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**Rhizospheric organic compounds in the soil-microorganism-plant system : their role in iron availability**

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## Summary

Poor iron (Fe) availability in soil represents one of the most important limiting factors of agricultural production and is closely linked to physical, chemical and biological processes within the rhizosphere as a result of soil–microorganism–plant interactions. Iron shortage induces several mechanisms in soil organisms, resulting in an enhanced release of inorganic (such as protons) and organic (organic acids, carbohydrates, amino acids, phytosiderophores, siderophores, phenolics and enzymes) compounds to increase the solubility of poorly available Fe pools. However, rhizospheric organic compounds (ROCs) have short half-lives because of the large microbial activity at the soil–root interface, which might limit their effects on Fe mobility and acquisition. In addition, ROCs also have a selective effect on the microbial community present in the rhizosphere. This review aims therefore to unravel these complex dynamics with the objective of providing an overview of the rhizosphere processes involved in Fe acquisition by soil organisms (plants and microorganisms). In particular, the review provides information on (i) Fe availability in soils, including mineral weathering and Fe mobilization from soil minerals, ligand and element competition and plant–microbe competition; (ii) microbe–plant interactions, focusing on beneficial microbial communities and their association with plants, which in turn influences plant mineral nutrition; (iii) plant–soil interactions involving the metabolic changes triggered by Fe deficiency and the processes involved in exudate release from roots; and (iv) the influence of agrochemicals commonly used in agricultural production systems on rhizosphere processes related to Fe availability and acquisition by crops.

## Introduction

The rhizosphere is defined as the soil volume influenced by root activity (Hinsinger, 1998). This small and particular soil volume is characterized by fluxes and gradients of both organic and inorganic compounds that are fundamental to rhizosphere processes. These latter, in turn, are able to influence considerably the transformations and flows of nutrients from soil to plant. For these reasons, and because they are the linkage between soil and plant, they are considered to be the bottleneck of nutrient mobilization in soil and subsequent acquisition by plants and, therefore, of crop yield.

Rhizosphere processes and the rhizosphere effects on plants are governed mainly by the release from roots, in a complex mixture, of low- and high-molecular-weight substances (such as protons, carbohydrates, organic acids, amino acids, phytosiderophores (PS), phenolics and enzymes; Dakora & Phillips, 2002), able to induce fundamental changes in the chemical, physical and biological characteristics of this part of soil closely surrounding the roots. These substances are involved in important pedogenic and rhizospheric processes involving fundamental functions such as (i) modulation of nutrient availability (Fe, P, Zn; Dakora & Phillips, 2002), (ii) root protection against toxic metals (Al, Zn, Cd; Jones, 1998) or pathogens (Bais *et al.*, 2004) and (iii) attraction and/or repulsion of microorganisms (Bais *et al.*, 2004). In this context, soil microorganisms, which may enhance or restrict these rhizosphere processes, can play an important role in determining nutrient availability for plants in the rhizosphere.

Physical, chemical and biological processes in soil are largely connected with iron (Fe) geochemistry (Carrillo-González *et al.*, 2006) and, in turn, with its availability for the soil-growing microorganisms and plants. However, despite the large natural abundance of Fe in soil, estimated to be about 20–40 g kg<sup>-1</sup> (Cornell & Schwertmann, 2003), its availability is very often far less than the requirements for optimal plant growth. Therefore, Fe deficiency is a frequent problem for many crops, particularly in calcareous soils, and represents one of the most important factors limiting agricultural production. As a micronutrient, Fe has a number of important functions in many vital metabolic reactions in plants (Vigani *et al.*, 2013) and its imbalance affects the whole cell metabolism, leading, for crops, to a loss of production. Iron is required as a co-factor for a wide range of enzymes belonging to both respiratory (RET) and photosynthetic electron transport (PET) chains in mitochondria and in chloroplasts, respectively (Vigani *et al.*, 2013). As a consequence, Fe-deficiency impairs chloroplast development, resulting in the chlorosis of leaves, a general reduction of plant growth, a reprogramming of metabolism and induction of Fe-acquisition mechanisms (Marschner, 2012). To cope with micronutrient shortage, plants have evolved strategies to enhance Fe concentration within the rhizosphere that include the release of inorganic (protons) and organic (organic acids, phenolics and PS) substances able, by acidifying the rhizosphere and reduction-complexation processes, to increase the availability of soluble Fe pools in soil. Plant organic exudates operate through Fe complexation mechanisms as well as low-molecular-weight Fe-binding molecules (microbial siderophores, MSs) (see the review by Lemanceau *et al.*, 2009), released by microorganisms in the rhizosphere.

