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Effects of Iron on Crops and Availability of Iron in Soil: A Review

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ABSTRACT: Iron (Fe) is the fourth most common element in soil. Among themicronutrients, Fe was the first micronutrient identified as essential for plant growth. In the metabolic processes of plants, Fe is necessary for a number of respiratory enzymes and metabolic activities related to photosynthesis. Legumes use iron extensively for nodule formation to fix atmospheric nitrogen. Green plant tissue contains between 50 and 100 mg of iron per kg of dry weight. Fe is therefore one of the most prominent micronutrients in plants. Although iron is the fourth most abundant element in soil, plant deficiency is the most common. In early, emerging leaves, iron-deficiency chlorosis (IDC) develops as interveinal to complete chlorosis; in the worst case, this can lead to crop damage and yield losses. There is a yield loss of between 16 and 32% due to Fe deficiency. An iron content of more than 7.5 mg kg^{-1} in soil samples is considered sufficient. Diethylene Triamine Penta Acetate (DTPA) extractable zinc, iron, copper, and manganese are presently deficient in 48.1%, 11.2%, 7%, and 5.1% of Indiansoils, respectively. In India, the states of Karnataka (35%), H.P. (27%), Maharashtra (24%), Haryana (20%), Tamil Nadu (17%), and Punjab (14%) are the most deficient in Fe. The addition of iron enriched manures improves the availability of nutrients due to stable organo-metallic/iron complexes formed with organic matter during the enrichment process, which prevents the nutrients fromfixing and makes them available to the plant root system during crop growth.

Key words: Iron (Fe), Iron deficiency chlorosis (IDC), pH, Available Fe, Toral Fe, Fe uptake.

INTRODUCTION

The most prevalent element in the crust of the planet is iron, and most plant species experience a scarcity of it on a regular basis. One form of this metal that permeates cells is iron chelate. Chelates are responsible for transporting irons, and are biologically synthesized in plants.

One of the most deficient micro-nutrients in the world is iron. The main causes of iron deficiency are calcareous soils, high pH levels in the soil and water, high HCO_3 concentrations, and irregular plant nutrient availability in the soil, i.e., improper and unscheduled applications of fertilizers. Shukla *et al.* (2016) reported that 12.6% of the Indian soils suffer from Fe deficiency. One of the major problems farmers have while cultivating plants on calcareous soils is an iron deficit. More than one-third of the soil in India is calcareous, with the majority of it being found in the low-rainfall regions of the western (Gujarat, Maharashtra, Rajasthan, and Karnataka) and central (M.P., U.P.) regions.

While iron being abundant in the soil, there are factors that affect the iron availability in soil. In soil solution, the iron exists in different forms *viz.*, Fe (II) (ferreous, Fe^{2+}) and Fe (III) (ferric, Fe^{3+}). In the presence of oxygen, Fe^{2+} quickly convert into Fe^{3+}. Further, it is commonly occurring in forms that plants cannot absorb, such as iron oxide, iron hydroxide, or iron phosphate.

Iron concentration in ranged from 7,000 to 500,000 mg kg^{-1} of iron. Most of it is stored as insoluble Fe^{3+}. It is simple to hydrolyze ferric ions into $Fe(OH)_2$, $Fe(OH)_3$, and $Fe(OH)_4$, with the Fe^{3+} ions constituting the total soluble inorganic iron.

Ferric ion concentration decreases from 10^{-8} to 10^{-20} M as soil pH increases from 4 to 8. The most prevalent Fe form in soils is hematite or ferric oxide (Fe_2O_3). It gives soil a reddish tint and is quite insoluble. Usually, the hydrated component is in oxide form.

Soils with Fe concentrations below 3.5 mg kg^{-1} are classified as Fe-deficient. The critical limits of Fe for calcareous and non-calcareous soils are 6.7 ppm and 3.7 ppm, respectively. Although total Fe is high in calcareous soils, it is present in chemical forms that are unavailable to plant roots. The main soil characteristics that contribute to IDC include an abundance of lime (15–40 % $CaCO_3$), a high pH (7.5-9.0), excessive irrigation, and an abundance of organic matter and P in the soil (Singh, 2004). In addition, low temperatures and soilmoisture are linked to the IDC. In calcareous soils, it has been calculated that theloss in pod yield caused by Fe shortage is to the extent of 13–15% (Tandon, 1998).

