0	1.0	6.7	-
Organic Matter					
Humic acid (soil)	$10^{-4.3}$ - $10^{-3.3}$	2.4	1760	3.2	-

Notes:
A_m = Langmuir adsorption maximum (umol/g)
K_L = Langmuir constant (log M-1)
A = Adsorption (umol/g)

Imposing reducing conditions on soils mobilizes the iron-oxide fraction, which becomes associated with the exchangeable, organic, and Mn-oxide fractions, making it more plant available. Increases in soil pH or Eh (oxidizing conditions) shift iron from the exchangeable and organic forms to the water-insoluble and iron-oxide fractions. Shuman (1988), in adding organic matter to soil, caused reducing conditions with alternate wetting and drying. Iron changed from the less soluble forms to the exchangeable and organic forms in response to the increased organic matter. Iron in fractions differed among marsh locations, probably due to different oxidation/reduction states (Lindau and Hossner, 1982). Tillage can affect pH and other soil properties.

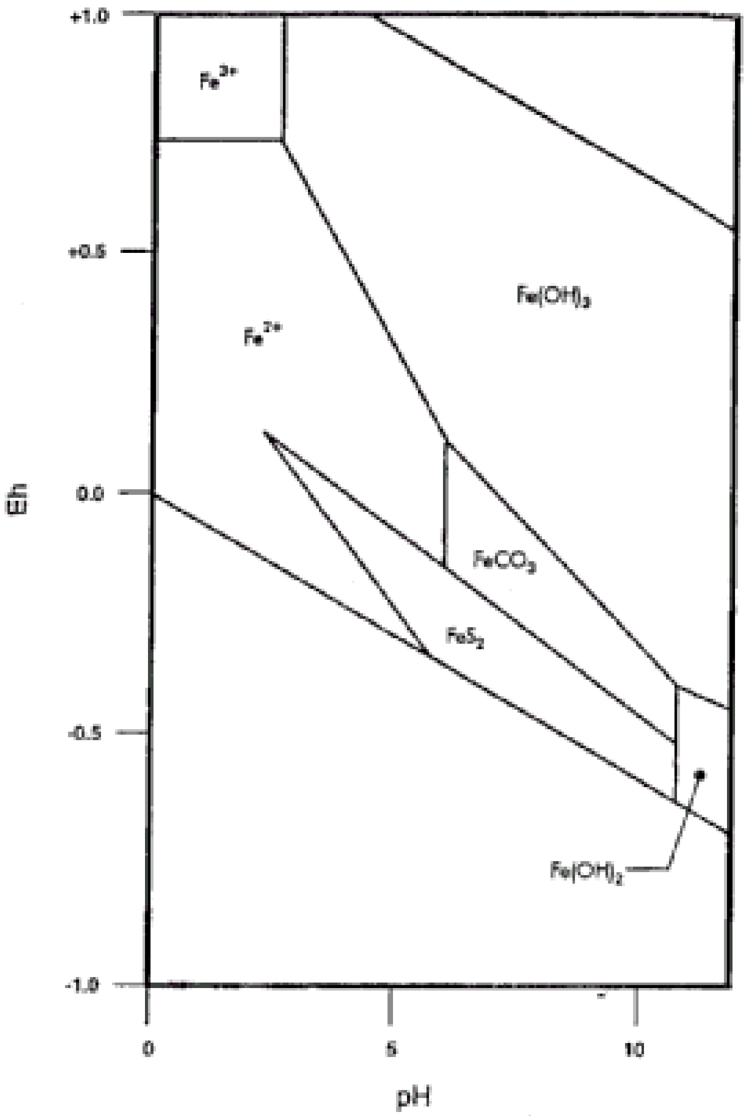

Figure 2.2 Typical forms of iron in soil under different conditions of pH and Eh (i.e., redox potential).

Figure 2.2 shows the typical forms of iron in soil under different conditions of pH and Eh (i.e., redox potential). The formation of certain iron compounds, such as FeS_2, is also dependent upon the availability of other chemicals, in this case sulfur, in the system. The solid phases shown in Figure 2.2 (e.g., precipitates) are $Fe(OH)_3$, $FeCO_3$ (siderite), FeS_2 (pyrite), and FeS. The chemical FeO_4^{-2} is not likely to be found in an environmental setting since it is strongly oxidizing.

One typical approach to evaluating whether there is any potential for iron's geochemistry to affect its environmental behavior is to superimpose the measured pH and Eh (collected concurrently in the field) on Figure 2.2. Based upon this result, the determination can be made of the valence state of the iron and its potential chemical compound (and resulting bioavailability and toxicity) in the environmental setting.

3.0 EFFECTS OF IRON ON PLANTS

Iron is considered a plant micronutrient. Iron is absorbed by plants as the ferrous ion (Fe^{+2}), which is necessary for the formation of chlorophyll and functions in some of the enzymes of the plant's respiratory system (Schneider et al., 1968). Much of the iron in well-drained soils is in the ferric (Fe^{+3}) form, which is unavailable to plants. Iron deficiencies may result if the soil minerals do not gradually release ferrous (Fe^{+2}) iron to replace that which is being oxidized to ferric iron over time (Thompson and Troeh, 1973). Iron deficiencies can also result from an excess of manganese and possibly copper (Sommer,1945). Manganese and copper are oxidizing agents that convert ferrous irons to the more insoluble ferric form. Iron deficiencies caused by manganese toxicity occur in acidic soils that otherwise would supply adequate iron for plant growth (Thompson and Troeh, 1973).

3.1 Essentiality

Iron is recognized as an essential element as early as 1845. Iron is essential for plant growth, and is generally considered to be a micronutrient Iron is necessary for the formation of chlorophyll and functions in some of the enzymes of the respiratory system. Iron is an abundant element in rocks and soils, but it is also one of the most commonly deficient micronutrients. This problem is associated with the extremely insoluble nature of certain compounds of ferric (Fe^{+3}) iron. These compounds accumulate in highly weathered soils and are major constituents of the red soils of tropical regions. Fossil remnants of some ancient soils contain enough iron to serve as iron ore. These compound, however, are too insoluble to meet plant needs, even as a micronutrient (Thompson and Troeh, 1973).

The mechanisms of iron uptake and transport by plants have received much study because they are the key processes in the supply of iron to plants. Almost all instances of iron deficiency in plants are considered to occur because of soil factors that govern iron solubility (Kabata-Pendias and Pendias, 1992).

The metabolic functions of iron in green plants are relatively well understood, and iron is considered the key metal in energy transformations needed for syntheses and other life processes of the cells. The essential role of iron in plant biochemistry can be summarized as follows (Kabata-Pendias and Pendias, 1992):

- Iron occurs in heme and nonheme proteins and is concentrated mainly in chloroplasts.
- Organic iron complexes are involved in the mechanisms of photosynthetic electron transfer.
- Nonheme iron proteins are involved in the reduction of nitrates and sulfates.
- Iron is likely to be directly implicated in nucleic acid metabolism.
- The catalytic and structural role of Fe^{+2} and Fe^{+3} are also known

3.2 General Effects

The interaction between soil and plant genotype is very important for iron nutrition (SSSA, 1991). Efroymson et al. (1997a) reviewed several studies which examined plant sensitivity to iron from soil solutions. Wallihan (1966) reported unspecified reductions in plant growth in a solution culture with the addition of 10 mg/L of iron. Wallace et al. (1977) evaluated the effects of iron (as $FeSO_4$) on leaf, stem, and root weights of bush bean seedlings grown for 15 days in nutrient solution. Iron at 28 mg/L reduced all three measures 67, 52, and 67%, respectively, while 11.2 mg/L had no effect. After 55 days, cabbage seedling plant weight was reduced 45% by 50 mg/L Fe added as $FeSO_4$ nutrient solution (pH 5), while 10 mg/L had no effect on growth (Hara et al., 1976). Based on these studies, the lowest-observed effect concentration (LOEC) values for iron are 28 and 50 mg/L, and the no-observed effect concentrations (NOECs) are 11.2 and 10 mg/L.

Many of the toxicity tests used to develop benchmarks are based on the addition of iron as a salt solution (e.g., $FeSO_4$) to the exposure medium. Thus, the results may conservatively represent effects of iron in its most bioavailable form, and not those that have undergone geochemical processes, valence changes, sorption/desorption, and other processes that are expected in an environmental soil matrix.

