IRON NUTRITION OF PLANTS: AN OVERVIEW ON THE CHEMISTRY AND PHYSIOLOGY OF ITS DEFICIENCY AND TOXICITY[1]

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ABSTRACT – Iron deficiency and toxicity are important yield limiting factors in crop production around the world. In this review, an attempt is made to summarize the information on diagnosis of Fe deficiency and toxicity, chemistry of Fe in soil, mechanism of Fe uptake, role of chelates in Fe nutrition, factors affecting Fe availability to crop plants and measures required to correct Fe deficiency and toxicity. A brief discussion about Fe toxicity in flooded rice is also included. Information presented in this review article should provide a basis for correcting this nutritional disorder in crop plants, and indicates new research efforts needed to solve Fe stress problems.

Index terms: flooded rice, Fe deficiency, Fe toxicity, Fe uptake mechanism.

NUTRIÇÃO DE FERRO DAS PLANTAS: QUÍMICA E FISIOLOGIA DA SUA DEFICIÊNCIA E TOXICIDADE

RESUMO – A deficiência e toxidez de Fe são fatores que limitam o rendimento das culturas. Nesta revisão é apresentado um resumo das informações sobre a diagnose da deficiência e toxidez química do Fe no solo, mecanismo de absorção, importância dos quelados de Fe na nutrição de plantas, fatores que afetam a disponibilidade de Fe e dos métodos de correção da deficiência e toxidez de Fe. É feita também uma discussão resumida sobre toxidez de Fe com arroz irrigado. Esta revisão fornece informações básicas para correção de desordens nutricionais que envolvem Fe, e sugere pesquisas a serem feitas visando solucionar problemas de estresse de Fe.

Termos para indexação: arroz irrigado, deficiência de ferro, toxidez do ferro, mecanismo de absorção de ferro.

INTRODUCTION

Iron stress (deficiency or toxicity) in crop plants often represents a serious constraint for stabilizing and/or increasing crop yields. Any factor that decreases the availability of Fe in a soil or competes in the plant absorption process contributes to Fe deficiency.

Iron deficiency occurs in a variety of soils. Affected soils usually have a pH higher than 6. Iron deficient soils are often sandy, although deficiencies have been found on fine-textured soils, mucks, and peats (Brown 1961). Factors that can contribute to Fe-deficiency in plants include low Fe supply from the soil; high lime and P application; high levels of heavy metals such as Zn, Cu, and Mn; low and high temperatures; high levels of nitrate nitrogen; high organic matter content; poor aeration; unbalanced cation ratios and roots infection by nematodes. This means soil, climate, and soil management practices are responsible for Fe deficiencies in crop plants.

Iron deficiency is potentially a problem on most calcareous soils (Chen & Barak 1982). It is estimated that as much as about 5.2 million hectares of the world land surface is calcareous (Dudal 1977) and might therefore be susceptible to Fe-deficiency problems. The most severely affected Fe-deficient areas tend to have less than 50 cm annual rainfall on

major soil association of xerosols, arenosols, solonetz, rendzinos and chernozems (Vose 1982). The latter are normally extremely fertile soils, but have high base status, high pH, and possibly contain free calcium carbonate. They have Fe-deficiency problems, especially under moisture stress.

Iron toxicity is not as common as Fe-deficiency. On acid soils, where Fe is most available, Fe^{2+} can become toxic to plants. Iron toxicity is most commonly found in rice soils where unfavorable factors such as poor drainage, highly reducing conditions, and high sulphide content occur (Foy et al. 1978, Yoshida & Tadano 1978). Iron toxicity is a serious problem in flooded rice, but very little attention has been paid to the problem. In many parts of the world (Africa, South America and Asia) where rice is grown on acid soils having great potential for rice production, Fe-toxicity is or will be a serious problem. Therefore, this topic needs special attention as far as management of flooded acid soils are concerned. Very little information exists about Fe-toxicity. Much of the reported work deals with either soil or plants, but not both. Therefore, in this review, Fe-deficiency as well as Fe-toxicity are discussed and both soil and plant factors are considered. This approach provides a more comprehensive understanding of the Fe mineral stress problem.

Various review articles about the Fe disorder have appeared in the last two decades (Anderson 1982, Chen & Barak 1982, Clark 1982, Foy et al. 1978, Viets 1962). However, in this review the authors will attempt to emphasize a slightly different viewpoint, bring out developments that have occurred since 1955, and provide a broader introduction to the literature.

Diagnosis of iron deficiency or toxicity

Iron deficiency or toxicity can be identified by visual symptoms in plants, and by soil and plant chemical analysis. Among the three methods of diagnosis, identification through visual symptoms is the cheapest and plant chemical analysis is the most expensive. At present, soil analysis is the method most commonly used to evaluate soil fertility. However, it is not necessarily the superior method. The best way to identify nutritional disorders in crop plant is a combination of all three diagnostic techniques. All these methods are discussed in the succeeding paragraphs.

Iron deficiency and toxicity symptoms

Severe Fe chlorosis of field crops generally occurs on calcareous, alkaline soils. Iron, as well as many other micronutrients, tend to become insoluble, immobile and unavailable in these soils. Iron deficiency has also been reported for upland rice grown on acid soils in Brazil where high doses of lime and P fertilizer were applied (Fageria 1984). Iron deficiency was also observed in upland rice growing on the high Mn-content cerrado soils of Brazil (Fageria 1984). The Fe-content of these soils is generally not low, but with increased pH, availability of Fe decreases. Above pH 4, each unit increase in pH decreases the solubility of Fe^{3+} by a factor of about 1000 (Latimer 1952).