The mineral Fe is involved in numerous metabolic activities, such as photosynthesis and cell respiration. Regardless of Fe nutritional status, over 80% of the Fe in green leaves is concentrated in the chloroplasts. Fe has the potential to form chelates and can undergo reversible oxidation-reduction reactions, two important features underlying its range of physiological effects (Mengel *et al.*, 2001). Fe is not incorporated into the actual chlorophyll structure, although it plays a catalytic role in numerous reactions leading to chlorophyll biosynthesis. Fe regulates the common precursor of heme and chlorophyll synthesis.

A. Role of Iron in Plant Growth and Metabolism

In plants, iron is an essential element of respiration, photosynthesis, oxidation, and reduction processes, as well as enzyme activity. For instance, iron is essential for the enzymes used by bacteria that fix nitrogen. The requirement for iron and subsequent intake are comparably low as compared to other essential elements.

Iron is an essential micronutrient for nearly all living organisms since it is vital for metabolic processes like photosynthesis, DNA synthesis, and respiration. The prosthetic groups of numerous enzymes contain iron, which is also a metabolic process activator.

The low availability of iron (Fe) in soils is one of the main issues affecting the yield and quality of agricultural commodities globally, especially in alkaline and calcareous soils. This poor availability is directly related to physical, chemical, and biological activities taking place inside the rhizosphere because of interactions between soil, microorganisms, and plants.

Fe fertilisers can be used to prevent iron deficiency in plants by applying them to the soil or leaves. Recently, Fe fertilisation has been used to enhance Fe allocation, overcome insufficient Fe uptake, and produce crops that are enriched in Fe (i.e., biofortification).

Iron has a vital function in a number of physiological and metabolic processes in plants. It is a component of various essential enzymes, including cytochromes of the electron transport chain, and is therefore necessary for a number of biological activities. Iron is essential for maintaining the structure and functionality of chloroplasts and is a component of plant chlorophyll synthesis. The long-distance and intracellular trafficking of this compound necessitates the use of certain proteins and low-molecular-mass chelates because it is insoluble and toxic in the presence of oxygen due to its redox properties.

Iron chlorosis is primarily brought on by an imbalance between the demand for iron by plants and the solubility of iron in soil. The appearance of root hairs, the transformation of rhizodermal cells into transfer cells, the yellowing of the leaves, the ultrastructural disorganisation of the chloroplasts, the increased synthesis of organic acids and phenolics, and the activation of root systems that increase their capacity to absorb iron are among these symptoms.

Fe deficiency has an impact on the entire plant because there are synergistic and/or antagonistic relationships between the elements in the plant-soil system. There must be a sufficient supply of Fe on hand in order to ensure maximum plant performance and growth. However, the speciation, or chemical form, of the metal, which can affect gene regulation, metabolic activity, and the distribution of elements within plants and cells, is also important.

One of the initial stages of this process is a transient increase in the concentration of the iron storage protein ferritin in the plastids, which reverses after a few days of iron replenishment. However, excessive iron can affect plants, causing oxidative stress and necrotic spots on the leaves.

The early induction of ferritin synthesis is another example of the plant's reaction to iron toxicity. Auxin, abscisic acid, and ethylene are examples of plant hormones that are important participants in the transduction pathways that allow plants to adapt to iron deficiency and excessive stressors.

In order to ensure Fe uptake, plants have evolved two distinct physiological strategies, one based on Fe (III) reduction (strategy I), and the other on Fe (III) chelation (Strategy II).

All plants, with the exception of grasses, rely on the reduction-based Fe acquisition Strategy I, which involves P-type ATPases acidifying the rhizosphere and root apoplast.

Gramineous monocots that like grass have evolved a second mechanism known as Strategy II. Moreover, this necessitates the production of phytosiderophores, which are metal ligands from the mugineic acid family. Both monocots and dicots produce nicotianamine (NA), but only grasses produce phytosiderophores.