3.2.1 Iron Deficiency

When iron deficiency occurs in plants, a sharp distinction develops between green veins and the less green (or yellow) tissue between veins (Wallihan, 1966). This shortage of chlorophyll in the plant's leaves is called chlorosis. The younger leaves are more affected than older leaves because iron is relatively immobile inside the plant (Thompson and Troeh, 1973). The major cause of chlorosis in plants on well-aerated soils is the insolubility of Fe^{+2} oxides. As the redox potential and/or soil pH increases, the availability of iron in soil solution to plants decreases. The critical redox potential for Fe^{+2} reductions is between +300 mV and +100 mV at pH 6 and 7, and -100 mV at pH 8 (Gotoh and Patrick, 1974).

Iron deficiency may occur in noncalcareous, coarse-textured soils (Chesney, 1972), but iron deficiencies are more common in calcareous soils (Miller et al., 1984). The equilibrium concentration of solution-phase iron in a calcareous system is very low (SSSA, 1991).
Iron availability in soils for plant uptake depends to a large extent on soil pH, complexing ligands and redox potential (Beckwith et al., 1975). Excess soil moisture increases the more soluble and mobile ferrous iron (Bjerre and Schierup, 1985), with waterlogging resulting in a decrease in redox potential (Sonar and Ghugare, 1982). Imperfectly drained soils often contain rust mottles which are formed by mobile ferrous iron moving to points where it is oxidized and precipitated as ferric iron (Thompson and Troeh, 1973).

The solubilities of ferric and ferrous iron are much higher at low pH than at high pH. Iron compounds, including $Fe(OH)_3$ and $Fe(OH)_2$, have low solubilities and can be precipitated at high pH because OH^- ions become more abundant when the pH rises. One of the hazards of over liming a soil is the precipitation of previously mobile iron and the resulting lime-induced chlorosis (Thompson and Troeh, 1973).

Research findings suggest that plants need in excess of 10^{-8} M of soluble Fe to supply their nutritional needs (Schwab and Lindsay, 1989). Inorganic Fe^{+3} oxides cannot maintain this level of soluble Fe in soils above pH 5.5 to 6. Either chelation by natural or synthetic chelates, or reduction of Fe(III) to Fe(II) is necessary to raise the solubility of iron in soils above this critical level (Lindsay and Schwab, 1982).

Iron deficiency is commonly accompanied by a reduced rate of growth, although it is not always certain whether this results from the deficiency or from the conditions that brought on the deficiency (Wallihan, 1966). Iron deficiency most commonly occurs in calcareous soils, poorly drained soils, and manganese rich soils (Wallihan, 1966). Soil management practices and other conditions which may produce or aggravate iron deficiency include: high concentration of soil moisture; high concentration of a heavy metal (notably copper, manganese, nickel and zinc) in an acid soil; excessively low or high soil temperatures; the presence of certain organisms (e.g., fungi or nematodes); and soil oxygen deficit (Wallihan et al, 1961; Wallihan, 1966).

Plant refuse, manures, sewage, sludges, peats, charcoal, byproducts of forest-product manufacturing (polyflavonoids and lignosulfonates), and even coal have been shown to be effective in alleviating iron chlorosis (Chen and Barak, 1982). Various plant species sprayed with iron and subsequently applied to problem soils are effective in supplying iron to plants (Matocha, 1984; Matocha and Pennington, 1982). Iron-organic compounds in manure are also effective in maintaining iron in an available form (Parsa et al., 1979).

3.2.2 Iron Toxicity

In general, iron toxicity is associated with increased iron uptake and translocation by plant tops (Brown and Jones, 1977; Chin, 1966; Clements et al., 1974; Perkins et al., 1972; Rhoads, 1971; Tadano, 1975; and Tanaka and Yoshida, 1970). For example, Rhoads (1971) found that in tobacco plants injured by iron toxicity, leaf strength decreased with increasing iron content between 450 and 1,126 ppm. Such leaves also contained lower manganese concentrations than normal (Perkins et al., 1972). Tanaka and Yoshida (1970) reported that the “bronzing” disease of rice is associated with accumulation of iron in necrotic spots on leaves. “Freckle leaf” in sugarcane is also associated with localized accumulations of iron in leaves (Clements et al., 1974). Maui leaf freckling” of sugarcane is associated with the accumulations of iron, aluminum, and manganese and with low levels of SiO_2 in leaves (Clements et al., 1974). Apparently, plants high in calcium and SiO_2 can tolerate higher internal levels of iron, aluminum, and manganese, perhaps by preventing localization into toxic spots. Clements (1974) concludes that silicon functions primarily as a detoxifier and is not essential for sugarcane if toxic factors are absent.

Symptoms of iron toxicity are expressed differently in different plants. Millikan (1949) notes that excess iron in flax produced dark green foliage and stunted top and root growth. Roots are reportedly thickened with large accumulations of inorganically-bound phosphate. Phosphate deficiency intensifies the dark green color while excess phosphates reduce the green color. These symptoms are very similar to those often described for aluminum toxicity. However, Skeen (1929) maintains that iron and aluminum are quite different in their effects on the roots of lupine and bean. He observes that root tips are flabby with excess iron and brittle with excess aluminum. In rice, iron toxicity is characterized by brown spots starting from the tips of lower leaves (Tadano, 1975). The spots spread over the leaves and then progress to the upper leaves while the lower leaves eventually turn gray or white. Symptoms differ widely with the age of the plant, the nutritional state, and the cultivar. Frequently, iron toxicity is difficult to identify by plant symptoms alone (Tadano, 1975). In tobacco, excess iron produces brittle, tender, dark brown to purple leaves with poor burning qualities and flavor (Perkins et al., 1972 and Rhoads, 1971). In navy bean, iron toxicity is associated with zinc deficiency which produces black spots on the foliage (Ambler and Brown, 1970 and Ambler et al., 1970).

Iron toxicity (foliar injury) has been produced in cigar wrapper tobacco by sprinkler irrigation with pond water containing > 1.5 ppm Fe (Purves (1972); Rhoads (1971)). The excess ferrous Fe in the pond water was attributed to the reducing conditions created by excess growth of aquatic plants. Wallace and Bhan (1962) suggest that some plants grow poorly in acid soils because of excess Fe absorption. Rogers (1973) report an iron-induced manganese deficiency in the Elberta peach. Brown and Jones (1977) suggest that Fe toxicity limits the growth of Bragg soybean on an acid Richland soil at pH 5.2. Olsen (1972) attributs the poor growth of hemp and mustard to iron toxicity in certain acid soils (below pH 6.0) (Foy et al., 1978).

Iron toxicity is believed to be involved in several extremely complicated physiological diseases of rice under flooded conditions. These include “bronzing” in Sri Lanka and elsewhere, “Alkagare Type” disorder in Japan, and “Akiochi” in Korea (Aizer et al., 1975; Howeler, 1973; Ponnamperuma, 1955; Tadano, 1975; Tanaka and Yoshida, 1970; and Thenabadu, 1974-1975). Howeler (1973) attributes bronzing in flooded rice to iron-induced deficiencies of several essential elements, mainly phosphorus, potassium, calcium, and magnesium (Foy et al., 1978). Roots of plants growing in soils high in soluble Fe may be coated with oxidized Fe (Howeler, 1973), which may reduce the uptake of other nutrients (SSSA, 1991). Mulleriyawa (1966) indicates that iron toxicity causes bronzing in plants, when the soil potassium level is low. He also suggests that excess H_2S could predispose plants to bronzing by reducing or inhibiting root respiration. Tanaka et al. (1976) and Tanaka and Yoshida (1970) found that in the presence of high iron concentrations, the rice root oxidizes iron and deposits it on root surfaces. Root tips accumulate considerable amounts of iron and translocate it to lower leaves if critical concentrations are exceeded. Cutting the roots increases iron uptake and the degree of toxicity. The lowest iron concentration found to produce toxicity is 100 ppm at pH 3.7, but sometimes 500 ppm are required, depending on many factors. Much less iron is required to injure young seedlings than older plants. Root damage by H_2S may aggravate or predispose plant roots to iron toxicity by destroying their oxidizing abilities. Even in nutrient solutions, the critical iron levels required to cause bronzing are difficult to determine. Iron toxicity is more severe when potassium levels are low in the growth medium (Foy et al., 1978).

