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Review Article

Dynamics of Iron in Rhizosphere

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A B S T R A C T

Iron (Fe) in the soil is present mostly in the form of insoluble Fe (III) oxides and hydroxides (*e.g.* haematite, goethite, ferrihydrite). The total iron in soil is much higher than most crops require. Nevertheless, the concentration of free Fe (III) in most agricultural soils is far below that required for optimal plant growth, which is between 10^{-9} and 10^{-4} M Fe (III) in the soil solution (Lindsay and Schwab, 1982). Generally, chelation of Fe (III) is the most successful mechanism by which plants roots can acquire Fe. Production of chelating compounds by microorganisms increases Fe solubility in the rhizosphere and hence increases plant Fe acquisition. Bacterial and fungal siderophores and other chelating metabolites are assumed to serve as major sources of plant-available Fe in the rhizosphere. Moreover, from the earlier literature it is well known that microbial chelates produced in the rhizosphere mobilize Fe (III) from insoluble Fe sources. In cultivated soil iron is oxidized to form ferric oxide and oxy hydroxides results in low availability of iron for living organisms. To face the demand of Fe (III) in the rhizosphere leads to strong competition for this nutrient among living organisms, plants and microorganisms have developed active strategies of iron uptake. Efficient siderophores of microbial populations from the rhizosphere do not compete with the plant harboring them, and even seems to contribute to the plant iron nutrition. The complex interaction between soil chemical properties, plants, and microbes affects the iron dynamics in the rhizosphere, which in turn impact the plant health and nutrition.

Introduction

Iron is essential for major metabolic processes in most organisms such as reduction of ribonucleotides and molecular nitrogen and the energy-yielding electron transfer reactions of respiration and photosynthesis (Guerinot and Ying, 1994). In the rhizosphere, this concentration is even lower due to the iron uptake by both roots and microbes, and the concentrations of Fe(III) species are generally far below those required for optimal growth of microbes and plants.

The combined low concentration of Fe (III) in soil solution (low supply) together with the requirements of aerobic organisms (plants and microorganisms) creates high demand lead to a considerable level of competition for Fe (III) in the rhizosphere. To acquire this essential element in spite of its low availability, plants and microbes have evolved active strategies of uptake which are based on a range of chemical processes (Loper and Buyer, 1991).

Iron dynamics in the rhizosphere are under the control of the combined effects of soil properties, uptake and activities of plants and microorganisms and interactions between them. In this review, the status of iron in soils and rhizospheres will be examined.

Iron status in soils

Iron is the 4th most abundant element in the earth's crust after O, Si and Al (Ma, 2005). And it ranges in soil from 1- 5 % total Fe in plough layer and in plants more than 50 ppm. It occurs in two oxidation states as Ferric (III), Ferrous (II). Availability of Fe is more in acidic pH predominantly included in the crystal lattice of a range of primary and secondary ferromagnesium silicates and in high pH Fe (III) precipitate as hydroxides, oxy hydroxides and oxides so concentration of Fe^{3+} in the soil solution is extremely low.

Chemical reaction of iron (Inglett *et al.,* 2006)

Aerobic condition

Oxidation - Fe^{2+} to Fe^{3+}.
Fe $(OH)_3 \leftrightarrows Fe^3 + 3OH$.
$FeOOH + 3H^+ \leftrightarrows Fe^3 + 2H_2O$
Soluble - Less soluble

Anaerobic condition

Reduction- Fe^{3+} to Fe^{2+}.
Fe $(OH)_3 \leftrightarrows Fe^{2+} + H_2O$
More soluble.

Role of iron

Iron plays critical role in metabolic processes such as DNA synthesis, respiration and photosynthesis. It is necessary for the synthesis and maintenance of Chlorophyll. It is a structural component of the molecules like Cytochromes, Peroxidase, Haematins and Catalase etc. It activates a number of enzymes like Pxygenase, Dioxygenases, Ferredoxin hydrogenase, Glutamate synthase (Rout and Sahoo, 2015).

Iron deficiency symptoms

Symptoms of iron deficiency appear on the youngest, newest leaves. The area between the leaf veins becomes pale yellow or white (Eskandar, 2011).

Under severe deficiency condition tissues show necrotic symptom Necrosis spreads from tip and margin into interveinal zones. In barley, maize and jowar leaves, reddish spots may be formed.