B. Effects of Iron on Plant Growth

Due to the limited solubility of the oxidized ferric form in aerobic settings, iron ranks third among nutrients in restricting plant growth and metabolism (Zuo and Zhang 2011; Samaranayake *et al.*, 2012). Poor yields and decreased nutritional quality are common nutritional disorders in many crop plants caused by iron deficiency. Iron is a component of chlorophyll production in plants and is necessary for the preservation of chloroplast structure and function.

Iron is the fourth most common element in the lithosphere. It is typically found in large amounts in soils, although its bioavailability is only moderate in aerobic and neutral pH settings. Iron is mostly found in the Fe^{3+} state in aerobic soils, mostly as a component of oxyhydroxide polymers with very little solubility. Most of the time, this form is insufficient to meet the needs of the plant. Interveinal chlorosis of young leaves and stunted root growth are the obvious symptoms of insufficient iron nutrition in higher plants.

Due to the low redox potential of wet soils, the concentration of soluble iron may increase by several orders of magnitude. In certain circumstances, iron absorption may be high. However, it has the potential to be hazardous and can promote the formation of reactive oxygen-based radicals, which can cause lipid peroxidation damage to vital biological components, including membranes. Plants exposed to above-optimal iron levels will exhibit symptoms such as bronzing (coalesced tissue necrosis), acidity, and/or blackening of the roots (Laan *et al.*, 1991).

Under various physiological situations, such as a high soil pH in alkaline soils, plants are ultimately unable to absorb iron because it is mostly present in the soil as Fe^{3+} chelate forms. As a result, plants growing in high-pH soils struggle to generate and stabilise chlorophyll, which causes leaf yellowing, poor growth, and decreased yield. However, plants have developed dynamic networks to absorb trace amounts of soluble iron. Non-graminaceous plants discharge protons, secrete phenolics, reduce Fe^{+3}, and uptake iron (Jeong and Connolly 2009 ; Cesco *et al.*, 2010).

Once iron has been solubilized, a membrane-bound Fe^{3+} reductase oxidase reduces Fe^{3+} to $Fe2^{+}$ (Jeong and Connolly 2009). An iron regulating transporter (IRT1) that regulates iron then transports Fe into the root. According to Ishimaru *et al.* (2011), plants use a Fe^{3+} chelation pathway to release phytosiderophores from the mugineic acid (MA) family. Through TOM1 transporters, MAs are secreted into the rhizosphere, where they chelate $Fe^{3+.}$ The yellow stripe family transporters (OsYSL15) in rice carry the resultant Fe-MA complex (Nozoye *et al.*, 2011). Additionally, rice plants can absorb the iron transporter, both tolerant and susceptible cultivars differed in terms of their total chlorophyll, total proline, total phenol, total protein, and total carbohydrate content. The oxidative enzymes differed between the genotypes of the tolerant and non-tolerant crops (Ishimaru *et al.*, 2011).

Iron is typically found in photosynthetic cells, where it is required for the electron transport system, the synthesis of Fe-S clusters, and the biosynthesis of cytochromes and other heme molecules, such as chlorophyll. Two or three iron atoms are present in molecules directly related to photosystem II (PS-II), 12 atoms are found in photosystem I (PS-I), five are found in the cytochrome complex, and two are found in the ferredoxin molecule in the photosynthetic apparatus. These ranges demonstrate that iron directly influences plant photosynthetic activity and, consequently, productivity (Briat *et al.*, 2007).

C. Iron Uptake Strategies in Plants

Reduction and chelation are two plant mechanisms for absorbing iron. According to Grotz and Guerinot (2006), plants have developed two primary strategies (Strategy I and II) for absorbing iron from the rhizosphere. The majority of non-grass plants use the strategy I (reduction approach), which is well understood in the model plant Arabidopsis thaliana (Fig. 1). The rhizosphere's H+-ATPase AHA2 releases protons when the Fe level is low. The released protons lower the pH of the soil and increase the solubility of Fe^{3+}. After entering the apoplast, soluble Fe^{3+} is chelated there by phenolics from the coumarin family that are exported via the ABCG37 transporter (Mladnka *et al.*, 2010). Plasma membrane ferric chelate reductase FRO2 (Ferric Reduction Oxidase 2) converts the chelated form of Fe^{3+} to Fe^{2+}.