Ponnamperuma (1955) associates bronzing disorder in rice with high concentrations of reduced products, particularly Fe^{+2}, in the soil solution. The conditions are improved by drainage, delayed submergence, or the addition of reduction retardants such as MnO_2.

The addition of MnO_2 at 0.4% by weight to the soil improved the growth of rice on three acid soils of pH 3.6 to 5.8. The beneficial effects of MnO_2 are attributed to an increase in the redox potential and reduced concentrations of Fe^{+2} and organic reduction products. Nhung and Ponnamperuma (1966) note that even after submergence, the pH levels of some acidic soils do not rise above 6.0. At pH levels below 6.0, a reduced soil can contain 5,000 ppm Fe^{+2} in the soil solution if the important solid phase is $Fe_3(OH)_8$. If FeS is the major solid phase, the concentration of Fe^{+2} depends on the pH and H_2S levels. In acid soil at a pH of 3.6, the death of rice seedlings is attributed to high concentrations of Al (68 ppm) and Fe^{+2} (490 ppm) in soil solution. Aluminum at 25 ppm and $Fe^{+2} > 500$ ppm are highly toxic to rice. Ferrous Fe concentrations > 400 ppm during most of the season are associated with toxicity. High salt (NaCl) concentrations aggravate the iron toxicity disorder by causing physiological drought (Nhung and Ponnamperuma, 1966). Iron toxicity was overcome by liming to pH 5.0 - 5.5 at planting, to give a pH of 6.0 a few weeks after flooding. Application of MnO_2 counteracted Fe toxicity by decreasing the concentration of Fe^{+2} in solution. The addition of $Fe(OH)_3$ aggravates iron toxicity. Ferrous iron concentrations of 730 ppm in an acid soil solution killed rice plants one day after transplanting; 365 ppm of ferrous iron at planting or 655 ppm 11 weeks after planting produced toxicity symptoms. However, water-soluble (Foy et al., 1978).

Certain management practices, such as periodic soil drainage to allow oxidation of the soluble Fe and the use of resistant cultivars (Gunawardena et al., 1982), can reduce Fe toxicity in rice. Winslow et al. (1989) planted rice on ridges to aerate the upper root zone. They found that ridging and resistant genotypes, especially when used in combination, appear to be effective management strategies for reducing yield losses in Fe-toxic soils.

Soil water status, through its effect on pH and iron reduction, greatly influences the availability of iron to plants. For example, while many rice cultivars frequently display iron-deficiency chlorosis in upland conditions (Reddy and Siva Prasad, 1986), the occurrence of chlorosis in lowland (and possibly waterlogged) conditions is rare, and is restricted to rice growing on alkaline soils low in organic matter (Ponnamperuma, 1985).

The reason that excess plant iron sometimes, but not always, reduces rice yields is not fully understood (van Mensvoort et al., 1985). Moore and Patrick (1989) concluded that the ratio of $Fe^{+2}/(Fe^{+2} + Mn^{+2} + Ca^{+2} + Mg^{+2})$ in the soil solution (identified as E1-Fe), rather than the activity of Fe^{+2}, controls iron uptake by flooded rice grown in some acid sulfate soils from Thailand. High levels of E1-Fe apparently stimulated Fe uptake and the likelihood of Fe toxicity. Drying and reflooding acid sulfate soils increases the risk of iron toxicity (Sahrawat, 1979).

3.3 Differential Tolerance of Plants to Iron Toxicity

Plants differ in their susceptibility to iron chlorosis. Soybeans become chlorotic grown in certain high-lime Iowa soils, but corn, oats, clover, and alfalfa are not affected. Peach trees become chlorotic on Houston clay soils, but cotton, corn, clover, and small grains show no signs of chlorosis. Most plants obtain adequate iron for their needs from neutral or acid soils, but rhododendrons and azaleas are likely to become chlorotic if the soil pH is above 6.0 (Thompson and Troeh, 1973).

Tolerance to iron toxicity appears to coincide with tolerance to waterlogging in soils. Bartlett (1960) found that the roots of plant species tolerant to wet soil oxidized iron more effectively and reduced its transport to plant tops than plants sensitive to wet soil. Alfalfa, which is sensitive to waterlogging, showed no ability to oxidize iron. Reed canary grass and rice, which tolerate wet soils, are efficient oxidizers of iron. Barlett (1960) suggests that wet-soil loving plants lower the toxicity of reduced substances such as Fe^{+2} by oxidation in the root zone.

Tadano (1975) concludes that rice plants may escape iron toxicity by lowering the Fe^{+2} concentration in the growth medium, excluding Fe^{+2} from the roots, and/or preventing iron translocation from roots to tops. Rice roots can increase the Eh (reduction potential) of the soil solution and, thereby, decrease the concentrations of Fe^{+2}; however, this effect is partly offset by the fact that growing plants lower the pH of the medium. Tanaka et al. (1966) report that rice roots secrete O_2 and oxidize Fe^{+2} to Fe^{+3}, and thereby prevent its penetration of critical root zones. Normal rice plants exclude excess iron, and respiration inhibitors increase iron uptake by roots (Foy et al., 1978).

4.0 UPTAKE AND ACCUMULATION OF IRON BY PLANTS

Reduction processes near respiring roots may increase Fe^{+3} reduction to Fe^{+2} and the subsequent disassociation of Fe^{+3} chelates (Römheld and Marschner, 1986). Although iron is quite abundant in the earth's crust, comprising approximately 5% of the lithosphere (Norrish, 1975), its availability in well-aerated soils is low, due to the specifics of iron chemistry in aerobic environments (SSSA, 1991). In aerobic systems, the solubility of inorganic iron depends on ferric oxides in the soil according to the reaction:

$$\text{soil } Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{+3} + 3H_2O$$

Hence, as solution pH is reduced from 8 to 4, the concentration of Fe^{+3} in solution will increase from about 10^{-17} to 10^{-5} mol/m^3 (Römheld and Marschner, 1986). Additionally, Fe^{+3} will readily hydrolyze; therefore, total soluble iron in solution is the sum of Fe^{+3} and its soluble hydrolysis products [e.g., $Fe(OH)_2$ and $Fe(OH)_4^-$] (Figure 4.1). Certainly, soil redox potential can influence iron solubility, as Fe^{+2} is considerably more soluble than Fe^{+3}. However, in the range of pH values associated with many soils (and physiological conditions; pH approx. 6.0 - 8.0), the Fe^{+3} species dominates, as Fe^{+2} is readily oxidized. Therefore, in most well-aerated soils, the minimum solubility of total inorganic iron is fixed in the range of 10^{-8} to 10^{-6} mol/m^3. The concentrations of soluble iron actually measured in soil solutions are usually higher than those calculated from equilibrium reactions, in the range of 10^{-5} to 10^{-3} mol/m^3, because of the

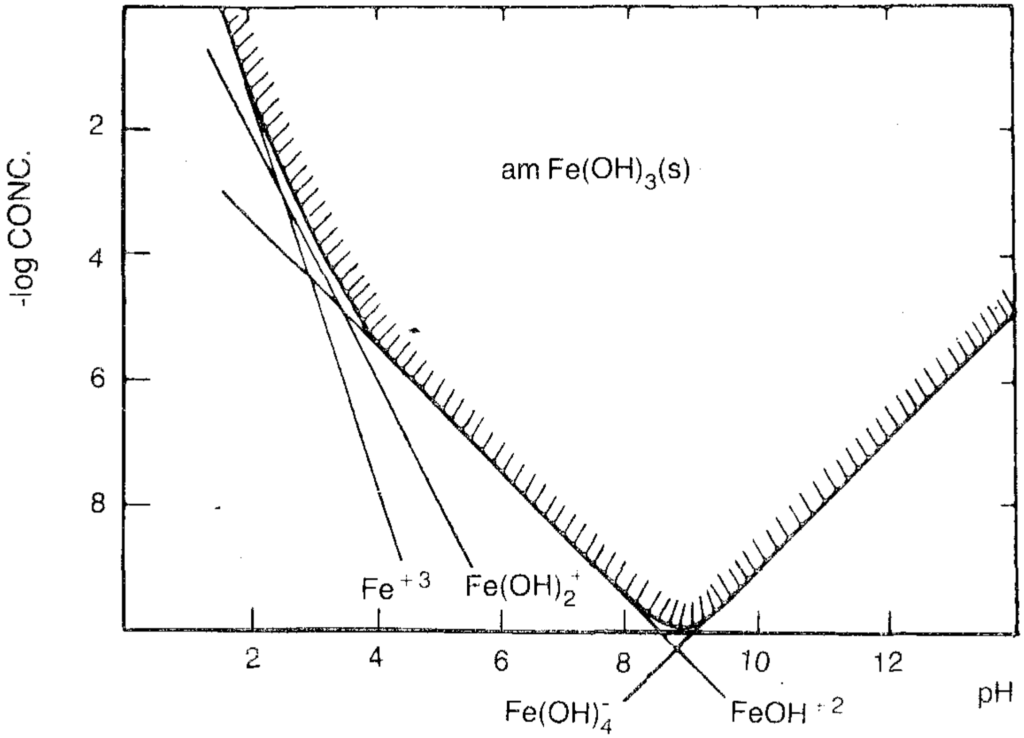

Figure 4.1 Eh-pH diagram for an Fe-H2O system, where Fe activity is 5.6 ppm (Dragun, 1988).