The present review focuses on the effect of low-molecular-weight organic compounds (rhizospheric organic compounds; ROCs) on rhizosphere processes involved in Fe acquisition by microbes and plants in cultivated soils and also considers the influence of agrochemicals. Because a link between the carboxylate and proton exudation has been already documented (Tomasi *et al.*, 2009), the contribution of rhizosphere acidification after proton release is also discussed in terms of Fe mobilization from soil particles. Attention will be paid to the plant metabolic changes involved in the enhanced production of ROCs and to the mechanisms adopted by roots for their release into the rhizosphere. Interactions between microbes and roots having a relevant effect on Fe acquisition are also discussed.

#### Low-molecular-weight organic compounds in the rhizosphere (ROCs)

Higher plants and microorganisms release significant amounts of assimilated carbon as organic compounds of high and low molecular weight into the rhizosphere as a response to Fe deficiency. For instance, it has been recently reported that maize releases up to 166 kg C ha<sup>-1</sup> as rhizodeposited carbon (C) in the soil, of which 50% was recovered in the upper 10 cm (Pausch *et al.*, 2013). The main classes of compounds, single components, residence time in soil and the stability constants of the complexes of ROCs with FeIII are listed in Table 1. Most of these substances will be discussed in this review. As can be seen in Table 1, in addition to high-affinity ligands, microorganisms and plants also produce a range of lower-affinity ligands such as phenolics and organic acids (Jones *et al.*, 1996; Reichard *et al.*, 2005; Robin *et al.*, 2008). Organic compounds derived from soil organic matter decomposition can also contribute to Fe dynamics in the rhizosphere.

**Table 1.** Rhizosphere organic compounds (ROCs) detected in exudates of plants and microorganisms

Class of compounds	Components	Residence time in soil	Range of stability constants (L-FeIII)
Sugars	Arabinose, glucose, fructose, galactose, maltose, raffinose, rhamnose, ribose, sucrose, xylose	—	—
Amino acids	All 20 proteinogenic amino acids, homoserine, cystathionine	30 minutes–12 hours (Jones & Kielland, 2012)	104–12 (Martell <i>et al.</i> , 2001)
Phytosiderophores (PS)	Mugineic acid, deoxymugineic acid (DMA), epi-hydroxymugineic acid, avenic acid	—	1018–20 (Murakami <i>et al.</i> , 1989)
Siderophores (MS)	Desferrioxamine-B (DFO-B), enterobactin, pyoverdine, ferrichrome	—	1025–51 (Kalinowski <i>et al.</i> , 2000)
Organic acids	Formic, acetic, propionic, malic, citric, oxalic, succinic, fumaric, shikimic, ketoglutaric, aconitic, malonic, maleic, tartaric, lactic	30 minutes–12 hours (Jones <i>et al.</i> , 2001)	103–20 (Martell <i>et al.</i> , 2001)
Phenolic acids	Caffeic, vanillic, hydroxybenzoic, p-coumaric, ferulic, gallic, syringic, sinapic	Hours–several days (Sosa <i>et al.</i> , 2010)	1010–28 (Perron & Brumaghim, 2009, and refs therein)
Flavonoids	Quercetin, genistein, genistin, rutin, kaempferol, formonnetin, biochanin, luteloin, apigenin, hyperoside	Hours–several days (Cesco <i>et al.</i> , 2012)	1040–49 (Perron & Brumaghim, 2009, and refs therein)
Fatty acids	Linoleic, oleic, palmitic, stearic	—	—
Sterols	Campesterol, cholesterol, sitosterol, stigmasterol	—	—
Enzymes	Amylase, invertase, cellobiase, desoxyribonuclease, ribonuclease, phosphatase, phytase, peroxidase, protease, sulphatase	—	—
Miscellaneous	Vitamins, auxins, sulphides, ethanol, protons, potassium, nitrate, phosphate, carbonate	—	—