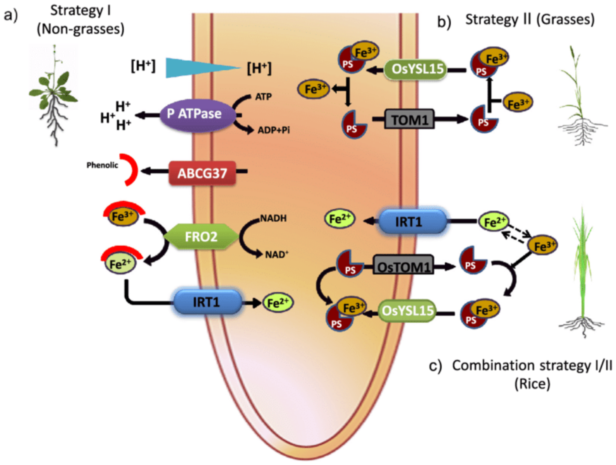

Fig. 1. Iron uptake strategies in plants (Snigdha Rai *et al.*, 2021).

This transformed Fe^{2+} is delivered into the root epidermal cells via high-affinity iron-regulated transporter 1 (IRT1). According to Morrissey and Guerinot (2009), strategy II, which is restricted to grasses and is comparable to many bacteria and fungi, is a chelation-based strategy. This technique might have developed as a response to alkaline soils, where it is challenging to achieve rhizosphere acidification (Fig. 1b). It is based on the manufacture and secretion of phytosiderophores (PS; a group of chemicals made of mugineic acids), which chelate Fe^{3+} and form PS-Fe (III) complex, in the rhizosphere. The complex uses transporters from the YS/YSL family to enter the root (Morrissey and Guerinot, 2009). The amount of PS produced and resilience to soils with low levels of iron are strongly correlated, and the chelation technique is less sensitive to pH than the reduction strategy. It's interesting to note that graminaceous species like rice can combine techniques I and II to get the best Fe levels (combination strategy, Fig. 1c) (Krohling *et al.*, 2016).

Fe binds with different chelators after symplastic entrance, preventing it from contributing to the production of reactive oxygen species (Morrissey and Guerinot 2009). Citrate and other organic acids attach to Fe^{3+}, while nicotinamide (NA) creates stable complexes with both Fe^{2+} and Fe^{3+}. Plant cells store excess Fe in iron complexes called phytoferritin, which lowers the availability of free Fe within cells (Briat *et al.*, 2010; Morrissey and Guerinot, 2009). Niacinamide (NA) forms stable complexes with both Fe^{2+} and Fe^{3+}.

Organic acids, such as citrate, bind with Fe^{3+}. Plant cells store excess Fe in iron complexes called phytoferritin, which lowers the availability of free Fe within cells (Briat *et al.*, 2010; Morrissey and Guerinot 2009). For iron-dependent enzymes to function, Fe must be transported across short or long distances to the sink tissues by Fe-chelator complexes (Krohling *et al.*, 2016). The vacuole is required for the transfer of Fe in the early stages of plant growth even though the majority of the Fe is found in chloroplasts (Morrissey and Guerinot 2009). Iron transporters unique to each kind of organelle have been found, as well as a significant amount of Fe utilised in plastids and mitochondria (Kim and Guerinot 2007). Seeds and leaves are two essential iron sinks. Iron returns to the symplast in leaves where it is primarily converted to Fe^{2+} by the action of FRO proteins, which is then used for photosynthesis. However, an OPT3 protein from the oligopeptide transporter family mediates this mechanism in Arabidopsis (Kim and Guerinot 2007). Iron is sometimes thought to have its final resting place in the seed, where it is necessary for germination.

D. Status of Available Iron in the Soil

In most Indian soils, the total amount of micronutrients (zinc, iron, manganese, and copper) is sufficient, but many soils insufficient in the concentrations of micronutrients required for crop growth. Iron is an essential micronutrient that limits plant growth. Its availability to plants is severely hampered by the frequent changes in its form (Fe^{2+} - Fe^{3+}), especially in rice-wheat cropping sequences. There are several different types/forms of iron in soil, such as the pool of immediately available iron, the available pool, iron that becomes available through decomposition, and prospective medium to long-term sources of available iron. A number of factors, including texture, $CaCO_3$ content, organic matter, and the quantity of Fe in solid form that is in equilibrium with that in the soil solution, affect the availability of Fe in soil. Higher plants can acquire a very small portion of the total Fe in the soil.