complexation of soil-Fe with soluble organic ligands (Olomu et al., 1973). These organic ligands can be the result of degradation of organic matter (e.g., fulvic acid) or can be siderophores (e.g., iron chelating compounds released by soil bacteria and fungi) or plant roots according to Powell et al. (1982).

Complexed ferric ion appears to be the dominant form of iron available for absorption by the plant (in well-aerated soils). The concentration of complexed iron required for optimal plant growth is around 10^{-4} to 10^{-2} mol/m^3, which is an order of magnitude higher than the levels of complexed iron in the soil solution (Lindsay and Schwab, 1982; Römheld and Marschner, 1986). Thus, it is necessary for plants to increase the availability of soil-Fe for absorption. Plants are successful in efficiently "mining" iron from the soil as indicated by their ability to maintain tissue-iron levels between 50 and 100 mg/kg dry weight in the face of low levels of available soil iron (Römheld and Marschner, 1986). The process that plants use to accomplish this aim has been the focus of much of the research in iron nutrition over the past 15 years (SSSA, 1991).

4.1 Iron Uptake by Plants

The uptake of iron appears to be mediated by the plant. Iron appears to be acquired in sufficient quantities for growth even though it may not be readily available (Bonner and Varner, 1976). Plants may also mediate the reduction of Fe^{+3} to Fe^{+2} to control uptake. It appears plants use two distinct strategies to solubilize and absorb iron from the soil. Either plants reduce Fe(III)-complexes at the root surface and absorb the Fe^{+2} ions produced via this root-associated reduction, or they excrete specific Fe(III)-binding, low molecular weight, organic polydentate ligands, known as phytosiderophores, which solubilize Fe^{+3} ions and make them available for absorption. These two strategies are used by distinctly separate taxonomic groupings of plants with the phytosiderophore-based mechanism restricted to the grass family (Poaceae), and the Fe(III) reduction mechanism restricted to the dicots and the monocots not included in the Poaceae (Römheld and Marschner, 1986).

4.2 Accumulation of Iron in Plants

Iron is absorbed by plants as the ferrous ion (Thompson and Troeh, 1973), with concentrations of total iron in plants typically ranging from 4 to greater than 16 ppm. These concentrations are approximately equal to boron, manganese, and zinc contents of plants. Many plants contain >16 ppm of iron, but not enough for iron to be considered a macronutrient (Thompson and Troeh, 1973). As shown by Mossbauer spectrometry, the main oxidation state of iron in plants is the ferric form. The ferrous form and the highly toxic, free Fe^{+2} are normally below the detection level in plants, but can reach values up to 20% of the total iron under certain circumstances (Machold et al., 1968; Goodman and DeKock, 1982).

Absorption of iron by plant roots is largely restricted to actively growing root tips (Clarkson and Sanderson, 1978). The appropriate content of iron in plants is essential both for the health of the plant and for the nutrient supply to man and animal. The variations among plants in their ability to absorb iron is not always consistent and is affected by changing conditions of soil and climate and by the stages of plant growth. Generally, certain forbs, including legumes, are known to accumulate more iron than are grasses. However, where iron is easily soluble, plants may take up a very large amount of iron. This is clearly shown by vegetation grown in soils derived from serpentine, where grass contained iron within the range of 2,127 to 3,580 ppm (dry weight). The natural iron content of fodder plants ranges from 18 to about 1,000 ppm (dry weight). The nutritional requirements of grazing animals is usually met at iron concentration ranging from 50 to 100 ppm (dry weight) in forage. Edible parts of vegetables appear to contain fairly similar amounts of iron, ranging from 29 to 130 ppm (dry weight), with lettuce being in the upper range and onion in the lower range. Iron in ash of a variety of plant species is reported to range from 220 to 1,200 ppm. Various cereal grains do not differ much in their iron concentrations. The common average iron content of different cereals ranges from 25 to around 80 ppm (dry weight). Values above 100 ppm are reported only for a few countries. The grand mean of 48 ppm (dry weight) for iron in grains was calculated by excluding the values of 100 ppm and above (Kabata-Pendias and Pendias, 1992). About 80% of the iron in leaves is localized in the chloroplasts (Terry and Abadia, 1986).

Iron is found in the phloem in concentrations that exceed those in the xylem (Ziegler, 1975). Iron is considered to be "intermediately mobile" in plants (Ziegler, 1975) and has been shown to be exported from the leaves (Brown et al., 1965; Bukovac and Wittwer, 1957). However, other than the recent work by Maas et al (1988), very little work has been conducted on the form of iron in the phloem. The alkaline pH of the phloem will have a significant influence on the form of the iron complex. Because Fe(III) ion is extremely insoluble at alkaline pH values, the possibility exists that both Fe(II) and Fe(III) ions exist in the phloem (SSSA, 1991).

In plant tissue, there are two major groups of iron-containing protein; heme proteins and Fe-S proteins. Heme proteins include the various cytochromes, which are characterized by a heme Fe-porphyrin complex as a prostetic group. Other heme proteins are cytochrome oxidase, catalase, peroxidase, and leghemoglobin, which occurs in root nodules of legumes. In Fe-S proteins, iron is coordinated to the thiol group of cysteine or to inorganic S as clusters, or to both. The most well-known Fe-S protein is ferrodoxin. Other Fe-S proteins have functions in metabolic processes, such as photosynthesis, SO_4 and SO_3 reductions, respiration, the tricarboxylic acid cycle, and N_2 fixation. In addition to its functions in heme and Fe-S proteins, iron activates a number of enzymes, including aminolevulinic acid synthetase, coproporphyrinogen oxidase, and plays a role in the synthesis of ribonucleic acid (SSSA, 1991).

5.0 EFFECTS OF IRON ON SOIL INVERTEBRATES

A preliminary review of the literature did not reveal a significant database on the toxicity of iron to earthworms. Rida (1996) evaluates the growth and bioaccumulation of five elements (cadmium, copper, iron, lead and zinc) in the earthworm *Lumbricus terrestris* from unfortified soils. Elevated trace element concentrations reduced earthworm growth. Bioaccumulation is related to the duration of exposure, tested element, and physiological condition (i.e., adult or cocoon) of the earthworm. The potential synergistic or antagonistic effects related to the geochemistry of the tested elements were not evaluated.

Efroymson et al. (1997b) provide some information on the toxicity of iron to other soil invertebrates. The reviewed study (Nottrot et al., 1987) evaluates the effects of iron in the diet of the springtail *Orchesella cincta* fed green algae (*Pleurococcus* spp.) containing various concentrations of iron for 21 days. Percent growth, feeding activity, and molting were determined. Growth of the springtails was reduced 42% by a diet containing 7,533 mg/kg of iron, but a diet containing 3,515 mg/kg of iron had no effect.

6.0 MEASURING IRON IN SOILS

For soil samples, iron is most commonly analyzed by ICP, following either the CLP protocols or SW-846 methods. The SW-846 methods include sample preparation by using either Method 3050B (acid-digestion) or 3051 (microwave assisted acid-digestion), followed by analysis following Methods 7380 or 7381. In all cases, the parameter measured is total iron. Speciation of iron is not commonly required as part of baseline site investigations, except when geochemical interactions are being evaluated.