## Iron mobilization from soil

Iron occurs in soil minerals in two oxidation states, FeII and FeIII. Both can be found in a wide range of primary and secondary minerals (Table 2). However, the main Fe mineral forms in soil are poorly soluble Fe (hydr)oxides. Iron may also be associated with clay minerals as a structural element or sorbed on them to a small extent in neutral or alkaline soils. In addition to the mineral fraction, Fe is also bound to organic matter in soluble or insoluble forms. The solubility of Fe crystalline minerals in soil is pH-dependent and decreases with increasing pH. Soil redox potential (Eh) is another important factor influencing mineral stability and therefore Fe solubility, as described by Colombo *et al.* (2013). Iron solubility in soil is mainly controlled by processes involving Fe (hydr)oxides (generically called 'soil iron oxides') and results in a soil solution concentration of about  $10^{-7}$ – $10^{-10}$  m over a pH range from 5.0 to 8.5 (Kraemer *et al.*, 2006), a quantity too small for plant growth. Nevertheless, the activities of living organisms can dramatically accelerate the weathering of soil minerals as shown for microorganisms (Brantley *et al.*, 1999) and plants (Hinsinger *et al.*, 2001). This enhances Fe solubility strongly by two or three orders of magnitude and meets microbe ( $10^{-5}$ – $10^{-7}$  m) or plant ( $10^{-4}$ – $10^{-9}$  m) requirements (Lemanceau *et al.*, 2009).

**Table 2.** Main Fe-bearing soil minerals

Mineral name	Chemical formula <sup>a</sup>	Group
<i>Primary minerals</i>		
Olivine	(Mg,Fe) <sub>2</sub> SiO <sub>4</sub>	Olivine
Augite	Ca(Mg,Fe,Al)(Si,Al) <sub>2</sub> O <sub>6</sub>	Piroxens
Hyperstene	(Mg,Fe) <sub>2</sub> SiO <sub>6</sub>	Piroxens
Hornblende	Ca <sub>2</sub> Na(Mg,Fe) <sub>4</sub> (Al,Si) <sub>8</sub> O <sub>22</sub> (OH,F) <sub>2</sub>	Amphiboles
Biotite	K(Mg,Fe) <sub>3</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>2</sub>	Micas
<i>Secondary minerals</i>		
Glauconite	(K,Na,Ca) <sub>2</sub> -1.2(Fe,Al,Mg) <sub>4</sub> (OH) <sub>4</sub> (Si <sub>7</sub> -7.6Al <sub>1</sub> -0.4)O <sub>20</sub>	Micas
Nontronite	(Ca,Na) <sub>0.7</sub> Fe <sub>4</sub> (OH) <sub>4</sub> (Si <sub>7.3</sub> Al <sub>0.7</sub> )O <sub>20</sub>	Smectites
Vermiculite	(Mg,Fe,Al) <sub>3</sub> (Al,Si) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	Vermiculites
Chlorite	(Mg,Fe) <sub>6</sub> (OH) <sub>4</sub> (Si,Al) <sub>8</sub> O <sub>20</sub> (Mg,Fe)(OH) <sub>12</sub>	Chlorites
		<b>Solubility product (pK<sup>°</sup>sp)<sup>b</sup></b>
<i>Iron oxides</i>		
Hematite	α-Fe <sub>2</sub> O <sub>3</sub>	11.820
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	13.026
Maghemite	γ-Fe <sub>2</sub> O <sub>3</sub>	10.486
Goethite	α-FeOOH	12.190
Lepidocrocite	γ-FeOOH	10.587
Ferrihydrite	Fe <sub>5</sub> H <sub>8</sub> O <sub>8</sub> ·4H <sub>2</sub> O	9.382
<i>Other minerals</i>		
Pyrite	FeS <sub>2</sub>	28.594
Siderite	FeCO <sub>3</sub>	16.723