Any factor that decreases the availability of Fe in soil or interferes with the absorption process, contributes to Fe-deficiency. This process is often referred to as lime-induced chlorosis or just Fe chlorosis. Factors such as high pH and excess phosphate, bicarbonate, and Ca salts in the growth medium can interfere with Fe uptake. Excesses of Cu, Mn, Ni, and Zn also can induce Fe chlorosis (Brown & Holmes 1956). Iron deficiency first starts in younger leaves in all crop plants. The deficiency is exhibited as a chlorosis developing intervenally in the new leaves. The area between the veins becomes light green, then turns yellow as the deficiency advances. The veins usually remain green except with extremely severe deficiency where the entire leaf becomes white and translucent (Anderson 1982). In the beginning, Fe-deficiency is similar to Mn-deficiency but at an advanced

stage, Fe-deficient leaves are bleached while Mn-deficient leaves form intervenal necrosis resulting in dead brown tissue. Most crop plants are more susceptible to Fe-deficiency in the early stage of growth. Plants become stunted in the early seedling stages. If the deficiency is severe and prolonged, plants die. Iron deficiency under field conditions commonly appears as irregular shaped yellow areas sporadically fading in and out of areas with normally colored plants.

Iron toxicity is most common in flooded rice grown on acid soils. Due to flooding, reducing conditions develop and Fe^{3+} is reduced to Fe^{2+}. Due to this reduction, Fe^{2+} concentration and uptake is increased. Metal toxicity, can be expressed in two ways. Direct toxicity occurs when an excess of the element is absorbed and becomes lethal to the plant cell. On the other hand, toxicity can be related to nutritional imbalance. When excess Fe is present in the growth medium, it may inhibit uptake, transport and utilization of many other nutrients and induce nutritional deficiency. In flooded rice grown on acid soils the second type of toxicity is most common. The most important nutrient deficiencies observed in irrigated or flooded rice in Brazil are P, K, and Zn (Barbosa Filho et al. 1983).

Unlike deficiency symptoms, Fe-toxicity symptoms first appear in old leaves. In rice, Fe-toxicity is characterized by brown spots starting from the tips of lower leaves (Tadano 1976). The spots spread over these leaves and the progress to the upper leaves.

Soil Analysis

Soil analysis is the most widely used test of nutritional status. It consists of chemical and physical measurements made on a soil. The success of soil analysis depends on proper soil sampling, the extractant used, interpretation of the analytical results and fertilizer recommendations. The most important part in the soil testing program is sampling to reflect the true nutrient status of the area sampled. This means that large numbers of soil samples are needed. A single sample can seldom accurately characterize the true nutrient status of the area. The error due to sampling is generally greater than that due to chemical analysis (Hemingway 1955, Peck & Melsted 1973). The question then is how to obtain the appropriate samples. It is beyond the scope of this article to discuss soil sampling methods, but readers may refer to good articles published in this field (Cline 1966, Hammond et al. 1959, Peck & Melsted 1973, Welch & Fitts 1956).

After soil sampling, the next step in soil analysis is extracting and measuring the nutrient. The best extractant is one where the quantities of extracted nutrient correlate well with plant uptake of the nutrient. In other words, the extractant should extract approximately that part of the nutrient pool that is a available to the growing plant. Various extractants have been tested and are reported in the literature. Sodium pyrophosphate (0.1 M), either at pH 10 or adjusted to pH 7 with phosphoric acid, is a good extractant of ferrihydrite, and does not extract Fe from more crystalline iron oxides (Wada 1977). Olson & Carlson (1950) evaluated the use of 1 M ammonium acetate, adjusted to pH 4.8 with acetic acid, and found that the critical level of Fe is about 2 mg kg^{-1} of soil. The best method so far reported for Fe extraction seems to be the DTPA (diethylene triamine pentaacetic acid) test developed by Lindsay & Norvell (1969), which involves 1:2 soil/solution extraction with 0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1 M triethanolamine, adjusted to pH 7.3. According to Lindsay (1979), a critical level of 4.5 mg Fe kg^{-1} of soil was found with DTPA extract for 77 Colorado soils. Boer & Reisenauer (1973) confirmed the effectiveness of the DTPA soil test and 5-6 mg kg^{-1} Fe was reported as a critical Fe level under greenhouse and field conditions.

The third step in soil analysis is interpretation of analytical results and recommendations for fertilizer. This is generally done through some type of previously determined correlation between test results and known

field crop responses. A basic principle of soil testing is that a soil test value can, under most circumstances, be treated and related as an independent variable to the percent yield and response obtained for a specific crop (Melsted & Peck 1973). To make appropriate fertilizer recommendations, it is important that fertilizer trials be carried out over the full range of soils, climatic conditions and crops of concern. Such calibration studies are successful only for immobile nutrients and all other management practices should be at optimum levels. Studies based on growth of seedlings under greenhouse conditions do not permit plant difference to be expressed as they would in the field. Therefore, they are not a valid basis for calibration of soil test values to be used as a guide for crop production (Cope & Rouse 1973). For food crops, cereals or legumes, grain yield is the most important parameter for evaluating crop response to fertilizers under field conditions. Experiments for calibration of chemical tests that provid the basis for recommendations to farmers must be conducted in the field.

Plant Analysis

Plant analysis is the determination of the concentration of an element or extractable fraction of an element in a sample from a particular part or portion of a crop sampled at a certain time or stage of morphological development (Munson & Nelson 1973). According to Fageria (1984), plant analysis, in its simplest terms, is a study of the relationship of the nutrient content of the plant to its growth. Plant analysis is based on the principle that the concentration of a nutrient within tha plant at any particular moment is an integrated value of all the factors that have influenced the nutrient concentration up to the time of sampling.

