AGRONOMIC APPROACHES FOR INCREASING IRON AVAILABILITY TO FOOD CROPS

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Summary

Iron availability in calcareous soils, and Fe uptake and translocation in plants are major factors limiting the agricultural use of land. The nutritional value of crops as Fe sources for humans is often reduced due to Fe-deficiency in plants. Agronomic approaches to overcome these shortcomings include: (i) methods aimed at increasing the availability of indigenous soil-Fe; (ii) soil and/or foliar application of external Fe using a wide array of organic and inorganic materials; and (iii) genetic and breeding practices aimed at enhancing the uptake and translocation efficiency of Fe in crops. Agronomic development during the last five decades, especially the introduction of synthetic chelates to agriculture, has opened doors for successful crop production on highly calcareous soils.

However, to date, no ultimate practice is available to overcome Fe-deficiency in all crops, and large areas of marginal soils are excluded from production, or produce low yields, due to Fe-deficiency. Available practices, along with the physiological and soil chemistry aspects of Fe nutrition of plants are addressed in this paper. New options for the remedy of lime-induced Fe-deficiency are described in detail, with the aim of inducing further discussion and research that will lead to improved solutions to the

problem of Fe-deficiency in crops.

1. Introduction - The Origin and Scope of the Problem

Iron, the fourth most widespread element in the Earths crust and in soils, was among the very first elements to be identified as essential nutrients for plants. Its deficiency, manifested as leaf chlorosis, was first recognized by Griss in 1843, and was later attributed to various soil, management, and plant physiology factors. Chlorosis may lead to yield loss or complete crop failure, even when the total Fe content of the soil exceeds by three orders of magnitude the plants demand for this element. Thus, Fe deficiency in plants is most often a matter of availability rather than quantity. Its correction may be complicated and Fe fertilization may often cost the farmer as much as all other nutrients applied to the field. Furthermore, Fe deficiency in human nutrition today is reported to afflict more than three billion people worldwide, with plants being the principal Fe source in most diets (see *Iron Nutrition in Man: Global Perspectives on Iron Deficiency and Malnutrition*). Some figures of Fe content in edible organs are shown in Table 1. It should be noted however, that a large range of Fe concentration can be found for each of the crops. For instance, reported Fe concentrations in lettuce range from 50 to 600 mg kg^{-1} dry weight and yet plant growth was normal. This large range of Fe concentration may reflect variation in the Fe nutrition status of the plant, as well as variation among cultivars within a species (see *Improving Micronutrient Value of Rice Through Breeding* and *Improvement of Common Bean for Mineral Nutritive Content at CIAT*). Thus, the problem of Fe availability to plants and its uptake, transport, activity within plant tissue and accumulation in edible plant organs, is of great concern.

Crop and organ	Fe content	Crop and organ	Fe content
Cereal, graminaceous		Legume, leguminosaes	
Rice, grain	10	Soybean	90
Oat, grain	50	Pea	85
Wheat, whole grain	40	Lentil	85
Vegetables		Other: Fruits, Vines, Nuts	
Tomato, fruit	100	Apple, fruit	22
Pepper, fruit	100	Orange, fruit	30
Potato, tubers	25	Papaya, fruit	42
Spinach, leaves	300	Banana, fruit	10
Lettuce, leaves	320	Grapes, fruit	22
Cabbage, head	57	Coconut, fruit flesh	36

Table 1. Iron content in edible plant organs (mg kg^{-1} dry weight).

Iron prevails in the plant, as well as in all cells of all living forms on Earth, in two oxidation states: reduced, as ferrous iron (Fe^{2+}), or oxidized, as ferric iron (Fe^{3+}). In aerated soils, Fe is readily oxidized to its ferric state and forms a group of very insoluble ferric oxides and hydroxide minerals, such as goethite and hematite. The general reaction of hydroxide precipitation can be described by the equation:

$$Fe^{3+} + 3(OH)^- \rightleftharpoons Fe(OH)_{3\,(solid)} \tag{1}$$

The stability constant of this reaction depends on the hydroxide type of mineral and its degree of crystallization, and it ranges between 37, for poorly crystallized ferrihydrite, to 44, for well-crystallized goethite. From equation 1, it is evident that the Fe^{3+} concentration in soil solution is intimately related to the pH of the soil. Indeed, the single most important soil characteristic leading to Fe-chlorosis in aerated soils is high pH, which results in diminished solubility of ferric oxides and hydroxides that control its concentration. Ferric ion speciation in soil solutions in the pH range relevant for plant growth (pH 4-9) consists of the following most abundant species: $Fe(OH)_2^+$, $Fe(OH)_3^0$, and $Fe(OH)_4^-$. The sum of all hydrated forms of the ferric ion when in equilibrium with poorly crystallized ferric hydroxide (freshly precipitated "soil Fe") is minimal at the pH range of 7.4 to 8.5. Its maximal value in this pH range is as low as 10^{-10} M. This extremely low Fe concentration is orders of magnitudes below the critical level needed for adequate Fe supply to plants, as demonstrated in a simplified, yet fairly realistic, calculation (Box 1). The sum of all inorganic species of the ferrous iron in equilibrium in the same pH range, with the same solid phase will exceed the above value only in anoxic or suboxic soils, which are deleterious to most crops grown in aerated soils. Therefore, this discussion is limited to the concentration of the ferric rather than ferrous ions.

- Soils rarely contain less than 0.7% Fe by weight. Thus a 50-cm layer of soil contains at least 40,000 kg Fe per hectare.
- The soil solution in a 50-cm layer of 1 ha of cultivated soil (assuming water content of 40% by volume) with Fe concentration of 10^{-10} M, contains as little as 10 mg Fe.
- A common critical Fe level in plant tissue is 50-70 mg Fe kg^{-1} plant dry weight. Thus, assuming 10,000 kg dry weight plant material per hectare, the crop contains 500-700 g Fe per hectare.
- The mass flow of soil solution to the plant when the annual water consumption of the crop is 10,000 m^3 ha^{-1} will supply it with as little as 50 mg Fe, which is only 0.01% of the plant's minimal need.
- Yet, plant roots are surrounded by an amount that exceeds 50,000 times the crop's annual demand for Fe.

Box 1. Representing figures of Fe in a soil: A comparison between the Fe content in the solid phase of a soil, in the soil solution containing 10^{-10} M soluble ferric iron, and between the Fe demand of a crop and the amount supplied by mass flow of the soil solution.

A pH range of 7.4 to 8.5, in which inorganic forms of Fe are at minimal concentration, is common to calcareous soils, which cover over 30% of the Earths land surface, especially in arid and semi-arid regions. Diffusion of Fe in the solution towards active sites of uptake in the roots might partially bridge the wide gap between the amount of Fe needed and the Fe available, and indeed it was found to be a principal means for Fe movement in soil towards plant roots. In accordance, while data presented in Box 1 suggest a µM-range of soluble Fe as a critical level for plant growth, it was shown in

nutrient culture, which represents the most favorable conditions for diffusion, that the actual critical level of soluble and available Fe for adequate supply of this element for various plants is in the range of 10^{-8} to $10^{-8.7}$ M. These data, found by the authors of this chapter and their co-workers, are based on a divalent Fe chelate buffered nutrient solution technique.

Long-term evolution of plants grown in aerated soils with low Fe availability has equipped them with various mechanisms for Fe acquisition from the soil. These mechanisms have been grouped by researchers into two strategies. The first strategy (strategy I), common to all plant families other than the gramineae family, relies on enhanced membrane bound reductase activity, proton extrusion, and release of reducing substances from the roots, in response to Fe deficiency. The other strategy (strategy II), confined to graminaceous plants, relies on enhanced release of phytosiderophores, a group of low molecular weight chelates with a high specific affinity to bind Fe^{3+}, in response to the deficiency, and a specific uptake system of the Fe-phytosiderophore complex. The efficiency of these mechanisms and strategies varies widely among and within plant families and species, and provides an explanation for the well-known phenomenon of large variation in plant resistance to Fe deficiency.

Acidification of soils by strategy-I plants would be a very efficient mechanism for increasing Fe solubility in soils, if soil-pH could be easily modified. Unfortunately, many of the high-pH soils are effectively pH buffered by $CaCO_3$. Therefore, acidification is actually limited to a very narrow layer next to the acidifying roots, namely the rhizosphere, and to the free space (apoplast) of the active roots. Thus, Fe-stress is not only related to high soil-pH, but also to the capacity of the soil to maintain high pH. The most efficient buffer system is the outcome of the reactions of $CaCO_3$-H_2CO_3-CO_2 in calcareous soils following the reactions:

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{2+} + H_2CO_3 \tag{2}$$

$$H_2CO_3 \rightleftharpoons CO_{2\,(g)} + H_2O \tag{3}$$

At equilibrium, the buffer capacity of a calcareous soil is merely related to its $CaCO_3$ content. Rhizosphere acidification, however, is the outcome of a biological process with its own rate. Hence, the kinetics of the buffer activity of the soil, which is related to the surface area of the $CaCO_3$ particles (or to the "active lime" content of the soil), is another factor that controls Fe availability to plants. The combined effect of high pH, high lime content, and high proportion of "active lime", is powerful in inducing Fe deficiency and is usually referred to as "lime induced chlorosis". Due to its potent effect on Fe availability and to the widespread occurrence of calcareous soils, it is by far the most common cause of Fe-chlorosis in cultivated land.