In Indian soils, the range of available (DTPA extractable) iron is very wide, ranging from 0.01 to 1461.70 mg kg^{-1} (Gupta, 2005). The main causes of the difference include agro-ecological conditions, extractant type, soil type, and soil characteristics. The iron deficiency was found to be highest in soils of Karnataka and Himachal Pradesh. Iron is readily found in significant amounts in the soils of many Indian states.

Sharma *et al.* (2006) examined the distribution of DTPA-extractable iron in Indian vertisols. He indicated that the weighted mean was 10.36 mg kg^{-1} and that all soils were sufficient (> 4.5 mg kg^{-1}) in DTPA-Fe. Like the other DTPA-micronutrients, the DTPA-Fe showed no constant trend over time and differed widely amongst profiles. Soils of the piedmont soils show a higher DTPA-Fe average value (11.08 mg kg^{-1}) than flood plain soils (9.52 mg kg^{-1}). DTPA-Fe levels in moderately well-drained soils were significantly higher (10.70 mg kg^{-1}) than in imperfectly to poorly drained soils (5.71 to 9.60 mg kg^{-1}). The high capacity of Fe to hydrolyze and the fact that Fe is sorbed to an extent that is approximately twice the cation exchange capacity in montmorillonite systems may be the reasons for the high DTPA-Fe levels in these soils (Roy and Chatterjee 1998).

While studying the soils of Sikkim, Lahiri and Chakravarti (1989) observed that high altitude soils have higher levels of available iron and organic matter than low altitude soils because of their acidic pH. They revealed uneven distribution in the soil solum and noticed an inverse relationship between Fe availability and soil pH. According to Tripathi and Singh, (1992), substantial correlation was found between DTPA-Fe and organic carbon (r=0.55**), the amount of organic carbon in soils has a significant effect on the amount of available Fe in certain soils.

According to Chander *et al.* (2014), the range of DTPA-extractable Fe in Himachal Pradesh's sub-humid zone ranged from 10.6 to 70.8 mg kg^{-1} and from 22.8 to 96.6 mg kg^{-1} in the wet-temperate zone; the available Fe content varies significantly between various locations. Simultaneously at different sites, it was found that Indian soils generally had sufficient and higher available Fe concentrations. With increasing soil depth, the available Fe content has also shown a trend toward diminishing.

According to Sidhu and Sharma (2010), the Trans-Gangetic Plains had DTPA-extractable Fe concentrations ranging from 1.05 to 97.9 mg kg^{-1}. The DTPA-extractable Fe in the Upper Gangetic Plains ranged from 3.48 to 90.2 mg kg^{-1}. The DTPA-extractable Fe ranged in the Middle Gangetic Plains from 9.22 to 256.7 mg kg^{-1}. The DTPA-extractable Fe in the Lower Gangetic Plains ranged from 0.04 to 3.46.

According to Singh *et al.* (2014), a micronutrient study with a range of 0.20 to 9.70 mg kg^{-1} and a mean value of 2.90 mg kg^{-1}, the DTPA-Fe test results showed that 54% of samples were deficient, 24% were medium, and 22% were sufficient.

The soil samples with a 7.92 percent Fe deficiency were reported by Regar and Yadav (2019) Semi variogram models for micronutrients had moderate nugget/sill ratios, with Fe having a value of 0.49.

Saha *et al.* (2019) conducted a study on micronutrient availability in Soil-Plant System in Response to Long-Term Integrated Nutrient Management under Rice-Wheat Cropping System and reported that the soil DTPA-extractable Fe status ranged from 44.23 to 71.48 mg kg^{-1}. Since farmyard manure (FYM), paddy straw (PS) and green manure (GM) were combined with mineral NPK fertilizers, the buildup of DTPA extractable Fe in surface soil (0–20 cm) ranged from 58.3 to 71.5 mg kg^{-1} in those treatments, as compared to 44.2 mg kg^{-1} in the unfertilized control.