The validity of plant tissue analysis is mostly dependent on the care taken in collecting, handling, preparation, and analysis of the plant tissue. Errors made in these different phases can result in misinterpretation

of analytical results and the purpose of plant analysis as a diagnostic instrument is defeated. Therefore, it is important that those employing plant analysis be familiar with recommended handling and analysis procedures. It is beyond the scope of this article to discuss these aspects, but the reader should refer to the articles by Jones Júnior et al. (1971) and Jones Júnior & Steyn (1973).

Studies have shown that chlorotic leaves may contain higher Fe concentrations than green leaves (Dekock et al. 1979, Dekock 1981, Wallace et al. 1982). Because of this it has been suggested that "active Fe" and not total Fe is the important fraction in plant tissues. Active Fe in plants has been reported to be Fe^{2+} (Dekock et al. 1979). Active Fe is considered to be that portion of Fe available for, or participating in metabolic reactions or incorporated into molecular structure (Pierson & Clark 1984). Katyal & Sharma (1980) developed a method for the determination of Fe^{2+} in plant tissues using OPh (1,10-o-phenanthroline) to extract Fe^{2+}. Significant differences between green and chlorotic leaf tissue were noted; chlorotic leaves had less Fe^{2+} than green leaves. However, this method had two main limitations. The first one is the use of fresh tissue would restrict Fe^{2+} determinations to presently growing plants (an important limitation for many investigations); and second, 16-hour extraction time appeared to be too long when reactions that can occur with Fe are considered. According to Pierson & Clark (1984), Fe^{2+} could be readily extracted from leaf tissue with aqueous solutions of the chelating agents OPh (1,10-o-phenanthroline) and PDTS [Ferrozine; 3-(2-pyridyl)-5,6-bis-4-phenyl-sulfonic acid)-1,2,4-triazine]. Since Fe^{2+} values remained constant after the second extraction of the same tissue, three extractions were considered adequate to obtain consistent Fe^{2+} values. An extraction time of 30 minutes was as effective as 16-hours. Even though fresh tissue yielded higher Fe^{2+} values than freeze-dried or oven-dried tissues, dried tissue could be used with-

out difficulty for Fe^{2+} determination (Pierson & Clark 1984).

Plant analysis is not as commonly used as analysis to evaluated soil fertility. The main reason for this is the high cost involved in plant tissue analysis and lack of calibration data for many plants and for many growing conditions. For interpretation of plant analysis results, it is essential to have preestablished critical or sufficiency nutrient levels for each crop and agroclimatic region. To determine critical or sufficiency level, a calibration curve is constructed relating nutrient concentration in a specific plant part to growth. Growth is usually expressed as a percent of the treatment giving maximum growth. If there is plant response to the applied nutrient, the calibration curve generally is represented by four zones. The first zone is known as the deficiency zone in which plant growth increases sharply as more nutrient is absorbed, but there is little change in the concentration of the nutrient in the plant part analyzed. The second zone is the transition zone, in which both nutrient concentration and growth increase as more nutrient is absorbed. The third zone, called adequate or sufficiency zone, is the region of the curve where each addition of the nutrient raises nutrient concentration without a corresponding increase in growth. If the applied nutrient is in excess, a fourth zone known as the toxic zone is developed. In this zone there is an increase in nutrient concentration, but yield is decreased. The critical concentration lies within the transition zone and is usually associated with a 10% reduction in growth. The sufficiency or adequate values of Fe reported for some important crops are presented in Table 1.

The sufficiency nutrient level in plants is influenced by several factors such as stage of plant growth, plant part sampled, soil fertility level, cultivar, climatic and management factors. These factors have been discussed in detail by Bates (1971). Bacause so many factors affect critical or sufficiency nutrient levels in plant tissue, developing standard values for each agroclimatic region, and for each crop under different management practices is advisable.

Plant analysis results are normally expressed in concentration (mg kg^{-1} or μg g^{-1}) and uptake (concentration x dry matter yield). Sometimes, it is doubtful which is the best way of expressing these results. Concentration is useful in identifying nutrient deficiency, sufficiency and toxicity whereas, uptake is useful in determining nutrient maintenance levels to apply for different soil test levels and crop yields. Research on this subject needs constant review, especially when improvements in varieties and management are being made.

Chemistry of iron in soils

Geochemical principles provide a basis for understanding the distribution of elements in soil parent material. They can be used to predict areas of micronutrient sufficiency and deficiency. Iron is a major constituent of the lithosphere, comprising approximately 5.1%; the average content of soils is estimated at 3.8% (Lindsay 1979). In primary minerals, Fe occurs largely as ferromagnesium minerals. During weathering, these minerals decompose, and the Fe released precipitates as ferric oxides and hydroxides. Iron is included in a group of heavy metal cations that held in soils principally on organic or inorganic surfaces or substituted as accessory constituents in common soil minerals (Hodgson 1963). The divalent form of Fe^{2+} is less strongly held by soil surfaces than Co, Cu, and Zn. When these elements area oxidized to higher valence states, they can form very insoluble oxides and phosphates, which renders these elements much less available to processes of leaching as well as to plants.