6.1 Total Iron

Total iron is often measured in soils because it provides useful information on the characterization of soils with respect to the origin of parent materials and weathering. It also serves as a basis for calculating the mineralogical composition of the sample (Bertsch and Bloom, 1996). Total soil iron as a direct measure of iron toxicity, however, appears to have little or no value based on the previously presented information. It is not possible to correlate the soil solution concentration of iron to the total soil iron measurement. Mulder et al. (1989) measured total soil iron (%) and soil solution iron in samples collected below plant rooting zones and found no relationship between the two concentrations.

6.2 Exchangeable Iron

A preliminary literature search did not identify any studies that evaluated exchangeable iron.

6.3 Soluble Iron

Soluble iron in soil pore spaces may be a useful parameter for evaluating potential toxicity or community effects for soil microfauna. For example, elevated iron in soil pore water may result in soil bacterial communities dominated by iron bacteria. The soil-water partition coefficient (K_d) for iron is pH-dependent. Baes et al. (1984) reported K_d values ranging from 1.4 to 1,000 L/kg over a pH range of 4.5 to 9.0; a value of 25 is used for their modeling assumptions.

The methods recommended for the collection of soluble aluminum (USEPA, 2003) can also be used to collect soluble iron, provided that speciation is not of concern. These techniques include *in situ* sampling with lysimeters, miscible displacement of soils in packed columns, centrifugation with or without a heavy liquid immiscible with water, and filtration of soil solution samples through a non-reactive membrane filter with pore sizes of 0.45-µm or less. Soil column studies can also provide useful information if potential release to groundwater is of concern. Fuller (1978) has summarized methods for performing these studies.

6.4 Iron and Waste Sites

Iron is often present at elevated concentrations at waste sites, since most used metal for either containerizing or conveying materials used in the manufacturing, disposal, or use of the materials. For example, flocculated iron (iron oxide) is commonly seen on the perimeters and in seeps from uncontrolled landfills. This is typically due to the metallic materials disposed at the site. Certain parts of the U. S. also have elevated iron in soils and waters due to natural deposits in the area. Acid mine drainage is also commonly observed in areas with iron mines or other mining operations where the acidic discharge may mobilize naturally occurring iron.

Traditionally, the main concerns with iron flocculation from a human health perspective include unsightliness, staining, and its effect on the taste of potable water. The iron stains the surface of the soil and can be carried to other areas via surface water routes. From an ecological perspective, the concern is not direct chemical toxicity *per se*, but the effect of iron as a mediator of the geochemistry of other (potentially toxic) metals and the potential physical hazard of depositing flocculent.

6.4.1 Interactions with Toxic Metals

Antagonistic interactions between iron and heavy metals has been observed in several crops, and results of recent studies suggest that chlorosis brought about by heavy metal excess is apparently the result of induced iron deficiency. Excess amounts of heavy metals, and of manganese, nickel, and cobalt in particular, caused a reduction in absorption and translocation of iron and resulted in a decrease of chlorophyll. On the other hand, high levels of iron compounds in soil are known to greatly decrease trace metal uptake. Reactions between iron and manganese are commonly observed, and the ratio of these two metals in both growth medium and plant tissue seems to be more important to plant metabolism than their concentrations (Kabata-Pendias and Pendias, 1992).

Although iron itself is not considered toxic, it is environmentally significant because of its interaction with metals that are toxic. Iron oxides adsorb many elements and participate in the attenuation of most trace and heavy metals. In soils and sediments where conditions are not strongly reducing, adsorption by solid iron oxides is one of the most important controls on the distribution of trace elements. In an aerobic sediment or water system, the metal bonding may be almost irreversible. If the oxides are dissolved by reduction, the adsorbed metals may be released and appear in solution, or they may be precipitated as some other phase, such as a sulfide (Bodek et al., 1988). However, if ferrous iron is present in large quantities, it can tie up the sulfide to the extent that insufficient amounts are available to precipitate heavy metals (Bodek et al., 1988).

The form of nitrogen applied may affect the availability of soil iron. Increasing NO_3-N uptake may cause an imbalance in the cation/anion ratio, resulting in exudation of HCO_3 into the rhizosphere with a subsequent reduction in iron uptake (Chen and Barak, 1982). Aktaks and van Egmond (1979) found that NO_3-N increased dry matter production of the iron-efficient Hawkeye soybean cultivar and decreased that of the iron-inefficient T-203 cultivar.

High soil phosphorus levels may decrease plant iron concentration. Azarbadi and Marschner (1979) reported that when phosphorus was depleted in the rhizosphere, corn roots were able to use iron from $Fe(OH)_3$ without decreasing the pH or redox potential. This depletion of phosphorus may enable some iron-inefficient plant species to use inorganic Fe^{+3} compounds (SSSA, 1991).

Zinc deficiency increases iron uptake in certain plant species (Francois and Goodin, 1972), sometimes to a toxic level (Adams and Pearson, 1967). Brown and Jones (1977) reported that, when the pH of a selected soil was increased from 5.2 to 7.1 by addition of lime, cotton became zinc deficient and accumulated higher levels of iron. Haldar and Mandal (1981) found that applied zinc decreased iron concentration in rice shoots and roots. This decrease in the concentration in the shoots was not due to a dilution effect or to a reduced rate of translocation from root to tops (SSSA, 1991).

The iron-manganese interaction is well documented (Brown, 1956). Although the iron-manganese interaction has been extensively studied, it is not fully understood. However, the importance of this interaction is evident from the finding that application of MnEDTA induced manganese deficiency in bean plants, apparently because the ligand increased soil-iron availability (Knezek and Greinert, 1971). Zaharieve et al (1988) recently suggested that: (i) iron hampers manganese uptake; and (ii) manganese decreases plant Fe^{+2} and adversely affects iron metabolism. Kuo and Mikkelsen (1981) reported that the translocation of iron in rice from roots to shoots was hindered at high manganese levels. Since coatings occurred on root surfaces and intensified with increasing manganese concentrations, part of the reduced iron levels in shoots was attributed to the formation of insoluble manganese oxides on the roots (SSSA, 1991).

An iron-efficient tomato and the soybean cultivar, A7, were unable to respond to iron deficiency stress in the absence of potassium in nutrient solutions (Jolley et al., 1988). The lack of a iron deficiency stress response in the absence of potassium resulted in reduced levels of leaf iron and greater chlorosis in both species. Potassium seems to play a very specific role in the plant for maximum utilization of iron (SSSA, 1991).

Olsen and Watanabe (1979) reported that an increase in molybdenum decreased iron uptake. This interaction may be important in alkaline soils in which iron availability may be low and soluble MoO_4^{2-} concentration high (SSSA, 1991).

Pulford suggested that the interaction of iron-zinc is apparently associated with the precipitation of franklinite ($ZnFe_2O_4$) that depressed the availability of both metals. Iron-phosphate interactions commonly occur in both plant metabolism and soil media. The affinity between Fe^{+3} and $H_2PO_4^-$ ions is known to be great, and therefore the precipitation of $FePO_4$ x $2H_2O$ can easily occur under favorable conditions. Furthermore, phosphate anions compete with the plant for iron, and thus phosphate interferes with iron uptake and with the internal iron transport. High iron concentrations are known to cause phosphate deficiency. The appropriate phosphate/iron ratio in plants is fundamental to plant health. Potassium deficiency is also often associated with iron toxicity because plants are not capable of oxidizing Fe^{+2} to Fe^{+3}. The antagonistic effect of calcium on iron is very complex and is related to both the growth medium and intracellular metabolism.

Other interactions between iron and micronutrients are not well understood. Thus, iron chlorosis in plants on calcareous soils may be thought to reflect a low iron availability in such soils because of the present insufficient evidence of iron-calcium metabolic interferences. Interaction between iron and sulfur seems to be erratic in that low soil sulfur levels may depress iron uptake, whereas, a high sulfur content may also result in low iron availability, depending on soil environments (Kabata-Pendias and Pendias, 1992).

Iron oxides adsorb and form coprecipitates with many elements (e.g., zinc, lead, manganese, nickel, copper, cobalt, and chromium), and in fact is a major controlling factor in the distribution of metals under non-reducing conditions (Bodek et al., 1988). If the oxides are dissolved under reduced conditions, the adsorbed metals become labile and available to a dissolved phase, or binding to other moieties, such as sulfide (Bodek et al., 1988). Metal lability from iron can also be mediated by bacterial action. Francis and Dodge (1990) showed that five heavy metals (cadmium, chromium, nickel, lead and zinc) were solubilized from the iron oxide, goethite (α-FeOOH), by anaerobic nitrogen-fixing bacteria. The authors were able to show that the dissolution of the metals due to microbial reduction varied with the type of metal, with the cadmium and zinc being the most labile when coprecipitated with the iron oxide tested. The mechanisms of this action by the bacteria appear to be a biochemical reduction of the iron, resulting in a release of the metals.