Singh *et al.* (2022) reported that the highest value was found to be in the surface layer of the Daulatpur profile, which retained more than 1 mg kg^{-1} DTPA-Fe throughout the depth, but the soil of Narahi profile could not maintain it beyond the soil depth of 90 cm. The available DTPA-Fe in the soil ranged from 0.28 to 3.80 mg kg^{-1}. Arunachalam *et al.* (2013) found that applying $FeSO_4$ to the soil increased the iron availability in the alfisol to 0.94 ppm (4.45 percent).

According to Shukla *et al.* (2021), the content of available Fe, Cu, and Mn in Indian soil ranged from 0.01-964, 0.01-99.2, and 0.01- 483 mg kg^{-1}, respectively.

E. Total Iron Content in Soil

According to other factors affecting plant availability, Bhattacharya *et al.* (2020) studied cationic micronutrient pools (Zn, Cu, Fe, and Mn) in 20 West Bengal soil series, 10 series from each of the Alfisols and Inceptisols. The order of the zinc fractions in the selected Alfisols and Inceptisols was Am FeOx > Cry FeOx > MnOx > OB > SE fractions. The percent predominance of the iron fractions followed the order: Cry FeOx > Am FeOx > MnOx > OB > SE fractions. It was discovered that the soil's clay content and the fractions of the corresponding elements that are organically bound are mostly responsible for the most phyto-available fractions, such as soluble and exchangeable Fe and Zn.

Indian soils have a high total iron concentration, ranging from 0.36 to 174 mg kg^{-1}. The total iron concentration of acid soils in India was investigated by Behera and Shukla (2015). The range of the mean values of the total Fe content in 400 surface soil samples (0-15 cm) from Orissa (Hariharapur series), Jharkhand (Debatoli series), Himachal Pradesh (Rajpora series), and Kerala (Neeleswaram series) were from 16,635 to 56,222 mg kg^{-1}. The average content of DTPA-extractable Fe in soils for the Hariharapur, Debatoli, Rajpora, and Neeleswaram series was 0.10%, 0.15%, 0.44%, and 0.11% of total Fe content, respectively. About 0.17% to 0.53%, 0.31% to 1.17%, 0.18% to 0.75%, and 0.31% to 0.58% of the mean total Fe content in different soil series were extracted using Mehlich 1, Mehlich 3, HCl (0.1 mol L^{-1}), and DTPA.

Singh *et al.*, (2009) indicated that the Gazipur district of Uttar Pradesh had a total Fe content in soil of 4000-273000 mg kg^{-1}. Singh *et al.* (2006) stated that certain vertisols soil of Rajasthan have a mean range of 24668 to 28046 mg kg^{-1} for total Fe.

Katyal and Sharma (1991) reported a wide range of total Fe concentrations in 8 soil orders representing 57 benchmark soils in India, with total Fe values ranging from 18,200 to 63,200 mg kg^{-1}. Fe of 1,800 to 3,400 mg kg^{-1} was found in highly to moderately acidic soils in Gazipur district of Bangladesh (Begum *et al.*, 2009).

Selvaraj and Basavaraj (2015) investigated the various iron fractions in the soils used for cultivating paddy in a few villages in North Karnataka, India. With a mean value of 450.21 ppm, the total Fe fraction ranged from 228.84 ppm in the Basapatna sample to 719.30 ppm in the Mallapura sample.

F. Chemistry of Fe in the Soil

Ferric oxides, hydroxides, and silicate minerals are forms of iron that are not readily available to plants as a source of iron. Iron content varied from 0.2 per cent to 55 per cent (20,000 to 550,000 mg kg^{-1}) depending on the soil type and depth, with the highest concentration occurring at 2 to 15 cm (Audebert and Sahrawat 2000). The total Fe concentration in Indian soil ranges from 0.4 to 27.3 per cent (40,000 to 273,000 mg kg^{-1}), but the amount available to plants varies widely, from 0.36 to 174 mg, depending on the plant, soil, and environmental elements factors (Singh *et al.*, 2009). In the soil, Fe can exist as divalent (Fe^{2+}) or trivalent (Fe^{3+}) ions. Due to the creation of soluble oxides or hydroxides, Fe^{3+} is not easily available to rice plants or microbes (Dotaniya *et al.*, 2013). According to estimates, the soil on Earth contains about one-third that is Fe deficient. Factors such as soil aeration (aerobic condition/dry soil), organic matter content, pH, soil redox potential, microbial populations, etc., influence the solubility and availability of Fe to plants (Becker and Asch 2005). Among these factors, soil pH is the single most dominant one that affects Fe availability, and it is reported that a one-unit increase in soil pH above neutral pH can cause a 95 per cent reduction in the availability of Fe (Rengel, 2015).