The solubility of Fe in soils is controlled by $Fe(OH)_3$ in well-oxidized soils, by $Fe_3(OH)_8$ (ferrosic hydroxide) in moderately oxidized soils, and by $FeCO_3$ (siderite) in highly reduced soils (Lindsay & Schwab 1982). The Fe^{3+} hydrolysis species $Fe(OH)_2^+$ and $Fe(OH)_3^0$ are the major solution species of inorganic Fe,

TABLE 1. Iron sufficiency level for different crops

Crop	Plant part analyzed	Stage of growth	Sufficiency range (mg kg^{-1})	Reference
Barley	Whole tops	Heading	50-150	Ward et al. 1973
Common bean	Fully developed Trifoliate	Flowering	100-450	Wilcox & Fageria 1976
Corn	Ear leaf	At silk	50-200	Jones Júnior & Eck 1973
Cotton	Mature leaves	Early bloom	30-300	Sabbe et al. 1972
Peanut	Upper Stem & Leaves	Flowering	50-300	Small & Ohlrogge 1973
Rice	Whole Top	Tillering	70-300	Fageria 1984
Sorghum	3rd leaf	At bloom below head	65-100	Lockman 1972
Sugarbeet 1966	Blade	Not given	60-140	Nagarajah & Ulrich 1966
Sugarcane	Blade	Not given	20-600	Schmehl & Humbert 1964
Soybean	Fully developed Trifoliate	Prior to pod set	51-350	Small & Ohlrogge 1973
Wheat	Whole Tops	Heading	50-150	Ward et al. 1973

but they are maintained at too low levels to supply available Fe to plants.

The dissolution and precipitation of ferric oxides is the major factor controlling the solubility of Fe in well aerated soils. The activity of Fe^{3+} maintaned by these oxides is highly pH dependent. The solubility of Fe^{3+} decreases 1000-fold for each unit increase in pH and is decreased to levels below 10^{-20}M as pH rises above 7.5 (Lindsay & Schwab 1982). Calcium carbonate buffers soils in the general pH range of 7.4 to 8.5. In this pH range, iron oxides attain their minimum solubility, and Fe deficiency in plants is most severe. The Fe^{3+} oxides have different solubilities which decrease in the order $Fe(OH)_3$(amorph.) > $Fe_2(OH)_3$(soil) > Fe_2O_3 (maghemite) > FeOOH(lepidocrocite) > Fe_2O_3(hematite) > FeOOH(goethite). Lindsay (1979) showed that Fe solubility in well-aerated soils tends to approach that of $Fe(OH)_3$(soil) or "soil-Fe". Its solubility is represented by the following reaction:

$$Fe(OH)_3(Soil) + 3H^+ = Fe^{3+} + 3 H_2O$$
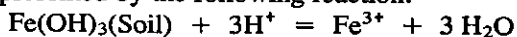
If soluble Fe salts are added do well-aerated soils, they quickly dissolve to precipitate $Fe(OH)_3$(amorph.). Over a period of several weeks the solubility of Fe decreases slowly and approaches that of "soil-Fe".

Ferric ions hydrolyze readily in aqueous media to give a series of hydrolysis products, mainly $Fe(OH)_2^+$, $Fe(OH)_3$ and Fe $(OH)_4^-$.

The sum of these various hydrolysis species and of Fe^{3+} gives the total soluble inorganic Fe. Measured Fe concentrations in soil solutions are usually in the range 10^{-8} to 10^{-6} M (Bradford et al. 1971, O'Connor et al. 1971, Uren 1984); and therefore, are higher than those predicted from thermodynamic equilibrium calculations. This higher Fe solubility is mainly due to soluble organic complexes (Olomu et al. 1973).

Besides concentration, nutrient mobility is also important. Mobility of an element in soils is no more than a reflection of its solution concentration as it is affected by the movement of water through the profile. As such, any factor that affects the solubility of an element in the same way affects the movement.

The presence of soluble substances leached from organic residues or produced through

microbial action influences the movement of Fe in two ways: 1) by stabilizing hydrosols of Fe in the soil solution, or 2) by forming strictly soluble organic complexes (Hodgson 1963). From the standpoint of soil fertilization, micronutrient amendments do not generally move far in the soil profile but organic chelates can promote the movement of Fe along with other heavy metals.

One of the most important factors affecting the mobilization and immobilization of Fe in soils is drainage. The manner and degree to which soil aeration alters the chemistry of Fe is well known. Oxidation of Fe in soils is, of course, a reversible process. As drainage becomes impeded and the oxidation potential (Eh) approaches 0.2 volts, oxides of Fe^{3+} can be reduced.

Mechanism of iron uptake

Plants primarily absorb Fe^{2+}, but in normal aerated soils Fe^{3+} is the form present. Iron (Fe^{3+}), therefore, has to be reduced to Fe^{2+}, before it can be absorbed by plant roots. Reduction of Fe^{3+} to Fe^{2+} is known to be an obligatory step in the Fe uptake by Fe-efficient species (Chaney et al. 1972). Two opposing hypotheses have been suggested for the mechanism of Fe^{3+} reduction. According to Brown & Ambler (1973) and Olsen et al. (1981), Fe deficiency causes a release of reducing substances from plant roots. These substances reduce Fe^{3+} in the apparent free space of the roots and/or in the external solution. This reduction is followed by uptake of Fe^{2+} into the root cells. The reductant produced by a stressed plant consists of several compounds which accumulate in relatively high levels in the periphery of young roots (Olsen et al. 1982). One of the reductants is caffeic acid. Its synthesis and oxidation is under enzymatic control in the roots. Release of reducing substances under Fe deficiency is reported under certain conditions such as acidification of the external solution by enhanced H^+-efflux from roots (Olsen & Brown 1980) or by addition of

acetic acid (Olsen et al. 1981). Many ions inhibit the reduction of Fe^{3+} by plant roots. Some of the more effective ions include P, Cu, and hydroxide. Other ions, including Mn^{2+}, Zn^{2+} and molybdate inhibit to a lesser extent. Therefore, these ions, when present in an excess amount in the growth medium, induce or aggravate Fe-deficiency in plants. As an alternative to the model of Fe^{3+} reduction by released reducing substances, Chaney et al. (1972) and Bienfait et al. (1982) put forward a hypothesis of enzymatic Fe reduction at the outer surface of the plasmalemma of the cortical cells. This hypothesis was supported by Romheld & Marschner (1983) working with peanut plants.