In view of the extremely low solubility of Fe in high-pH soils, it might be surprising that Fe-deficiency in plants does not prevail throughout the entire calcareous land area. Indeed, in many cases, even under high-pH conditions, soil solutions were found to contain Fe in micro-molar concentrations, up to five orders of magnitude higher than the equilibrium concentration of the inorganic ferric Fe. In these cases, most of the Fe is probably present as natural organo-metal complexes or as fine colloidal Fe hydroxides

that might move in water almost as a soluble species.

Other factors that restrict Fe availability to plants include: High water content and poor aeration and oxygen supply for root respiration, which impair active energy-dependent Fe uptake in the roots; high HCO_3^- content of soil solution; extreme, usually low, soil-temperature; and high concentration of elements such as P, Mn, and sometimes Cu and Zn, that might behave as antagonistic elements in Fe uptake or translocation within the plant. Each of these factors may impose additional stress on Fe availability to plants. In many instances, Fe deficiency is not related to any single factor. On the contrary, it is related to numerous factors that control Fe solubility, the kinetics of various soil reactions, and physiological processes in the roots and within the plant. Each of these factors can potentially be alleviated by certain agronomic practices that will be addressed in this chapter. However, in many cases, the impact of an agronomic practice is not straightforward. It may well have some side effects that will impede its efficiency in the remedy of Fe deficiency. Such cases will be addressed where appropriate.

2. Agronomic Methods for Correction of Iron Deficiency

2.1. General Considerations

Whenever Fe nutrition hampers plant growth and crop production, agronomic steps should be taken to alleviate the deficiency by one or more of the following approaches: (i) Increase the availability of indigenous soil-Fe; (ii) supply the plants with an external source of available iron; and (iii) increase the efficiency of the plant mechanisms involved in the uptake and translocation of Fe. Although our level of understanding of the chemistry of Fe in soils and of the mechanisms and regulation of Fe uptake in plants have greatly increased in the last two decades, many side effects and interactions cannot be well predicted, and to date, no ultimate practice is available to completely overcome Fe-deficiency. Furthermore, since the problem is not merely scientific and theoretical, but an issue of applied agronomic practices that should be practical for agriculture worldwide, economic constrains are also involved.

2.2. Historical Review

Just four decades ago, before synthetic chelates were widely introduced for plant nutrition, it was assumed that "the most practical solution to lime-induced chlorosis is learning to live with it..." (Wallace and Lunt, 1960). At the beginning of the 1950s, first reports from field trials showed the efficiency of Fe-EDTA (ethylenediamine-tetraacetic acid) as a Fe source for citrus orchards grown on acidic sandy soil. However, this chelate was found to be inefficient in high-pH calcareous soils. Among other chelates tested in following years, Fe-EDDHA (ethylenediaminedi-o-hydroxyphenilacetic acid) emerged in the 1960s as the most effective chelate for relieving lime-induced chlorosis. Using chelates has since become the most common agricultural practice for improving the Fe nutrition of plants. However, as concluded in a review of the unsolved problems of Fe nutrition of plants, four decades after synthetic Fe-chelates were first introduced for agriculture, Fe chelates have probably failed to reach expectations as micronutrient carriers in soils. Even though considerable progress has been made, many questions concerning the Fe nutrition of plant still remain open. Among these, the high cost of the

chelate treatment which limits their application to predominantly high-cash crops, and their unclear environmental impact often lead to land abandonment.

2.3. Iron Fertilizers

2.3.1. Inorganic Fe Fertilizers

The simplest technology used to fertilize soils with Fe is soil application of mineral soluble or insoluble Fe-compounds. However, this approach is usually ineffective due to the high capacity of the soil to reduce Fe solubility and availability. Application of $FeSO_47H_2O$ was found to be efficient in sandy soils with low buffer capacity, or in acid soils, where quantity rather than availability of the Fe is the main cause for the deficiency, or where high concentration of other microelements, such as Mn or Cu, interfere with Fe uptake. In such cases, the application of 30 kg Fe ha^{-1} could possibly alleviate Fe stress and increase yields.