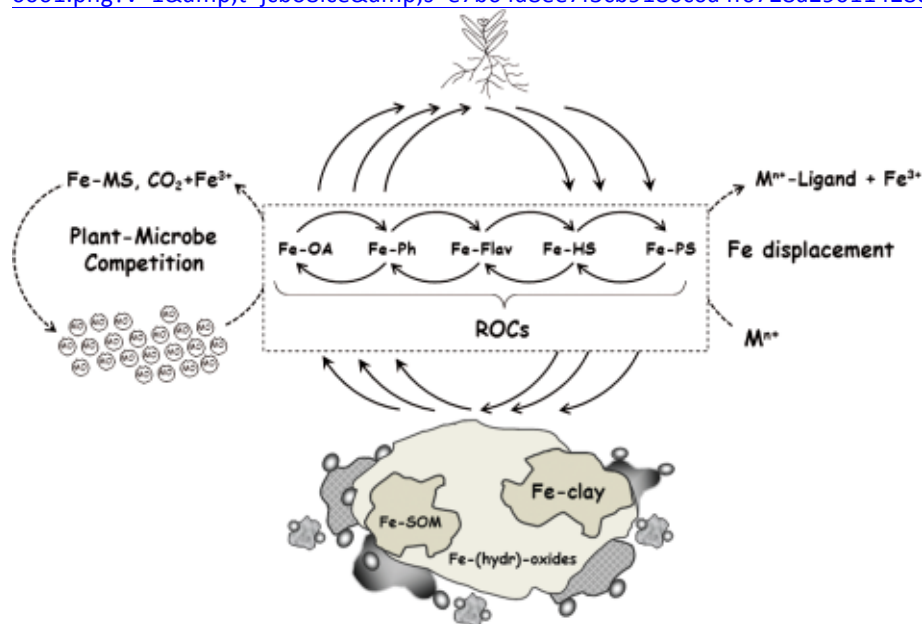
### Mineral weathering and Fe mobilization from soil minerals

The literature about the weathering of Fe (hydr)oxides is vast (Reichard *et al.*, 2007, and references therein), but is limited with respect to other Fe-bearing soil minerals, especially clay minerals. In addition, the dynamics of mineral weathering in the rhizosphere have not been widely studied, particularly the role of organic compounds in soil Fe biogeochemistry (Hinsinger *et al.*, 2006). For instance, Tuason & Arocena (2009) observed the weathering of chlorite and micas in the rhizospheric soil of white spruce (*Picea glauca* Moench) and subalpine fir (*Abies lasiocarpa* Hook.). Vermiculite and smectite were the products of the weathering process. Hinsinger *et al.* (1993) reported the ability of rape (*Brassica napus* L.) to promote the transformation of a mica (phlogopite) into a vermiculite. The vermiculitization of the same mineral was also observed in the rhizosphere of ryegrass (*Lolium perenne* L.) where the process occurred over a period ranging from a few days up to one month (Hinsinger & Jaillard, 1993).

Iron solubilization and mobilization from soil minerals in the rhizosphere and the extent of mineral weathering is influenced strongly by the presence of ROCs and protons (Courchesne & Gobran, 1997). Figure 1 shows the main processes involving ROCs in Fe mobilization from soil. The main insoluble Fe sources subjected to this weathering process are Fe-containing primary silicates and Fe (hydr)oxides (Kraemer, 2004). In the mobilization process, ROCs can act alone or in combination, which has an additive effect on Fe dissolution from minerals (Dehner *et al.*, 2010). A synergistic effect on the dissolution of goethite has been documented for oxalate, a common root exudate when P-deficiency and/or Al toxicity occurs, and deoxymugineic acid (DMA, a PS, Reichard *et al.*, 2005); similarly, Cheah *et al.* (2003) detected goethite dissolution in discrete quantities but only when oxalate and desferrioxamine-B (DFO-B, an MS) were simultaneously in contact with the mineral. It is interesting to note that ROCs could also remove Fe from

organic sources such as Fe complexed by humic substances (HS) *via* a ligand exchange mechanism, as described for PSs and Fe-HS (Cesco *et al.*, 2000, 2002).

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**Figure 1.**

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Schematic representation of important processes involved in Fe mobilization in soil; ROCs = rhizosphere organic compounds, OA = organic acids, Ph = phenolic compounds, Flav = flavonoids, HS = water soluble humic substances, PS = phytosiderophores, MS = microbial siderophores, Mn<sup>+</sup> = metal cation present in soil solution such as Ca<sup>2+</sup> competing for Fe<sup>3+</sup>.

Because Fe solubility is governed by soil pH, the acidification of the rhizosphere through the release of protons, organic acids and root respiration plays an important role in mineral weathering. In addition, in nutrient-deficient conditions plant roots enhance the qualitative and quantitative root-exudate pattern, increasing mineral dissolution and thus Fe mobilization even more (Hinsinger *et al.*, 2003). Rhizosphere microorganisms can also promote mineral weathering through their own metabolism (Calvaruso *et al.*, 2006).