This reduction hypothesis mostly operates in dicotyledonous plants. In grasses, uptake of Fe^{3+} is of major importance (Lindsay & Norvell 1969). Grasses have developed a different strategy for responding to Fe-deficiency. In general, they are less susceptible to lime-induced chlorosis than most dicotyledonous species. In Fe-deficient grasses, nonproteinogenic amino acids accumulate in and are released from the roots (Takagi 1976). Some of them, including avenic acid, have been identified (Fushiya et al. 1982). These amino acids form highly stable complexes with Fe^{3+}, but no with Fe^{2+} (Benes et al. 1983) and are very effective in dissolving FeOOH at high pH (Sugiura et al.1981). Chemically they are closely related to nicotianamine, which is widely distributed in higher plants (Marschner 1986). Nicotianamine is an effective chelator for Fe^{2+}, but not Fe^{3+}. In response to Fe deficiency, grasses obviously transform nicotianamine into substances such as avenic acid which are released into the rhizosphere for mobilization of Fe^{3+} by chelation. These Fe^{3+} chelates are transported into the root cells.

Role of chelates in iron nutrition

Chelating agents have been used to correct Fe deficiency for more than five decades (Wallace 1962). The most commonly available

chelating agents are EDTA (ethylenediamine-tetraacetic acid - $C_{10}H_{16}O_8N_2$), DTPA (diethy-lenetriaminepentaacetic acid - $C_{14}H_{23}O_{10}N_3$) CDTA (cyclohexanediaminetetraacetic acid - $C_{14}H_{22}O_8N_2$),EDDHA (ethylenediaminedi-o-hydroxyphenylacetic acid - $C_{18}H_{20}O_6N_2$), HEEDTA (hydroxyethylethylene-diaminetri-acetic acid - $C_{10}H_{18}O_7N_2$), and EGTA (ethy-leneglycol-bis (2-aminoethylether) tetraacetic acid - $C_{14}H_{24}O_{10}N_2$). Lindsay (1976, 1979) has pointed out that chelates do not increase the activity of Fe^{3+} or Fe^{2+} in soils, they only increase the concentration of chelated iron. Chelated Fe is important, because it establi-shes a larger diffusion gradient to aid in the transport of Fe to plant roots. The ability of chelating agents to maintain chelated Fe in solution as pH rises follows the order: EDTA < DTPA < CDTA < EDDHA. Iron is displaced from EDTA above pH 6.7, and from DTPA and CDTA above pH 7.7 (Lindsay & Schwab 1982). The driving force that enables chelating agents to function in the vicinity of plant roots is the release of H^+ and e^- and the uptake of Fe^{2+}. The rate limiting step of diffusion is overcome by the presence of chelated Fe which is generally added at levels of 10^{-6} or 10^{-5} M (Lindsay & Schwab 1982).

Factors affecting the availability of iron

Soils and plants are the most important factors affecting Fe availability to plants. The availability of Fe is particulary sensitive to changes in the soil environment. Part of the sensitivity to these changes is related directly to the performance of the root system in exploring the soil volume for this nonmobile element, and part is related to the pool or bonding of the element in the soil (Viets 1962). Soil conditions important to the availability of Fe have not been fully defined largely because solubility relationships for Fe are very complex. In the case of an insoluble nutrient like Fe, the transport process from soil to plant roots is generally the rate limiting step in nutrient uptake. A number of the factors that influence these relationships are known and are briefly discussed below.

Soil pH

Soil reaction is one of the most important factors affecting Fe availability to plants. The soil pH is known to influence the solubility of Fe in soil (Bohn et al. 1979, Elgala et al. 1976). As pH increases, Fe is converted to less soluble forms, principally to the oxide Fe_2O_3. The reaction responsible for the reduced solubility of Fe with increasing pH is well understood. It results in the precipitation of $Fe(OH)_3$ as the concentration of OH^- ions is increased as indicated by the following reaction:

$$Fe^{3+} \quad + \quad 3OH^- \quad = \quad Fe(OH)_3$$

The $Fe(OH)_3$ is chemically equivalent to the hydrated oxide, $Fe_2O_3.3H_2O$. Acidifi-cation shifts the equilibrium, causing a greater release of Fe^{3+} as a soluble ion. Liming is and essential management practice for crop production in acid soils. But when the pH values of cerrado soils in Brazil are increased from 5 to 6, Fe-deficiency has been observed in upland rice, bean and corn, even when soil analysis showed a high Fe concentration (Fageria 1984).

Oxidation-reduction

One of the soil properties which has a marked effect on Fe behavior is the oxidation-reduction or redox potential. Oxidation-reduction factors affect the valence of Fe and thereby its uptake by plants. Oxidation-reduction reactions involve the transfer of electrons from one ion or molecular to another. Oxidation is the donation, and reduction is the acceptance, of electrons from other substances (Bohn et al. 1979). Oxidizing agents accept electrons from other substances and thereby undergo reduction. Reducing agents donate electrons to other substances. Iron (Fe^{2+}) loses an electron to form Fe^{3+}. The oxidation-reduction of Fe is described by the following equation:

$$Fe^{3+} \quad + \quad e^- \quad = \quad Fe^{2+} \qquad \log K_0 = 13.04$$

Oxidation-reduction processes affect the valence of Fe and thereby its uptake by plants.