Both Fe^{+2} and Fe^{+3} readily form complexes with cyanide (i.e., ferrocyanide, Fe(CN) and ferricyanide, Fe (CN) which can decompose in the presence of light to yield free cyanide (Broderius and Smith Jr., 1980). The decomposition of ferrocyanide also results in the elevation of the pH (Bodek et al., 1988). The iron cyanide complexes are of special concern at Manufactured Gas Plant sites since they are a residual of the gasification process (Theis et al., 1994). However, due to light attenuation processes in soils, it is not likely that this would be a significant process for soils contaminated with these complexes unless the contamination is very near-surface.

Cohen et al. (1998) have also reported an apparent induction of the uptake of some heavy metals (e.g., cadmium) by plants grown in iron-deficient soils. Using pea seedlings, the authors were able to show that an iron transport mechanism was induced when the plants were grown under iron-deficient conditions, resulting in increased uptake of cadmium by the seedlings. Although currently reported only from a laboratory setting, this phenomenon could be important in areas with alkaline soils (i.e., parts of the western U. S.). The authors also reported that this mechanism has potential applications for phytoremediation.

Precipitation of iron oxides during dredging operations has been reported to decrease dissolved concentrations of cadmium, copper, lead and zinc (Windom, 1973). Iron (and manganese) oxides are used as scavengers in wastewater treatment and may be very effective in retarding the migration of pollutants in the subsurface (Drever, 1982). Deep-sea nodules, concretions of manganese and iron oxides growing on the ocean floor, are known to concentrate trace elements, such as cobalt, nickel, zinc and lead, from seawater. As the oxides aggregate and settle, they act as scavengers for trace elements (Bodek et al., 1988).

In soils, various trace elements are concentrated by iron oxides, including zinc, lead, manganese, nickel, copper, cobalt, vanadium, molybdenum and chromium. The most widely observed sorption capacities of iron oxides are those for phosphates, molybdates, and selenites. The adsorption is dependent on pH and is greatest for various irons on iron oxides at pH 4-5. Iron oxides also react with carbonates in soil systems. Fe(III) can be incorporated in hydrated phosphates, and Fe(II) reacts with sulfur to form the stable minerals pyrite and jarosite (Kabata-Pendias and Pendias, 1984).

6.4.2 Deposited Floc

As the reduced ferrous oxide comes into contact with air, it oxidizes to the ferric state that is not soluble in water, resulting in a precipitate. The precipitate can accumulate on soils in areas where groundwater seeps to the surface. This is commonly observed at older municipal and industrial landfill sites, in areas which may be influenced by acid mine drainage, and natural background (but non-minable) settings. For example, the total iron concentration in landfill leachate has been reported up to 2,820 mg/L, with a median concentration of 94 mg/L (Miller, 1980). The flocculated iron covers the soil surface, smothering any plants and microbial communities that may have been present.

7.0 SUMMARY AND CONCLUSIONS

Iron is a commonly occurring metallic element, with typical soil concentrations ranging from 0.2% to 55% (20,000 to 550,000 ppm). Concentrations can vary significantly even within localized areas due to soil types and presence of other sources. Iron can occur in either the divalent (Fe^{+2}) or trivalent (Fe^{+3}) valence states under typical environmental conditions. The valence state is determined by the pH and Eh of the system, and the chemical form is dependent upon the availability of other chemicals.

Iron is essential for plant growth, and is generally considered to be a micronutrient. Iron is considered the key metal in energy transformations needed for syntheses and other life processes of the cells (Thompson and Troeh, 1973). Consequently, plants regulate its uptake. In well-aerated soils between pH 5 and 8, the iron demand of plants is higher than the amount available (Römheld and Marschner, 1986). Because of this limitation, plants have evolved various mechanisms to enhance iron uptake (Marschner, 1986). Under these soil conditions, iron is not expected to be toxic to plants.

The main concern from an ecological risk perspective for iron is not direct chemical toxicity *per se*, but the effect of iron as a mediator in the geochemistry of other (potentially toxic) metals and the potential physical hazard of depositing flocculent. Soil pH and Eh should be included as standard soil chemical field parameters when conducting any field investigation. Although some EPA analytical methods require the collection of soil pH prior to analysis, this information is not always made available to the ultimate data users. In addition, the pH measured in the lab may no longer be representative of field conditions since the samples can be exposed to oxygen during storage prior to analysis. A determination of the geochemical conditions (i.e., pH and Eh at a minimum) of the environmental setting, as well as the presence of iron floc and the toxic metals, is critical to the determination of the relative importance of iron at a site.

8.0 LITERATURE CITED

Adams, F., and R.W/ Pearson. 1967. Crop response to lime in the southern United States and Puerto Rico. In: *Soil acidity and Liming*, R. W. Pearson and F. Adams, editors. Agron. Monogr. 12. ASA, Madison, WI, pp. 161-206.

Aizer, R. S., Rajagopel, C. K., and N. S. Money. 1975. Available zinc, copper, iron, and manganese status of the acid rice soils of Kuttanad, Kerala State. *Agric. Res. J. Kerala*. (13): 15-17.

Aktaks, M., and F. van Egmond. 1979. Effect of nitrate nutrition and iron utilization by an Fe-efficient and an Fe-inefficient soybean cultivar. *Plant Soil.* 51: 257-274.

Al-Khafaji, A. A., and M. A. Tabatabai. 1979. Effects of trace elements on arylsulfatase activity in soils. *Soil Sci.* 127 (3) : 129-133.

Ambler, J. E., Brown, J. C., and H. G. Gauch. 1970. Effect of zinc on translocation of iron in soybean plants. *Plant Physiol.* 46: 320-323.

Azarbadi, S., and H. Marschner. 1979. Role of the rhizosphere in utilization of inorganic iron-III compounds by corn plants. *Z. Pflanzenernaehr. Bodenkd*. 142: 751-764.

Baes III, C. F., R. D. Sharp, and A.L. Sjoreen. 1984. A Review and Analysis of Parameters for Assessing transport of environmentally released radionuclides through agriculture. ORNL-5786.

Bartlett, R. J. 1960. Iron oxidation proximate to plant roots. USDA, ARS, SWC, East. Soil Water Manage. Res. Branch Field Location Ann. Rep. Burlington, VT., pp. 15-16.

Beckwith, R. S., Tiller, K. G., and E. Suwadji. 1975. The effects of flooding on the availability of trace metals to rice in soils of differing organic matter status. In: *Trace Elements in Soil-Plant-Animal Systems.* D. C. D. Nicholas and A. Egan, editors. Academic Press, New York, pp. 135-149.

Bloom, P. R., and W. P. Inskeep. 1988. Factors affecting bicarbonate chemistry and iron chlorosis in soils. *J. Plant Nutr*. 9: 215-228.

Bodek, I., Lyman, W. J., Reehl, W. F., and D.H. Rosenblatt. 1988. *Environmental Inorganic Chemistry: Properties, Processes, and Estimation Methods.* SETAC Special Publication Series, B.T. Walton and R.A. Conway, editors. Pergamon Press. New York.

Broderius, S. J., and Smith Jr., L. L. 1980. *Direct Photolysis of Hexacyanoferrate Complexes: Proposed Applications to the Aquatic Environment.* USEPA. EPA-600/3-80-003.

Brown, J. C. 1956. Iron chlorosis. *Annu. Rev. Plant Physiol*. 7:171-190.

Brown, J. C., and W. E. Jones. 1977. Manganese and iron toxicities dependent on soybean variety. *Commun. Soil Sci. Plant Anal.* 8: 1-15.

Brown, J. C., Yamaguchi, S., and J. Leal-Diaz. 1965. Evidence for translocation of iron in plants. *Plant Physiol.* 40: 35-38.

Bukovac, M. J., and S. H. Wittwer. 1957. Absorption and mobility of foliar applied nutrients. *Plant Physiol.* 32: 428-435.