In the rhizosphere, fractions of humified organic matter are present together with mineral constituents. Therefore, in this specific volume of soil, interactions between these humified organic fractions and ROCs released by plants and microorganisms occur (Piccolo *et al.*, 2003), with a consequent impact on the extent of mineral weathering. An additional influence could be also exerted by the interactions between HS and minerals in the rhizosphere, which lead to the formation of stable organo–mineral complexes; these complexes are more refractory, particularly in acidic conditions, to mineral weathering (Ochs *et al.*, 1993; Colombo *et al.*, 2012). In addition to these indirect effects, HS, because of their ability to interact with Fe, are also able to affect Fe biogeochemistry directly in the soil. The soluble low-molecular-weight HS fractions, because they can form Fe soluble complexes, can enhance the dissolution and solubility of Fe in soil, as shown for ferrihydrite (Cesco *et al.*, 2000). The extent of this effect is comparable to that observed for PSs or organic acids (Tomasi *et al.*, 2013). In monocotyledons (Strategy II plant species as defined by Römheld & Marschner, 1983), the depletion of Fe in the rhizospheric solution occurs simultaneously to that of PSs involved in the Fe-complexation process. The same effect could occur with microbes where the major active strategy of Fe acquisition relies on the release of MSs and then the transport of the Fe–MS complex into microbial cells by a specific transporter (see review by Lemanceau *et al.*, 2009). In contrast, dicotyledons (Strategy I plant species as defined by Römheld & Marschner, 1983) have an impact on the Fe concentration in the rhizosphere but not on the availability of ROCs.

After Fe reduction by the root Fe-reductase associated with the plasma membrane of the root cell, the complex splits with the release of the organic ligand, which is then, theoretically, available again for the Fe mobilization process. For those ROCs with a reducing capacity such as phenolics and some organic acids, the dissolution of FeIII-bearing minerals could be the result of both reduction and complexation processes (Tomasi *et al.*, 2008; Cesco *et al.*, 2010). It has been suggested that, for these compounds, part of the root reducing capacity is ascribable to the redox properties

of these compounds when released into the rhizosphere (Römheld & Marschner, 1983). In addition, because the extent of this Fe solubilization and mobilization from minerals is strongly dependent on ROCs concentration and microbial activity in the rhizosphere (Courchesne & Gobran, 1997), compounds having effects on soil (bio)activities such as flavonoids could promote or restrict Fe solubilization processes (Tomasi *et al.*, 2008; Cesco *et al.*, 2012). The availability of elements other than Fe can also be influenced by the weathering action of organic ligands on Fe-bearing minerals. In soils where Fe oxides are responsible for making phosphate insoluble (Borggaard *et al.*, 1990), ROCs (organic acids and flavonoids) are able to promote indirectly the mobilization and the availability of P by solubilizing Fe from an insoluble Fe-phosphate through an exchange of the anion adsorbed onto Fe oxides (Tomasi *et al.*, 2008).

#### *Ligand and element competition*

As outlined in Figure 1, ligand exchange processes between ROC complexes with Fe are mainly influenced by the affinity of the ligands (ROCs) for Fe and their stability constants (Table 1). Because of their large stability constants (1025–1051), FeIII-MS complexes represent only rarely a source of exchangeable Fe for other ROCs such as oxalate or citrate (108 and 1011, respectively) or even PSs (1018–20) (Murakami *et al.*, 1989). However, MSs could restrict Fe complexation reactions mainly to themselves (Figure 1). In this case, the Fe-free ROCs derived from the ligand exchange process, can participate again in the processes of Fe mobilization in the rhizosphere.

In the rhizosphere, ROCs could act as ligands for cations other than Fe and thereby influence Fe mobilization. For instance, in calcareous soils the large amount of soluble calcium (Ca<sup>2+</sup>) can compete with Fe (Figure 1) thus strongly reducing the effect of the ROCs on Fe solubility, as described for citrate in the presence of calcite (Kraemer *et al.*, 2006). In contrast, PSs have only a small affinity for Ca, which makes them very efficient in mobilizing Fe in calcareous soils. As observed by Zhang *et al.* (1991), the solubility of ferrihydrite in the presence of DMA remains approximately the same in the presence of calcite. On the other hand, most PSs can chelate a number of divalent cations efficiently, especially Zn<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> (Murakami *et al.*, 1989). The larger stability constants of Cu-PS compared with those of Fe-PS (Reichman & Parker, 2005) could explain the Fe-Cu antagonism and Cu toxicity observed in durum wheat grown in calcareous soils contaminated with Cu (Michaud *et al.*, 2007).