When Fe^{3+} is reduced to Fe^{2+}, its concentration increases and so does uptake. On the other hand, when Fe^{2+} is oxidized to Fe^{3+}, its concentration is reduced and uptake by plants is also reduced.

The critical redox potentials for Fe reduction and consequent dissolution are between +300 mV and +100 mV at pH 6 and 7, and -100 mV at pH 8, while at pH 5 appreciable reduction occurs at +300 mV (Gotoh & Patrick Júnior 1976).

Organic matter

The relative influence of soluble and insoluble organic compounds and their relation to inorganic soil constituents in the average mineral soil is still debatable. The presence of organic matter may promote the availability of Fe, presumably by supplying soluble complexing agents that interfere with its fixation. When Fe is added to a soil in chelated form, or when chelation occurs by soluble organic compounds, the concentration and gradient in soil solution is usually higher than the concentration and gradient of unchelated Fe and transfer by diffusion is greatly enhanced (O'Connor et al. 1971).

Several investigators, such as Miller & Ohlrogge (1958), Kononova (1966), and Schnitzer (1969) have found that under normal soil conditions, relatively high amounts of water-soluble Fe are present in organic forms and natural organic chelating agents play a role in keeping Fe in solution under alkaline soil conditions and the presence of $CaCO_3$ (Elgala et al. 1976). Fulvic acid and amino acids were among the active organic components that have been found to play a role in binding Fe and transporting Fe in soils (Hodgson 1969, Shnitzer 1969).

Microbial

Alexander (1962) gives five ways that microorganisms may affect the availability of Fe. These are: 1) the release of inorganic Fe ions during the decomposition of organic material, 2) immobilization of Fe by

incorporation into microbial tissue, 3) oxidation of Fe generally to a less available form, 4) reduction of an oxidized form of Fe under conditions where oxygen is limited, and 5) indirect transformations; e.g. changes in pH or oxidation potential.

Soil sterilization is known to increase Fe^{2+} in soil. It is well established that flooded soils are subject to a succession of Fe transformations from the Fe^{3+} to the Fe^{2+} state under reducing conditions. This is caused by a wide variety of facultative anaerobic soil bacteria (Bromfield & Williams 1963, Ottow & Glathe 1971, Takai & Kamura 1966). Takeda & Furusaka (1970) found that the number of facultative anaerobes was greater than that of strict anaerobes when the bacteria were anaerobically separated from paddy soil.

In the event aeration becomes limiting in a soil, e.g. under flooded conditions, microorganisms can also play a very significant role in lowering the redox potential (Eh) and accordingly, the relative concentrations of Fe^{3+} and Fe^{2+} as shown by the equation (Olsen et al. 1982).

$$E_h = E^0 + 59 \log [Fe^{3+}]/[Fe^{2+}]$$

This equation indicates that a decrease in Eh of 59 millivolts will increase the concentration of Fe^{2+} tenfold if Fe^{3+} remains constant.

Plant genetic variability

The total quantity of Fe in a soil is usually sufficient for plant growth, but the use of this Fe by the plant is genetically controlled by an adaptive mechanism. This mechanism is activated in Fe-efficient plants in response to Fe stress, but remains inactive if Fe is sufficient (Brown et al. 1972).

Iron-efficient plants release H^+ ions and reductants from their roots when they are under Fe stress. The pH at their root zone is lowered which favors Fe^{3+} solubility and reduction of Fe^{3+} to Fe^{2+}. The Fe is reduced externally by the root where it can be prevented from entering the plant by trapping

with the ferrons chelator BPDS-bathophenanthrolin-edisulfonate (Brown & Ambler 1974, Chaney et al. 1972). The factors activated in response to Fe stress are associated with the plant's increased Fe uptake.

Interaction with other nutrients

Two or more growth factors are said to interact when their influence individually is modified by the presence of one or more of the others (Sumner & Farina 1986). Interactions may be positive or negative depending on the growth response. If the growth response is greater with two combined factors as compared to the sum of their individual effects, it is a positive interaction, and when the combined effects are less, the interaction is negative.

A number of nutrients appear capable of reducing the availability, absorption and utilization of Fe in crop plants. These so-called negative interactions may result from interactions that occur either outside the root or within the root. Those taking place in the external root environment are usually precipitation or similar reactions that reduce the chemical availability of the nutrient. Those that influence absorption or utilization processes alter the effectiveness of a nutrient by reducing its physiological availability.

Iron deficiency of plants is difficult to correct by application of inorganic salts (Olsen 1972). Some synthetic chelates such as FeEDDHA effectively supply Fe to plants, but they are expensive. Since the correction of Fe deficiency is not simply achieved by a management practice, knowledge of interactions leading to Fe deficiency becomes very important in Fe nutrition of plants.

Iron deficiency induced by heavy applications of P has been widely reported (Brown et al. 1955, Sumner & Farina 1986, Wallace 1951, Watanabe et al. 1965). Some experiments indicate that Fe phosphate may precipitate externally on the roots (Ayed 1970, Biddulph 1953), but the interaction of Fe and P leading to Fe chlorosis appears to be caused by an internal immobilization of Fe probably due to the formation of Fe phosphate (Biddulph 1953, Rediske & Biddulph 1953).