Rhizosphere soil

Hiltner (1904) proposed the name rhizosphere for designing the volume of soil surrounding roots in which microorganisms are influenced by those roots. Since then, further studies have shown that living roots modify the biological, physical, and chemical properties of the surrounding soil. The Rhizoplane is the medial zone directly adjacent to the root including the root epidermis and mucilage**.**

Iron status in soils and rhizospheres (Robin *et al.,* 2008)

Iron in primary and secondary minerals

Ex: Biotite, Hornblende, Olivine, Augite.

Soluble iron

Ex: Hydrous ferric oxide, Goethite, Hematite

Iron bound to organic matter

More than 95 % of Fe in soil solution - Chelated (organic ligands)

Microbial siderophores

Siderophores (Greek: "iron carrier") are small, high affinity iron chelating compounds secreted by microorganisms such as bacteria, fungi. The production of siderophores is an efficient strategy of bacteria, fungi and graminaceous plants to overcome a lack of iron. The stability of the siderophore iron complex is an important factor for the efficiency of the siderophores (Wittenwiler, 2007).

Example

Short-Term Effects of Rhizosphere Microorganisms on Fe Uptake from Microbial Siderophores by Maize and Oat

When FePSB was supplied to maize plants under varied microbial population density in the nutrient solution, dramatic differences in "Fe uptake rate i.e concentrations in roots and shoot were observed. These differences did not correspond with Fe translocation rate *i.e* concentration in shoots. Under Fe deficiency, the 55Fe uptake rates from FePSB increased with increased microbial population density, but the translocation rate remained at a similarly low level as in the Fe sufficient plants.

The increase in Fe concentration was more distinct by inoculation with *P. putida*, which is the producer of PSB and utilizes it via a specific membrane-bound receptor. When ferrated phytosiderophores (FeHMA) were used as the Fe source, the uptake and translocation rates of "Fe were higher than those with FeEDDHA or FePSB. Similar results were obtained for oat plants. The uptake and translocation rates of "Fe from FeHMA were higher than the bacterial siderophore FeFOB. The uptake and translocation rates of "Fe from FeHMA were higher than the bacterial siderophore FeFOB.

A low rate of translocation associated with high root accumulation is a strong indication for involvement of rhizosphere microorganisms.

Population of ferric iron-reducing bacteria the rhizoplane of a wetland rice during the growth cycle in a micro plot experiment. Iron-reducing bacteria greatly increase in number at the beginning of the reproductive growth phase of rice. In the case of iron-reducing bacteria, this increase can be ascribed to an enhanced exudation of carbohydrates and other metabolites during heading of rice panicles, finally leading to severe iron toxicity ((Prade, 19871).

Plant root exudates

Photosynthates are released from plant roots to soil through a process called rhizodeposition. Ex: Lysates, mucilage, dead cell material and ethylene. Increasing root exudates in soil enhances the soil fertility level as well as microbial biomass. These soil microbes play vital role in nutrient transformation reactions in soil and nutrient uptake by crop plants (Dotaniya *et al.,* 2013).

This increase in Fe content was about two times higher in the Fe sufficient (+Fe pretreated) plants compared with the Fe deficient (-Fe pretreated) plants. The calculated uptake rate for Fe during the 4 d treatment was about 2.5 times higher in the Fe deficient seedlings (Awad *et al.,* 1994) this enhancement in Fe solubility is mainly due to phytosiderophores released by the roots of wheat seedlings.

It has been shown that in chlorotic graminaceous plants the main component of the low-molecular-weight root exudates (more than 80 %) are phytosiderophores which has been characterized as non-proteinogenous amino acids.

Phytosiderophores

Organic substance produced by the plants under Fe deficient condition, which can form organic complexes with Fe^{3+} and increases the movement of Fe in soils (Mori and Nishizawa, 1987).

Phytosiderophors are secreted from plant root, and it is a lifesaving mechanism in plants. It enhances the plant nutrient uptake and improves the soil health. Iron availability is low in most aerobic soil, and microorganisms and plants release low molecular-weight compounds (chelators) which increase Fe availability.

It spe-cially enhances the uptake of Fe and Zn in lower concentration (Dotaniya *et al.,* 2013). In the rhizosphere the concentration of phytosiderophores may be in the range of 1 mM and even higher, suggesting that they also play an important role in Fe transport to the root surface.