#### *Plant-microbe competition*

As previously described, ROCs could form a mix of Fe complexes available for uptake by plants and microbes (Figure 1). Depending on their capability to use these Fe sources and to release new ROCs, Fe concentration could be quite different over time. For this reason and because of the need to meet the specific requirements of microbes and plants, a strong competition among the users of these Fe sources is easily established (Colombo *et al.*, 2013). Microorganisms are very competitive for Fe because they (i) are able to take up Fe complexes formed not only with their own ligands (MSs) but also with those released by other organisms, (ii) use ROCs as a source of nutrients and energy, and (iii) synthesize and release ligands (MSs) (Figure 2). In addition, rhizospheric microorganisms can contribute to the solubilization of Fe from minerals by decreasing soil pH through nitrification, reducing FeIII or complexing FeIII with small-affinity ROCs which can be used by plants (Colombo *et al.*, 2013). These latter complexes, in order to be exploited by plants, must have a sufficiently large redox potential for enzymatic reduction (Strategy I) or a sufficiently small thermodynamic stability to undergo ligand-exchange reactions with PSs (Strategy II) (Kraemer *et al.*, 2006; Figures 1, 2). It has been demonstrated that Strategy II plants are able to use, to a limited extent, Fe from FeIII-MSs complexes *via* indirect mechanisms (Duijff *et al.*, 1994). For Strategy I plants the involvement of a putative transporter for the intake of the integral FeIII-MSs complex has been hypothesized (Vansuyt *et al.*, 2007). It has been demonstrated recently that FeIII-DMA complexes could be absorbed directly by Strategy I plants by using a transporter codified by a gene belonging to the yellow stripe1-like (YSL) family and located at the root epidermis (Xiong *et al.*, 2013).

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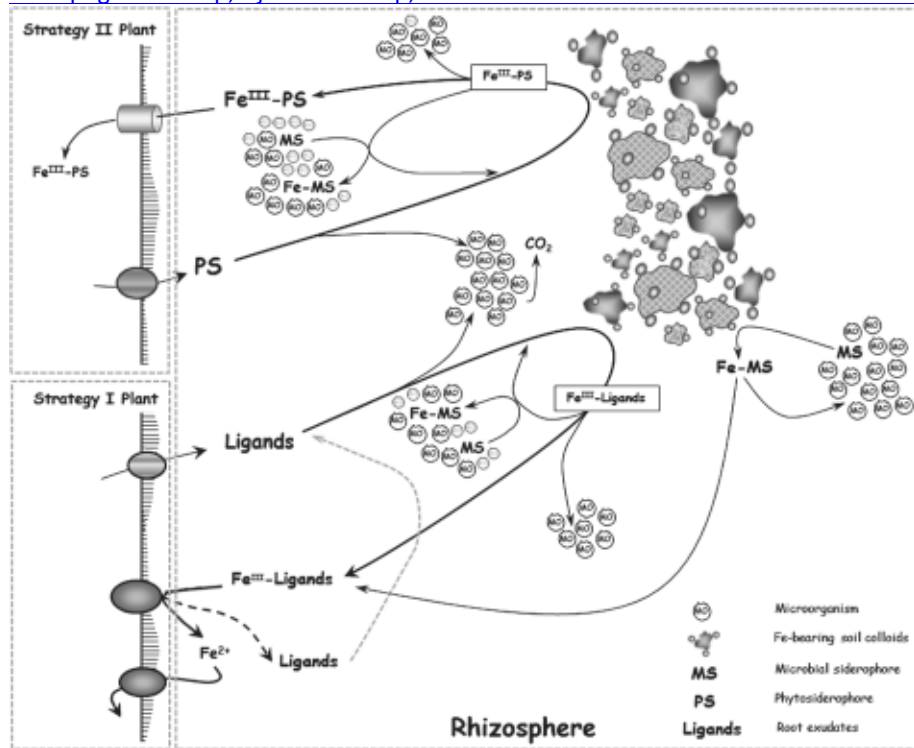


Figure 2.