Similarly, Fe deficiency is caused by the accumulation of excess Mn and Cu in the soil (Bingham et al. 1958, Brown et al. 1955, Nason & McElroy 1963, Olsen & Watanabe 1979). The interactions of Fe with Mn and Cu appear to be of a physiological nature. They may reflect the joint participation of these nutrients in some of the same biochemical systems, the proper functioning of which depends on the relative proportions of each of the nutrients present. High Mn in soils or plants may oxidize Fe to an inactive state. Competitive effects on Fe uptake have also been observed with excess Ca^{2+}, Mg^{2+}, K^+, Zn^{2+} and Mo (Dekock 1956, Hanger 1965, Lingle et al. 1963).

Phytosiderophores

Phytosiderophores are defined as Fe containing chelates of microbial origin and are wide-spread among fungi and bacteria (Winkelmann 1982). There are two classes of phytosiderophores: the catechols, produced by bacteria and the hydroxamates produced mainly by fungi (Powell et al. 1982). The microbial siderophores are generally produced under Fe stress and are and important factor in determining Fe acquisition by plants.

According to Marschner (1986), grasses respond quite differently to Fe deficiency by sharply increasing the release of nonproteinogenic amino acids (phytosiderophores) from the roots. The release of these compounds is typical for grasses but cannot be found in dicots (Takagi et al. 1984). These amino acids mobilize sparingly soluble inorganic Fe^{3+} in the rhizosphere by the formation of Fe^{3+} chelates. Most likely, these chelates are taken up readily by the roots of grasses. Neither the pathway of biosynthesis of phytosiderophores, nor the mode of regulation by Fe are known (Powell et al. 1982).

Iron toxicity in flooded rice and its correction

Rice is an important food crop for the world's population. Globally, it ranks second to wheat in terms of area harvested, but rice provides more calories per hectare than any other cereal crop (Fageria 1984). Based on water source and land preparation method, rice can be divided into two groups; upland and lowland rice. Upland rice refers to rice grown on both flat and sloping fields that are prepared and seeded under dryland conditions and depend on rainfall for moisture. This type of rice cultivation is most common on small and medium size farms in South America, Asia, and Africa. Brazil is the world's largest producer of upland rice (Fageria et al. 1982). On the other hand, flooded rice is grown on flat land with controlled irrigation. It is also known as irrigated rice, lowland rice and waterlogged rice. The common practice of flooded rice culture is flooding when seedlings are 25 to 30 days old. The water level varies from 10-15 cm and is maintained until one week to 10 days, before harvesting.

Due to reducing conditions, the chemical properties of flooded rice soils are entirely different from those of drained soils. The reduced conditions of flooded rice bring some changes which are beneficial as well as harmful. One harmful effect is increased concentrations of Fe^{2+} which sometimes reach levels toxic to rice plants.

No other food crop except rice can be grown under submerged or flooded conditions because all other food crops are sensitive to waterlogging. If other crops have to be grown, these soils first need to be drained. Since rice is such an important world food crop, it is worthwhile to discuss Fe-toxicity in flooded rice.

Iron toxicity in flooded rice has been reported in Southeast Asia, Africa, and South America (Fageria et al. 1984), Fageria & Rabelo 1987, Inada 1966, Ottow et al. 1982). In Brazil, this problem has been reported in the states of Minas Gerais, Goiás, Pará, Santa Catarina, and Rio Grande do Sul. Iron toxicity may be attributed to high Fe content in the soil, low soil pH, low soil fertility as well as to accumulation of harmful organic acids and/or hydrogen sulphide (Inada 1966, Ota & Yamada 1962, Sahu 1968, Tanaka et al. 1966, Trolldenirer 1973). Plants generally show bronzing if dissolved Fe in the rooting mediun is in the 300 to 500 mg kg^{-1} range.

Reduction is the most important chemical change brought about by flooding, and oxidation-reduction potential or redox potential is a quantitative measure of the intensity of this change (Ponnamperuma 1972, Ponnamperuma et al. 1967, Savant & McClellan 1987). The most drastic changes that occur when a soil is submerged and its Eh falls, are reduction of NO_3^- to nitrous oxides, Mn^{+4} to Mn^{+5} and Fe^{3+} to Fe^{2+}. The concentration of water-soluble Fe, which prior to submergence rarely exceeds 0.1 mg kg^{-1}, may rise to 600 mg kg^{-1}, or it may reach plateau seldom exceeding 20 mg kg^{-1} (Ponnamperuma 1978). In some acid sulfate soils the peak values may be as high as 5,000 mg kg^{-1} (Ponnamperuma et al. 1973).

The increase in concentration of water-soluble Fe following flooding can be described for most mineral soils by the equation (Ponnamperuma 1978):

$$Eh = 1.06 - 0.059 \log Fe^{2+} - 0.177 \, pH$$
or
$$pE = 17.87 + pFe^{2+} - 3 \, pH$$

Effective measures to ameliorate Fe toxicity include periodic surface drainage, liming and good fertilizer management. If Fe toxicity is not severe, the use of tolerant rice cultivars alone may serve as an alternative to these measures (Fageria et al. 1984). The existence of an oxygen transport system from shoot to root in the rice plant prevents suffocation of root tissues in an anaerobic root environment. The rate of diffusion of oxygen from shoot to root varies markedly among different rice cultivars. Tadano (1976) proposed that three functions of rice roots

account for the tolerance of rice to high concentrations of Fe in soil solution: 1) oxidation of Fe in the rhizosphere, 2) exclusion of Fe at the root surface, and 3) retention of Fe in the root tissues which prevents translocation of Fe from the root to the shoot.