Chen, Y., and P. Barak. 1982. Iron nutrition of plants in calcareous soils. *Adv. Agron.* 35: 217-240.

Chesney, H. A. D. 1972. Yield response of pangolagrass grown on Tiwiwid fine sand to Mg and fritted micronutrients. *Agron. J.* 64: 152-154.

Chin, T. F. 1966. Iron and manganese absorption by rice plants. *Soils Fert. Taiwan.* 1-6.

Clarkson, D. T., and J. Sanderson. 1978. Sites of absorption and translocation of iron in barley roots. *Plant Physiol.* 61: 731-736.

Clements, H. F., Putnam, E. W., Suehisa, R. G., Yee, G. L. N., and M. L. Wehling. 1974. Soil toxicities as causes of sugarcane leaf freckle, macadamia leaf chlorosis (Keaau) and Maui sugarcane growth failure. *Hawaii Agric. Exp. Stn. Tech. Bull.* 88. 52 pp.

Cohen, C. K., Fox, T. C., and D.F. Garvin. 1998. The role of iron deficiency stress responses in stimulating heavy metal transport in plants. Agricultural Research Service, U. S. Department of Agriculture.

Dragun, J. 1988. *The Soil Chemistry of Hazardous Materials*. Hazardous Materials Control Research Institute. Silver Spring, MD.

Drever, J. I. 1982. *The Geochemistry of Natural Waters*. Prentice-Hall, Englewood Cliffs, NJ.

Efroymson, R. A., Will, M. E., and G. W. Suter II. 1997a. *Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants, 1997 Revision.* ES/ER/TM-85/R3.

Efroymson, R. A., Will, M. E., and G.W. Suter II. 1997b. *Toxicological Benchmarks for Contaminants of Potential Concern for Effects on Soil and Litter Invertebrates and Heterotrophic Process, 1997 Revision*. ES/ER/TM-126/R2.

Electric Power Research Institute. 1984. *Chemical Attenuation rates, Coefficients, and Constants in Leachate Migration.* Volume I: Critical Review, EPRI EA-3356, February.

Foy, C. D., Chaney, R. L., and White, M. C. 1978. The physiology of metal toxicity in plants. *Ann. Rev. Plant Physiol.* 29: 511-566.

Francis, A. J., and C. J. Dodge. 1990. Anaerobic microbial remobilization of toxic metals coprecipitated with iron oxide. *Environ. Sci. Technol*. 24 (3): 373-378.

Francois, L.E., and J. R. Goodin. 1972. Interaction of temperature and salinity on sugar beet germination. *Agron. J.* 64: 272-273.

Fuller, W.H. 1978. Methods for conducting soil column test to predict pollutant migration.

Goodman, B. A., and P. C. DeKock. 1982. Mössbauer studies of plant material. I. Duckweed, stocks, soybeans and pea. *J. Plant Nutr*. 5: 345-353.

Gotoh, S., and W. H. Patrick, Jr. 1974. Transformation of iron in a waterlogged soil as influenced by redox potential and pH. *Soil Sci. Soc. Am. Proc*. 38: 66-71.

Grussak, M. A. 1996. Plant Breeding Strategies for Improving Human Mineral and Vitamin Nutrition. Federation of American Scientists. http://www.fas.org/mnp/micro.htm#iron.

Gunawardena, I., Virmani, S. S., and F. J. Sumo. 1982. Breeding rice for tolerance to iron toxicity. Oryza (Cuttack, India) 19:5-12.

Haldar, M., and Mandal, L. N. 1981. Effect of P and Zn on the growth and P, Zn, Cu, Fe, and Mn nutrition of rice. *Plant Soil* 59:415-420.

Hoffman, S. J., and Fletcher, W. K. 1978. Selective sequential extraction of Cu, Zn, Fe, Mn, and Mo from soils and sediments. In: *Geochemical Exploration*, J. R. Watterson and P. K. Theoblad, editors. IMM Publ., pp. 289-299.

Howeler, R. H. 1973. Iron-induced oranging disease of rice in relation to physio-chemical changes in a flooded Oxisol. *Soil Sci. Soc. Am. Proc*. 37:898-903.

Jolley, V. D., Brown, J. C., Blaylock, M. J., and Camp, S. D. 1988. A role for potassium in the use of iron by plants. *J. Plant Nutr*. 11.1159-1175.

Juma, N. G., and Tabatabai, M. A. 1977. Effects of trace elements on phosphatase activity in soils. *Soil. Sci. Am. J.* 41 : 343-346.

Kabata-Pendias, A., and Pendias, H. 1992. *Trace Elements in Soils and Plants*, second ed. CRC Press, Boca Raton, FL.

Kabata-Pendias, A., and Pendias, H. 1984. *Trace Elements in Soils and Plants.* CRC Press, Boca Raton, FL.

Knezek, B. D., and Greinert, H. 1971. Influence of soil iron and manganese chelate interactions upon the iron and manganese nutrition of bean plants (*Phaseolus vulgaris* L.). *Agron. J.* 63:617-619

Kuo, S., and D. S. Mikkelsen. 1981. Effect of P and Mn on growth response and uptake of Fe, Mn and P by sorghum. *Plant Soil*. 62:15-22.

Lee, J. 1998. Suicidal plant gives researchers insights on iron. Agricultural Research Service, U. S. Department of Agriculture. http://www.ars.usda.gov/is/cgi-bin/ffp.pl/is/pr/1998/981223.htm?iron. December 23, 1998.

Liang, C. N., and M. A. Tabatabai. 1977. Effects of trace elements on nitrogen mineralisation in soils. *Environ. Pollut*. 12 : 141-147.

Lindau, C. W., and L. R. Hossner. 1982. Sediment fractionation of Cu, Ni, Zn, Cr, Mn, and Fe in one experimental and three natural marshes. *J. Environ. Qual*. 11:540-545.

Lindsay, W. L. 1979. *Chemical Equilibria in Soils*. John Wiley and Sons, Inc., Wiley-Interscience, New York.

Lindsay, W. L., and A. P. Schwab. 1982. The chemistry of iron in soil and its availability to plants. *J. Plant Nutr.* 4: 821-840.

Maas, E. V., D. A. M. van de Wetering, M. L. van Beusichem, and H. F. Bienfait. 1988. Characterization of phloem iron and its possible role in the regulation of Fe-efficiency reactions. *Plant Physiol*. 87: 167-171.

Machold, O., Meisel, W., and Schnorr, H. 1968. Bestimmung der Bindungsform des Eisens in Blättern durch Mössbauerspektrometrie. Naturwissenschaften 55:499-500.

Marschner, H. 1986. *Mineral nutrition of plants*. Academic Press, New York.

Matocha, J. E. 1984. Grain sorghum response to plant residue-recycled iron and other iron sources. *J. Plant Nutr.* 7: 259-270.

Matocha, J. E., and D. Pennington. 1982. Effects of plant iron recycling on iron chlorosis of grain sorghum grown on calcareous soils. *J. Plant Nutr*. 5: 869-882.

McGovern, E. C. 1987. Background concentrations of 20 elements in soils with special regard for New York State. Wildlife Pathology Unit, New York State Department of Environmental Conservation.

Miller, D. E. 1980. Waste disposal effects on ground water. Premier Press, Berkeley, CA.

Miller, G. W., J. C. Pushnik, and G. W. Welkie. 1984. Iron chlorosis, a world wide problem: The relation of chlorophyll biosynthesis to iron. *J. Plant Nutr*. 7: 1-22.

Millikan, C. R. 1949. Effects on flax of a toxic concentration of boron, iron, molybdenum, aluminum, copper, zinc, manganese, cobalt, or nickel in the nutrient solution. *R. Soc. Victoria Proc.* 61: 25-42.

Moore, P. A., and W. H. Patrick, Jr. 1989. Iron availability and uptake by rice in acid sulfate soils. *Soil Sci. Soc. Am. J.* 53: 471-476.

Morel, F. M. M., and J. G. Hering. 1993. *Principles and Applications of Aquatic Chemistry*. John Wiley and Sons, Inc., New York City, NY.

Mulleriyawa, R. P. 1966. Some factors influencing bronzing, a physiological disease of rice in Ceylon. MS thesis, Coll Agric., Univ. Phillipines.