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Schematic representation of Fe acquisition of Strategy I and II plants and the pathways of Fe mobilization at the soil-root interface, including the influence of microorganisms.

In addition, as outlined in Figure 2, plants could use Fe as an Fe<sup>III</sup>-MS source only after their microbial degradation and the following release of Fe for new sequestration by poor affinity ROCs (Leong, 1986; Guerinot, 1994). In this case, the driving force determining the plant use of Fe<sup>III</sup>-MS complexes is strictly linked to their microbial or chemical degradation rates (Kraemer *et al.*, 2006).

#### Residence time of ROCs in soil

The maintenance of structure and concentration of ROCs in the rhizosphere is a prerequisite to fulfil their function in Fe mineral weathering and mobilization. However, these compounds in soil are readily degraded by microorganisms and/or sorbed onto soil minerals. As recently noted for flavonoids (Cesco *et al.*, 2012), the processes in the rhizosphere are still poorly understood and focused research is needed.

It has been observed that organic acids and amino acids applied to soil are rapidly degraded, exhibiting half-life values ranging from 30 minutes to 12 hours (Jones *et al.*, 2001; Jones & Kielland, 2012). In contrast, a half-life of up to several days was described for flavonoids (Sosa *et al.*, 2010). The information for PSs is poor and most of the studies are based on hydroponic systems (Crowley, 2001). Römheld (1991) suggested that for barley there is a slower PS degradation rate in soil than in non-sterile cultures because of the diurnal pulse timing of PS release and location near the root (Marschner *et al.*, 1987) where the microbial activity is still small. This spatial separation along the root axis might not only limit the microbial degradation but also the competition for Fe between PSs and MSs. In general, the degradation rate of ROCs is strongly dependent on soil type and horizon, soil temperature and water availability, the vegetation type and the microbial community. In addition, molecular size and chemical structure might further influence the degradation rate. van Hees *et al.* (2002) observed that citrate (a tricarboxylate) was mineralized faster than oxalate (a bicarboxylate) and acetate (a monocarboxylate). A different trend was observed for soil sorption processes (oxalate > citrate > acetate; van Hees *et al.*, 2003). Sorption of ROCs can decrease their availability in soil solution and, in turn, their efficacy in Fe mobilization, but also preserve them from microbial degradation.

#### Microbe-plant interactions

Microbes can interact with plants as pathogens, by attacking roots, or as beneficial organisms. As the main goal of this review is further understanding of rhizosphere processes, only the latter effect is discussed.

#### Beneficial microbial communities

Among beneficial microbes, pollutant degraders, bio-pesticides, auxin producing phytostimulators and nitrogen-fixers rhizobia have been investigated and often used as inoculants (Bloembergen & Lugtenberg, 2001). Despite the different



roles that beneficial microorganisms can have when interacting with plant roots, common mechanisms are used to achieve different purposes (Lugtenberg *et al.*, 2002). Growth and development of rhizosphere microorganisms, mostly heterotrophic, depend on exogenous carbon and nutrient sources, mainly derived from root exudates including ROCs. In turn, plant roots may control the surrounding microflora by secreting specific mixtures of compounds in order to create selective conditions (Weisskopf *et al.*, 2005). Thus each plant is colonized by specific microbial populations. The first results regarding the different composition of bacterial communities on plant roots were determined by cultivation-dependent methods about two decades ago (Lemanceau *et al.*, 1995). More recently, culture-independent techniques have been used to determine the taxonomic diversity of bacteria associated with roots of wheat cultivars and the variation of rhizosphere microbial communities in response to different crop species and cultivars (Wieland *et al.*, 2001; Salles *et al.*, 2004). The impact of plant species on the composition of *nirk*-type denitrifiers (Bremer *et al.*, 2007) and of rice cultivar on ammonia-oxidizing bacteria (Briones *et al.*, 2002) was demonstrated. Salles *et al.* (2004) demonstrated that the bacterial community composition in the rhizosphere is also affected by soil type and root location. Studies with sugar beet showed that the bacterial community is affected by soil type and geographical regions that can affect solubility and diffusion of root exudates and, as a consequence, their fate and availability to microbiota (Zachow *et al.*, 2008).