Characteristics

PS are produced 3hr after onset of the light period

Highly affinity for Fe^{3+} and removes from minerals

Highly soluble Fe chelate

Regulates the mechanism for the biosynthesis under Fe deficient condition

Usually, the amounts of ferrous iron in the soil solution of flooded soils are significantly higher in planted than in unplanted soil (Fig. 1). This result shows that, despite the aeration mechanism of the roots, iron-reduction processes in the bulk soil are stimulated by the physiological activity and by the growth of rice roots (Jacq *et al.,* 2000).

Fe movement in the growth medium is also influenced by the chelating ligand species

Chelating ligands have been used in agriculture as an additive in micronutrient fertilizers in order to increase Fe bioavailability (Alvarez-Fernandez *et al.,* 2005). Ferric ions and their complexes have low solubility in aquatic systems, but they are extensively buffered by chelation (Morel and Hering, 1993), which increases their dissolved concentration. The dissolved concentration of Fe determines its rate of uptake by organisms.

The growth of radish sprouts was correlated with the Fe concentration in the plant tissues. The heights of the radish sprouts increased with higher tissue Fe concentrations (Fig. 2). The Fe concentration in the tissues of the radish sprouts was dependent on the chelating ligands, since the Fe was not readily bioavailable under experimental conditions (at pH 10) before the addition of ligands. Compared to the control, the Fe concentration in the sprouts increased with the addition of chelating ligands. The Fe uptake in radish sprouts was increased by 79 % with the addition of HIDS to the growth medium (Hasegawa *et al.,* 2011). Synthetic Fe (III)-chelates, such as EDTA and EDDS, are the most common and effective ligands used to increase Fe bioavailability. HIDS is a new chelating ligand with high biodegradability and a high stability constant with Fe^{3+} (Hasegawa, 2011).

Iron solubilization in the rhizosphere

Acidification through proton extrusion and organic acid secretion (and possibly respiration)

Chelation through secretion of complexing molecules with variable affinity for iron (phytosiderophores, siderophores, phenolics, and carboxylic acids), and reduction through

secretion of compounds characterized by reducing properties or through the expression of a membrane-bound reductase activity (Darrah, 1993; Hinsinger et al., 2003; Siebner-Freibach et al., 2003).

Fig.1 Fe (I1) - concentrations (ppm) in the rhizospheric soil solution of differently fertilized wetland rice (IR-8 cultivar) in comparison with an unplanted soil during a field experiment in Senegal
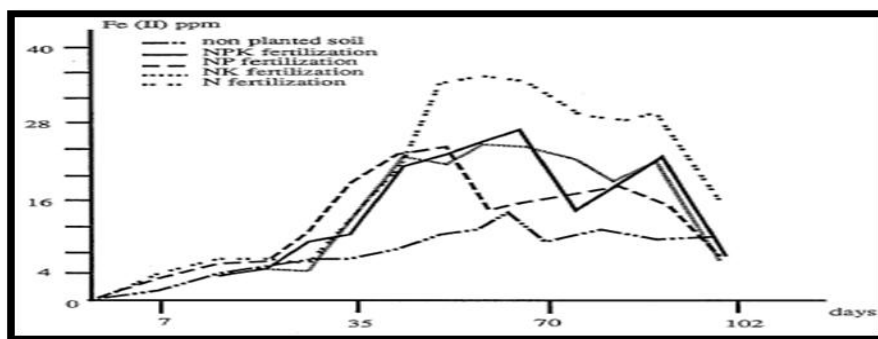

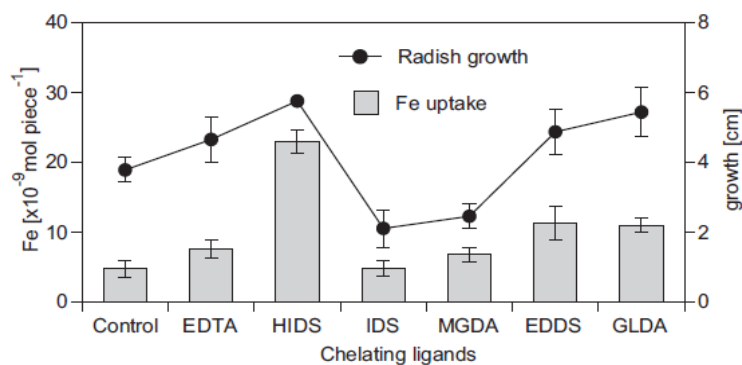**Fig.2** Iron uptake and growth of radish sprouts in medium with Fe-complexing chelators