Due to conversion of Fe into the insoluble Fe-hydroxyl complex, saline, alkaline, sodic, and calcareous soils are naturally deficient in Fe, which restricts their ability to absorb and uptake it by roots. However, Fe is excessively freely available in acid sulphate soils with pH lower than 5, which cause iron transports to plants (2000 mg kg^{-1}) (Fageria *et al.*, 2002; Fageria *et al.*, 2008). Due to the excessive formation of bicarbonates and phosphates, which prevent Fe absorption, the amount and rate of organic matter in the soil also affect Fe availability (Koh *et al.*, 2007; Onaga *et al.*, 2013). Other nutritional elements like phosphorus and potassium become less available and are absorbed due to increase in Fe concentration in the rhizosphere (White and Brown 2010). However, the improvement in Fe availability and the effective uptake of Fe^{2+} across the plasma membrane of root epidermal cells is improved by soil acidity caused by root exudates.

Fe^{2+} oxidation and reduction are regulated by high root density and the presence of aerenchyma in the root zone (Vejchasarn *et al.*, 2016; Steffens and Rasmussen 2016). In addition to producing organic acids, soil microbial populations like *Pseudomonas*, *Bacillus megaterium*, *B. pumilus*, *Geobacter*, *Clostridium*, and *Bacillus* sp. also have an impact on the availability of iron by controlling the oxidation and reduction of iron in the root zone as well as the mobilization of iron oxides.

These facultative anaerobic chemo-organotrophic fungi have a variation of tolerance mechanisms, including the secretion of siderophores, Fe exclusion through the development of a Fe plaque permeability barrier, enzymatic detoxification, modification of root architecture, efflux pumps, etc., which restrict the uptake and mobilization of Fe (Nworie *et al.*, 2017). Fe^{3+} serves as an electron acceptor for facultative anaerobic microbes once oxygen is depleted under flooded soil conditions, and the subsequent reduction of Fe-oxides and hydroxides can accumulate a significant amount of Fe^{2+} in the soil solution.

G. Iron Deficiency in Soil

Geochemical composition (total micronutrient contents of the parent soil material), soil type (clay mineralogy, particle size distribution, soil horizon, soil age, and soil formation processes), intrinsic soil properties like pH, redox potential (Eh), soluble salt concertation (EC), quality and quantity of soil organic matter, calcium carbonate content, and inputs of trace elements supplied through the atmospheric (Fageria *et al.,* 2002; Alloway, 2008; Shukla and Tiwari 2016). In addition to these issues, the development of agriculture without adequate replenishment of micronutrients through fertilisation is blamed for the low levels of available micronutrients and their widespread deficiencies in Indian soils. Additionally, the soils' supply of available micronutrients has been rapidly depleted due to leaching, soil liming, sparing use of manures, and increased use of chemical fertilizers that are pure sources of micronutrients without micronutrient additions. Parent material and pedogenic processes have a complex role in determining the total soil micronutrient concentration. In terms of overall micronutrient content, Indian soils are largely sufficient. However, despite the generally high total contents, micronutrient deficits have been recorded regularly in various crops as a result of low levels of readily available micronutrients in soils (Shukla and Tiwari 2016).

One of the significant nutritional problems that affects aerobically grown rice on upland alkaline and calcareous soils and lowers production is iron (Fe) deficiency. Shukla *et al.* (2018) investigated the status of soil micronutrients. The status of the micronutrient deficiencies was evaluated in different soils between 2011 and 2017 based on the critical limits observed in various Indian states. Over 2.0 lakh soil samples were analyzed between 2011 and 2017, and it was found that, on average, 12.8% of soils had Fe deficiencies. While states like Uttar Pradesh, Telangana, Andhra Pradesh, Bihar, Goa, and Tamil Nadu had deficiencies in 10 to 20% of soils, states like Rajasthan (34.4%), Gujarat (25.9%), Haryana (21.7%), and Maharashtra (23.1%) had Fe deficiencies in more than 20% of soils.