Correcting iron deficiency

Iron is an essential element and its deficiency can reduce plant growth and yield. Of course it is a micronutrient but as cropping systems become more intensive in modern agriculture, changes in soil management practices frequently alter micronutrient availability, and depletion of nutrients not added in fertilizers becomes more rapid. As the demand for higher yield increases and the plant's requirements for major elements are more effectively met, other nutrients are more likely to become limiting. Correcting Fe-deficiency and toxicity is important for yield improvement of food crops. The question then becomes what is the best method of correcting this nutrient disorder.

The most widespread incidence of Fe-deficiency in plants occurs on alkaline and calcareous soils characterized by high pH and the presence of free $CaCO_3$ (Berger & Pratt 1963, Wallace 1962). This abnormality has often been termed, "lime induced chlorosis." A large part of the world's land area is calcareous. Iron, as well as many other micronutrients, tends to become insoluble, immobile, and unavailable in these soils. Iron chlorosis or deficiency can be corrected by soil and foliar application of Fe. Anderson (1982) investigated several sources of Fe applied to soil and as a foliar spray on peanuts. Of the several soil applied Fe sources (Fe^{2+} and Fe^{3+} sulfates, chelates, lingnosulfonates, finely powdered elemental Fe by-products), only the chelate FeEDDHA (Chel 138) at the rate of 10 kg Fe ha^{-1} alleviated the visual Fe chlorosis. Iron deficiency was also corrected by foliar application of 3% $FeSO_4$ solution to peanuts

and sorghum (Anderson 1982). If the deficiency is severe, multiple applications at 10 day intervals may be required. Most sources were somewhat effective in alleviating Fe chlorosis when soil applied at sufficiently high rates (50 kg Fe ha^{-1}), however, few were economically feasible in severe Fe chlorosis situations. Another alternative for correcting Fe-deficiency is use of Fe-efficient cultivars. There are varietal differences in Fe-uptake by corn (Zaharieva 1982), oat (McDaniel & Brown 1982), sorghum (Williams et al. 1982), dry beans (Coyne et al. 1982), and wheat (Vittal & Subbiah 1982).

Soil applications of some synthetic Fe chelates are effective for crops under some conditions, but their high cost restricts their use. Wallace & Lunt (1960) reported that FeEDTA (ethylenediaminetetraacetic acid) was effective in controlling Fe chlorosis of citrus Florida, but this chelate is not effective on calcareous soils. The most effective chelate for calcareous soil systems is FeEDDHA (ethylenediaminedi - o - hydroxyphenylacetic acid). Differences in agronomic effectiveness of synthetic chelates are related to how their stabilities vary with soil pH (Norvell 1972). The stability constant for FeEDTA is much lower than that for FeEDDHA; the former is effective mainly in acid soils, while the later is effective at all soil pH levels.

Soil applications of inorganic Fe sources usually are not effective in correcting Fe chlorosis unless the rates are very high. Withee & Carlson (1959) reported that optimum yields of grain sorghum were achieved with a broadcast application of 600 kg of $FeSO_4$ ha^{-1}. Mathers (1970) also showed that high $FeSO_4$ rates were required for correction of sorghum chlorosis in greenhouse and field tests. The effectiveness of $Fe_3(SO_4)_3$ and Fe $(NH_4)_2(SO_4)_2$ generally is similar to that of $FeSO_4$, while $FeCO_3$ and Fe_2O_3 are not effective as soil applications. Greenhouse results by Mortvedt & Giordano (1971) showed that banding $FeSO_4$ or $Fe_2(SO_4)_3$ with ammonium polyphosphate fertilizers was more effective than applying

these Fe sources alone to soil. Soil application of Fe sources would be preferred by most growers if the effectiveness was equal to that of foliar sprays. Works by Tan et al. (1971), Miller et al. (1969), and Thomas & Mathers (1979) indicate that animal manures can be good sources of Fe and other micronutrients as well as possible complexors or chelators of supplemental Fe mixed with the manures. Sulphur has been used in the past as a means of acidifying soil to correct Fe chlorosis, but the quantities required were too large to be economically feasible for food crops (Olson 1951, Viets 1962).

Iron is usually considered to be immobile within growing plants (Salisbury & Ross 1969). The new growth of a plant deprived of Fe soon becomes chlorotic while the older tissue remains green. Because of the immobile nature of Fe in growing plants, foliar application of Fe to chlorotic plants is recommended.

In certain types of crop production, foliar sprays area popular and used on a world-wide basis (Mengel & Kirby 1978, Murphy & Walsh 1972). But Fe-deficiency has been particularly difficult to correct by foliar sprays and controversy remains on the subject.

CONCLUSION

Iron deficiency has been observed in important food crops such as corn, sorghum, peanuts, soybeans, common beans, oats and barley in many parts of the world. Whereas, Fe-toxicity is mostly restricted to flooded or lowland rice. Much research work has been conducted under laboratory and greenhouse conditions concerning Fe chemistry, Fe uptake, and Fe transport and storage mechanisms. But very little attention has been given to determining the most effective and economical ways to solve this nutritional disorder. At present, foliar application is the only feasible means for overcoming Fe-deficiency in most crop plants. Inorganic sources of Fe are ineffective for soil application when applied at low or moderate

rates and higher doses are uneconomical. However, foliar application of nutrients is not the right solution in modern agriculture where higher productivity is the goal. In addition, foliar appplication is restricted by weather conditions and cost.

This means more field research is needed to solve Fe-deficiency or toxicity problems. One feasible and economical approach may be selection of crop genotypes which are more efficient or tolerant under low and high Fe concentrations, respectively. To achieve this objective, it is necessary to have a cooperative effort among soil scientists, plant physiologists and plant breeders. A lot of work has been done in identifying genotypes with high efficiency or resistance to toxicity, but these results have not been taken to farmers.

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