Fig.3 Schematic representations of mechanisms affecting iron availability in the rhizosphere. Plants and microorganisms may increase iron availability
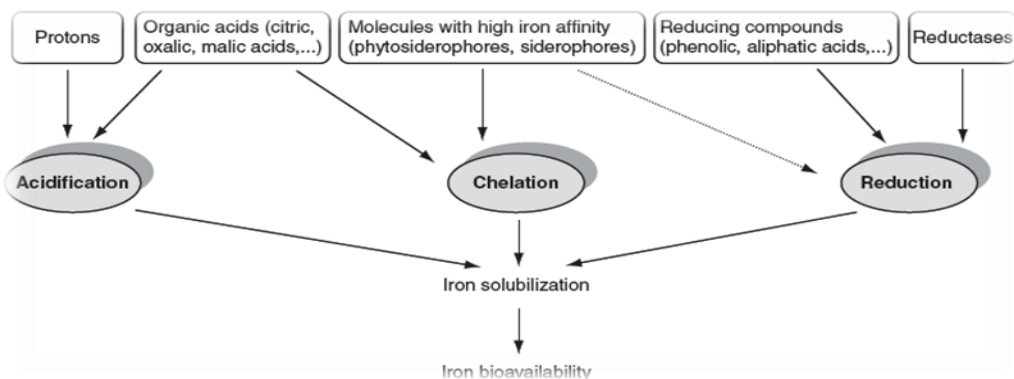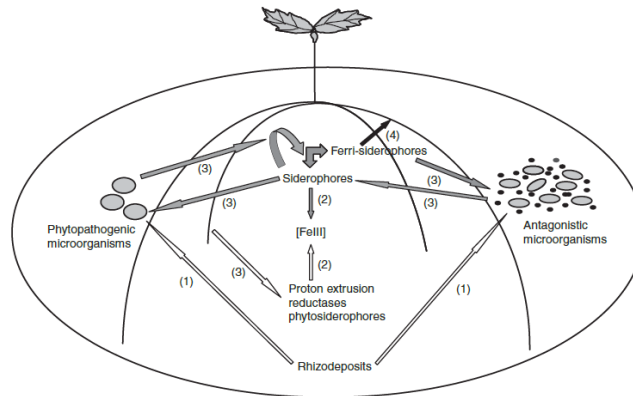
Fig.4 Schematic representations of iron-mediated interactions between plants and microbes promoting plant health and iron nutrition

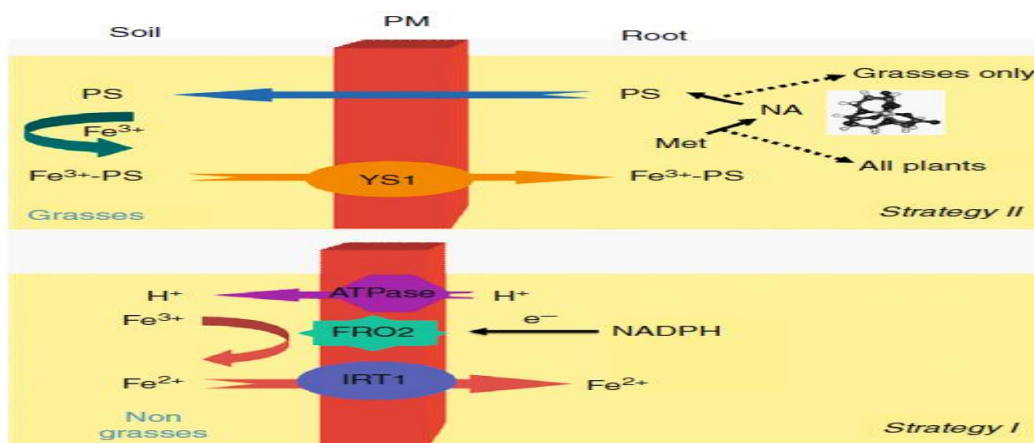**Fe deficiency differs according to the strategy of iron uptake**