According to Shukla *et al.* (2014), the amount of extractable Fe in the soils of the various states of the India ranges from 0.01 to 1461.70 g kg^{-1}. Although, the analysis results of 97,464 georeferenced soil samples showed that overall, Fe deficiency in India stayed close to 13%, its deficiency is rapidly increasing in some states, such as Gujarat (23.9%), Haryana (21.6%), Maharashtra (21.5%), Telangana (17.0%), and Andhra Pradesh (16.8%).

H. pH and Availability of Iron in Soil

Dissolution-precipitation equilibria regulate the solubility of minerals containing iron, and the extent of this solubility is influenced by the ionic strength and pH of the soil. Only at extremely acidic pH levels (pH 3) does iron exist as trivalent ions, and at neutral pH, the solubility of Fe^{3+} rapidly decreases. When the pH is between 7.5 and 8.5, Fe oxides have a minimum solubility of near to 10^{-10} M (Lindsay and Schwab 1982). Due to the lack of Fe, bacteria and numerous graminaceous plants have developed various methods to solubilize Fe in soil by increasing soil acidity and producing chelating compounds. The latter are released as rhizo deposits, which are a number of different of complex compounds and simple organic acids with low molecular weight.

The availability of soluble Fe is increased at lower pHs in soil solutions (Robin *et al.,* 2008). In this way, the metabolism of bacteria allows them to contribute to the acidity of the soil. In fact, the bacteria involved in the oxidation of ferrous sulphide, such as pyrite, and ammonium, leading to the formation of sulfuric and nitric acids, are also capable of acidifying the surrounding soil. This is because their respiration raises the pCO_2, increasing the concentration of carbonic acid (Yu and Bishop 2001). Plants respond with their roots to this rhizosphere acidification phenomenon. Furthermore, in addition to the metabolism of roots, the release of carboxylates from these tissues in the rhizosphere, when the exudation is combined with proton efflux can significantly lower the pH of this particular volume of soil. In fact, rhizosphere pH has been reported to be up to 1-2 pH units below or above bulk soil pH. It has been proven that the roots of white lupin have a relationship between the excretion of organic acid and proton extrusion (Tomasi *et al.,* 2009). It is also known that soil humic substances stimulates the plasma membrane H^+ - ATPase activity of roots, which is primarily involved in proton extrusion combined with the release of citrate (Pinton *et al.,* 1997). When organic acids (citric, malic, and oxalic) are present in soils with limited Fe availability, their presence also causes pH to decline when their exudation is combined with proton efflux; the concentration in the rizo-deposition varies among plant species and is dependent on soil pH (Hinsinger *et al.,* 2003). The bacterial metabolism of small organic acids also contributes to pH decline. This is true of oxalic acid, which fungi and lichens produce in considerable proportions (Jones and Wilson, 1985). Proton-promoted dissolution reactions of primary minerals containing iron are widely thought to be the rate determining step for weathering processes under acidic conditions, but are neglectable in soil environments and sediments due to the predominance of neutral conditions.

Fe availability to plants depends on soil characteristics and plant species. Soil pH and soil organic carbon (SOC) content are significant components of a variety of soil characteristics. The solubility of Fe in soil decreases by a fold of 1000 with each unit increase in soil pH between 4 and 9 (Lindsay, 1979).

CONCLUSIONS

Iron is one of the most essential for plant growth. This element is abundantly present in the soil. It required for enzyme activities in plant *viz.,* cytochromes, peroxidase, and catalase, phytoferritin and ferredoxin. Iron deficiency is commonly occurred in calcareous soils. It is the one of the major problems in groundnut crop, because groundnut is highly susceptible to iron deficiency which affects economic yield.

In recent years, the productivity of crops getting reduced due to inadequate soil fertility along with imbalanced fertilizer management. To overcome these problem, good management practices and integrated fertilizer management with right kind of nutrients at right time by adapting right method of application has significantly increased availability of iron thereby increasing crop yield.

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