However, in calcareous soils, 10-fold higher rates were shown to have merely a partial effect, and to last only for a short time. Much higher and impractical rates, in the range of several tons $FeSO_47H_2O$ ha^{-1}, are needed to effectively supply Fe for crops grown on calcareous soils, and even these high rates affected crops only for a short period. Other mineral Fe compounds, soluble or insoluble, were tested with similar results. All of them face the same problem of low effectiveness in calcareous soils. In some cases, a band application of the nutrient will minimize its contact with soil particles, slow down various processes that decrease availability, and result in improved efficiency.

Another approach, which is easily applied in irrigated fields, is the application of soluble compounds, such as $FeSO_47H_2O$, through fertigation. This practice, however, if applied above ground on soil of neutral to high-pH, results in Fe precipitation on the soil surface with a very small, if any, part of it reaching deeper soil in the active root zone. Drip irrigation, which keeps much of the roots near the surface, mulching above drippers, or underground drip irrigation may improve this practice. Another practical problem, unless irrigation water is acidified, is the rapid oxidation and precipitation of the Fe^{3+}, which may take place within the irrigation system thereby plugging small openings of the drippers. Combined application of $FeSO_47H_2O$ and a chelating agent through fertigation system will be discussed later.

2.3.2. Industrial By-Products

Low-grade pyrite (Fe_2S) based mining residues, Fe-dust from the steel industry, coal slurry solids, and some other waste and by-product materials are often an available source for large quantities of low-priced Fe minerals. In many places where Fe-deficient fields are close enough to a source of such material, attempts have been made to make use of the available Fe-source by applying it to the soil. These materials were found, however, to face the same problems as those previously discussed. Thus, inorganic Fe-compounds are bound to be of limited value in highly calcareous soils that tend to induce severe Fe-deficiency. Decreasing particle size, acidification, and band application rather than surface broadcast, may slightly increase the effectiveness of these materials.

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Biographical Sketches

Yona Chen received his B.Sc., M.Sc. and Ph.D. degrees from the Hebrew University of Jerusalem in 1968, 1970, and 1975 respectively. Dr Chen was recognized as a fellow of the American Society of Agronomy in 1990, and of the American Society of Soil Science in 1991.

In 1977, Dr. Chen was appointed as lecturer of soil chemistry at the Department of Soil and Water Sciences at the Hebrew University of Jerusalem. He was promoted to senior lecturer in 1979, to associate professor in 1983, and to full professor in 1987. He was Head of the Department of Soil and Water Sciences from 1985 to 1989, and Dean of the Faculty of Agricultural, Food and Environmental Quality Sciences from 1993 to 1997.

Dr. Chen and his collaborators have made major contributions to research in the basic aspects of chemistry and biochemistry of soil and water. Among other topics, emphasis has been given to research on: (i) Organic matter-micronutrient reactions of agricultural importance; complexes of humic material, peat, manure and composts with Fe, Zn, and B have been investigated with emphasis being given to solubilities and uptake by plants; and (ii) Effects of biochemicals and humic substances on plant growth; defined biochemicals (siderophores) produced by soil microbes were found to enhance plant growth and to support Fe uptake. Strains of microbes and fungi efficient in the production of siderophores have been isolated and grown in fermentors, and their effect on Fe uptake has been investigated recently by Dr. Chen and his group.

Dr. Chen has co-edited six books, and authored or co-authored about 200 scientific articles, book chapters, and monographs. Among others, he has served as Associate Editor of *Plant and Soil*, *Agrochimica*, the *Journal of Environmental Quality*, and *Critical Reviews in Environmental Quality*.
Dr. Chen currently serves as the President of the International Humic Substances Society, and as President of the Israeli Society for Ecology and Environmental Quality Sciences.

Moshe Shenker was born in 1953. He received his B.Sc., M.Sc. and Ph.D. degrees from the Hebrew University of Jerusalem in 1985, 1989, and 1995 respectively.

In 1995-96, Dr. Shenker worked in the Israeli Ministry of the Environment, where he was in charge of municipal and industrial solid waste landfills. In 1997, after Post-Doctoratal research at the Department of Soil and Environmental Sciences, University of California, Riverside, USA, Dr. Shenker was appointed as a lecturer of soil chemistry and soil fertility at the Department of Soil and Water Sciences, Faculty of Agricultural, Food and Environmental Quality Sciences, the Hebrew University of Jerusalem.

Dr. Shenker and his groups research focuses on agronomic and environmental aspects of chemical processes and transformations occuring in the soil environment. Topics of research include: (i) Hydro-

geochemistry of phosphorus in re-wetted peat soils; (ii) Evaluation of nutrient availability for plants; (iii) Phosphorus reactions and availability in soils amended with sewage sludge; and (iv) Heavy metals in soils and their uptake by plants.