Table.1 55Fe Uptake and Translocation Rates in Fe-Sufficient (+Fe) and Fe-Deficient (-Fe) Maize Plants Supplied with 55FePSB, 55FeEDDHA, and 55FeHMA under Various Densities of Microorganism Population Eli *et al.,* 1992

Treatment	^{55}Fe Uptake Rate		^{55}Fe Translocation Rate		Microorganisms
	+Fe	−Fe	+Fe	−Fe	
	nmol·g^{-1}·10 h^{-1}				*CFU mL^{-1}*
FePSB					
Uninoculated	17.6 cd	37.2 d	3.3 a	1.9 c	1.6·10^3
Axenic	–	24.2 e	–	8.8 a	<1
Soil bacteria	56.4 b	115.6 b	1.8 b	0.8 d	7.0·10^9
Pseudomonas	121.5 a	1125.7 a	1.7 b	0.8 d	2.0·10^{10}
Antibiotics	23.6 c	55.8 c	4.1 a	5.6 b	5.0·10^1
FeEDDHA					
Uninoculated	15.1 b	25.2 c	4.4 c	7.1 a	1.8·10^3
Soil bacteria	27.4 a	37.3 b	10.4 a	5.0 ab	3.0·10^{10}
Pseudomonas	25.5 a	79.1 a	10.1 a	2.7 bc	5.0·10^{10}
Antibiotic	14.0 b	10.8 d	5.2 bc	3.5 b	2.0·10^2
FeHMA					
Uninoculated	2578 b	3465 b	1572 b	2217 b	1.8·10^3
Soil bacteria	1231 c	1578 c	743 c	707 c	9.0·10^9
Antibiotic	4758 a	5057 a	3257 a	3822 a	6.0·10^1

Time-course of changes in the available iron concentration in the rhizosphere of peanuts induced by intercropping

The different cropping systems affected the available Fe concentration in the rhizosphere of peanut and maize. Generally, the available Fe concentration was increased in the rhizosphere in intercropped peanuts at all growth stages (34-76 days). Indicating that intercropping could consistently provide more available Fe to peanut than monocropping over a longer period of time. The available Fe showed no significant change with time under monocropping.

Intercropping significantly improved the available Fe concentration in peanut rhizosphere during the reproductive stage, at 60-76 days. In particular, at 60 days, where there was obvious Fe-deficiency chlorosis in the monocropped peanuts, the intercropped system could maximize DTPA-Fe concentrations in the rhizosphere of peanut plants (Guo *et al.,* 2014).

Fe deficiency differs according to the strategy of iron uptake

Active strategies (Römheld and Marschner 1986)

In soil low concentration of Fe (III) and Requirement of aerobic organisms creates high demand for Fe so competition for Fe (III) in the rhizosphere than Plants and microbes have evolved active strategies

Acidification of the soil solution based on the excretion of protons or organic acids,
Chelation of Fe (III) by plant and microbial ligands showing a high affinity for Fe^{3+}

Reduction of Fe^{3+} to Fe^{2+} mostly by plant reductases and reducing compounds.

Strategy I

Crop species (Peanut, Cotton, Cucumber, Pea, Carnation).

Strategy II

Graminacious plant species (Barley, Maize, Sorghum, Oat) are more efficient to overcome the deficiency of iron

Iron-mediated interactions between plants and microbes promoting plant health and iron nutrition (Robin *et al.,* 2008)

Plants release a variety of organic and inorganic substances (rhizodeposits) which exert a direct influence on soil borne microorganisms including antagonistic and phytopathogens populations. The concentration of Fe (III) in solution is decreased in the rhizosphere due to its uptake by roots and microbes.

Active iron acquisition strategies are activated; antagonistic microorganisms produce siderophores showing a higher affinity for iron than those of phytopathogens leading to their suppression (microbial antagonism).

Microbial siderophores may also elicitate defense reactions in the host plant and promote plant iron nutrition. Altogether, these different actions promote plant health and iron nutrition.

Synthetic Fe (III)-chelates, such as EDTA and EDDS, are the most common and effective ligands used to increase Fe bioavailability. The performance of HIDS with respect to Fe movement in growth medium and radish growth was higher than that of other chelating ligands tested. Thus, HIDS would be a good alternative to EDTA and other poorly biodegradable chelating ligands.

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