Nhung, Mai-Thi-My, and F. N. Ponnamperuma. 1966. Effects of calcium carbonate, manganese dioxide, ferric hydroxide, and prolonged flooding, chemical and electrochemical changes and growth of rice in a flooded, acid sulfate soil. *Soil. Sci*. 102:29-41.

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

Nottrot, F., Joosse, E. N. G., and van Straalen, N. M. 1987. Sublethal effects of iron and manganese soil pollution on *Orchesella cincta* (Collembola). *Pedobiologia* 30: 45-53.

NSCSS. 1999. Proper use of 2,2'-dipyridyl indicator dye. National Society of Consulting Soil Scientists (NSCSS). http://www.nscss.org/dipyridyl.html.

Olsen, S. R. 1972. Micronutrient interactions. In: *Micronutrients in Agriculture,* first ed., J. J. Mortvedt, P. M. Giordano, and W. L. Lindsay, editors. SSSA, Madison, WI, pp. 243-64.

Olsen, S. R., and Watanabe, F. W. 1979. Interaction of added gypsum in alkaline soils with uptake of iron, molybdenum, manganese and zinc by sorghum. *Soil Sci. Soc. Am. J.* 43: 125-130.

Olumu, M. O., Racz, G. J. and C. M. Cho. 1973. Effect of flooding on Eh, pH and concentrations of Fe and Mn in several Manitoba soils. *Soil Sci. Soc. Am. Proc.* 37: 220-224.

Parsa, A. A., Wallace, A., and J. P. Martin. 1979. Enhancement of iron availability by some organic materials. *J. Agric. Sci*. 93: 115-120.

Perkins, H. F., Gibson, E. J., and A. R. Bertrand. 1972. Influence of iron content on quality of cigar wrapper tobacco. *Commun. Soil Sci. Plant Anal.* 3: 459-466.

Ponnamperuma, F. N. 1955. Physiological diseases of rice attributed to iron toxicity. *Nature.* 175:265.

Powell, P. E., Staniszlo, P. J., Cline, G. R., and C. P. P. Reid. 1982. Hydroxamate siderophores in the iron nutrition of plants. *J. Plant Nutr.* 5: 653-673.

Purves, D. 1972. Consequences of trace-element contamination of soils. *Environ. Pollut.* 3: 17-24.

Reddy, C. K., and G. V. S. Siva Prasad. 1986. Varietal response to iron chlorosis in upland rice. *Plant Soil* 94: 289-292.

Rhoads, F. M. 1971. Relations between Fe in irrigation water and leaf quality of cigar wrapper tobacco. *Agron. J.* 63: 938-940.

Rida, A. M. 1996. Growth and trace element concentration in the earthworm and plants in non-contaminated soils and soil contaminated with cadmium, copper, iron, lead, and tin: Soil-earthworm interactions. *Soil Biol. Biochem*. 28 (8): 1029-1035.

Rogers, E. 1973. Iron-induced manganese deficiency in 'July Elberta' peach trees. J. Am. Soc. *Hortic. Sci*. 98:19.

Römheld, V., and H. Marschner. 1986. Mobilization of iron in the rhizosphere of different plant species. In: *Advances in Plant Nutrition, Volume 2*, B. Tinker and A. Läuchli, editors. Praeger Scientific, New York, pp. 155-204.

Sahrawat, K. L. 1979. Iron toxicity to rice in an acid sulfate soil as influenced by water regimes. *Plant Soil* 51: 143-144.

Schwab, A. P., and W. L. Lindsay. 1989. A computer simulation of Fe(III) and Fe(II) complexation in nutrient solution. II. Experimental. *Soil Sci. Soc. Am. J.* 53: 34-38.

Schwertmann, U. 1988. Occurrence and formation of iron oxides in various pedoenvironments. In: *Iron in Soils and Clay Minerals*, J. W. Stucke et al., editors. NATO ASI Series C 127. D. Reidel Publ. Co., Boston, pp. 267-308.

Shuman, L. M. 1988. Effect of organic matter on the distribution on the distribution of manganese, copper, iron, and zinc in soil fractions. *Soil Sci*. 146: 192-198.

Shuman, L. M. 1985. Fractionation method for soil microelements. *Soil Sci*. 140:11-22.

Shuman, L. M. 1979. Zinc, manganese, and copper in soil fractions. *Soil Sci*. 127:10-17.

Skeen, J. R. 1929. The tolerance limit of seedlings for aluminum and the antagonism of calcium. *Soil Sci.* 27:69-80.

Sonar, K. R., and Ghugare, R. V. 1982. Release of Fe, Mn and P in a calcareous Vertisol and yield of upland rice as influenced by presowing soil water treatments. *Plant Soil* 68: 11-18.

SSSA. 1991. *Micronutrients in Agriculture*, Second Ed. J. J. Mortvedt, F. R. Cox, L. M. Shuman, and R. M. Welch, editors. Soil Science Society of America, Inc., Madison, WI.

Tadano, T. 1975. Devices of rice roots to tolerate high iron concentrations in growth media. *Jpn. Agric. Res*. Q. 9:34-39.

Tanaka, A., and S. Yoshida. 1970. Nutritional disorders of the rice plant in Asia. Int. Rice. Res. Inst. Tech. Bull. 10. *Makati, Rizal*, P. I. 51 pp.

Tanaka, A., Loe, R., and S. A. Navasero. 1966. Some mechanisms involved in the development of iron symptoms in the rice plant. *Soil Sci. Plant Nutr*. 12:32-38.

Terry, N., and J. Abadia. 1986. Function of iron in chloroplasts. *J. Plant Nutr*. 9: 609-646.

Theis, T. L., Young, T. C., and M. Huang. 1994. Leachate characteristics and composition of cyanide-bearing wastes from manufactured gas plants. *Environ. Sci. Technol*. 28 (1) : 99-106.

Thenabadu, M. W. 1974-1975. Iron in the nutrition of the rice plant. *J. Natl. Agric. Soc. Ceylon* 11/12:87-102.

Thompson, L. M. and F. R. Troeh. 1973. *Soils and Soil Fertility*, third ed. McGraw-Hill Book Company.

van Mensvoort, M. E., Lantin, R. S., Brinkman, R., and N. van Breemen. 1985. Toxicities of wetland soils. In: *Wetland Soils: Characterization, Classification, and Utilization*. Int. Rice Res. Inst., Los Banos, Philippines, pp. 123-138.

Wallace, A., and Bhan, K. C. 1962. Plants that do poorly in acid soils. In: *A Decade of Synthetic Chelating Agents in Inorganic Plant Nutrition*. A. Wallace, editor, pp. 36-38.

Wallace, A., Alexander, G. V., and F. M. Chaudhry. 1977. Phytotoxicity and some interactions of the essential trace metals iron, manganese, molybdenum, zinc, copper, and boron. *Commun. Soil Sci. Plant Anal*. 8 (9) : 741-750.

Wallihan, E. F. 1966. Iron. In: Chapman, H. D. *Diagnostic Criteria for Plants and Soils.* University of California, Div. Agric. Sci., Riverside, CA, pp. 203-212.

Windom, H. L. 1973. Investigations of changes in heavy metals concentrations resulting from maintenance dredging of Mobile Bay Ship Channel, Mobile Bay, Alabama. Mobile District, U. S. Army Corps of Engineers, Mobile, AL. *As cited in:* Khalid, R. A., Gambrell, R. P, Verloo, M. G., and Patrick, Jr., W. H. 1977. Transformations of heavy metals and plant nutrients in dredge sediments as affected by oxidation reduction potential and pH. U. S. Army Contract No. DACW39-74-C-0076. May 1977.

Winslow, M. D., Yamauchi, M., Alluri, K., and T. M. Masajo. 1989. Reducing iron toxicity in rice with resistant genotype and ridge planting. *Agron. J.* 81: 458-460.

Water Quality Association (WQA). 1997. WQA Glossary of Terms. Water Quality Association. www.wqa.org/Glossary/Default.htm.

Zaharieve, T., Kasabov, D. and V. Römheld. 1988. Response of peanuts to iron-manganese interaction in calcareous soil. *J. Plant Nutr*. 1:1015-1024.

Ziegler, H. 1975. Nature of transported substances in plants. In: *Transport in Plants, Encyclopedia of Plant Physiology*. New Ser., Vol. 1,. M. H. Zimmermann and J. A. Milburn, editors. Springer-Verlag, Heidelberg, W. Germany, pp. 59-100.