The colonization of plant roots depends also on microbial characteristics. The plant root surface is not covered homogeneously by microbes: there are vacant areas as well as those with micro-colonies and biofilms, where cell-cell communication and competition among bacteria occur as a consequence of the expression of many bacterial genes involved in root colonization (Lugtenberg *et al.*, 2002).

#### *Microbe-plant association and plant mineral nutrition*

Dennis *et al.* (2010) provide a detailed description of types and amounts of root exudates and define them in terms of stimulatory (carbon sources, mostly sugar and amino acids, vitamins, complexing agents and specific substrates) or inhibitory (antimicrobials and quorum sensing inhibitors) factors. The role of root exudates as mediators of direct mineral acquisition in nutrient-poor environments is well known (Dakora & Phillips, 2002), as are their effects on soil microorganisms, which further impact plant nutrition by influencing plant growth promotion, nutrient availability and uptake (Richardson *et al.*, 2009).

Though the role of microbe-plant association in N and P plant nutrition has been much investigated, there is still a lack of information on Fe acquisition. Certain bacteria in the rhizosphere can use PSs as a source of Fe or may alter Fe availability to plants and other competing microorganisms (Von Wiren *et al.*, 1993). As Fe stress becomes more severe, the proportion of PSs in root exudate increases. Yang & Crowley (2000) used barley plants grown in a Fe-limiting soil and foliar treatments to ameliorate Fe deficiency or suppress PS production. They demonstrated (with a culture-independent method (PCR-DGGE of 16S rDNA) and canonical correspondence analysis), that rhizosphere communities may be altered by up to 40% by changes in root exudates caused by changes in plant Fe nutrition status (Yang & Crowley, 2000).

Plants release ROCs to increase Fe availability while bacteria such as fluorescent *Pseudomonas* synthesize pyoverdines, an MS that has a large affinity for Fe and can contribute to plant Fe acquisition (Lemanceau *et al.*, 2009). In general, plant growth-promoting (PGP) rhizobacteria, as well as producing hormones such as indole acetic acid, release MSs and maintain Fe concentration in soil solution (Lemanceau *et al.*, 2009; Table 1, Figure 2). Recently, some studies have attempted to isolate PGP microorganisms from different habitats that potentially improve soil fertility and enhance plant nutrition, with a consequent reduction of external input necessary for successfully enhanced crop production (Dastager *et al.*, 2011).

#### **Plant-soil interaction**

Under limited Fe availability, the metabolic reprogramming of plants to take up more Fe from soil represents not only a survival mechanism for the plant but is responsible for the production of large amounts of compounds/metabolites that are exuded (ROCs) into the rhizosphere under the nutritional stress. The main ROCs are (i) carboxylates, such as citrate and malate, which originate from the primary metabolism, and (ii) many compounds such as phenolics and flavins, which are produced by secondary metabolism (Cesco *et al.*, 2010, 2012; Vigani *et al.*, 2012).

In addition to the role played in the rhizosphere, carboxylates act also within plants as Fe-chelates, aiding transport of Fe within the plant, and play a central role in metabolism (Vigani *et al.*, 2013). Under Fe deficiency the phosphoenolpyruvate carboxylase (PEPC) activity is strongly increased and produces much oxaloacetic acid (OAA) and in turn malate, by malate dehydrogenase activity (Zocchi, 2006) (Figure 3). Furthermore, elevated production of OAA and/or malate could be used to replenish the tricarboxylic (TCA) cycle. It has been observed that Fe deficiency affects the TCA cycle activity, leading to an accumulation of citrate in roots (Vigani, 2012). The accumulated citrate in roots could provide (i) carbon skeleton to chlorotic leaves to sustain growth and respiration (Abadía *et al.*, 2002), (ii) reducing equivalents for ferrioxalate reductase (FCR) through the cytosolic NADP<sup>+</sup>-dependent isocitrate dehydrogenase (ICDH) activity and (iii) 2-oxoglutarate, which contributes to nitrogen metabolism (Zocchi, 2006;

Borlotti *et al.*, 2012). The citrate and malate accumulated in Fe-deficient plants can be released by roots to facilitate acquisition of Fe from the soil (see next section and Figure 1) or transported to the shoot *via* the xylem.

[<img class="inline-figure image" alt="Figure&nbsp;3." data-bbox="90 111 480 126"/>](#)

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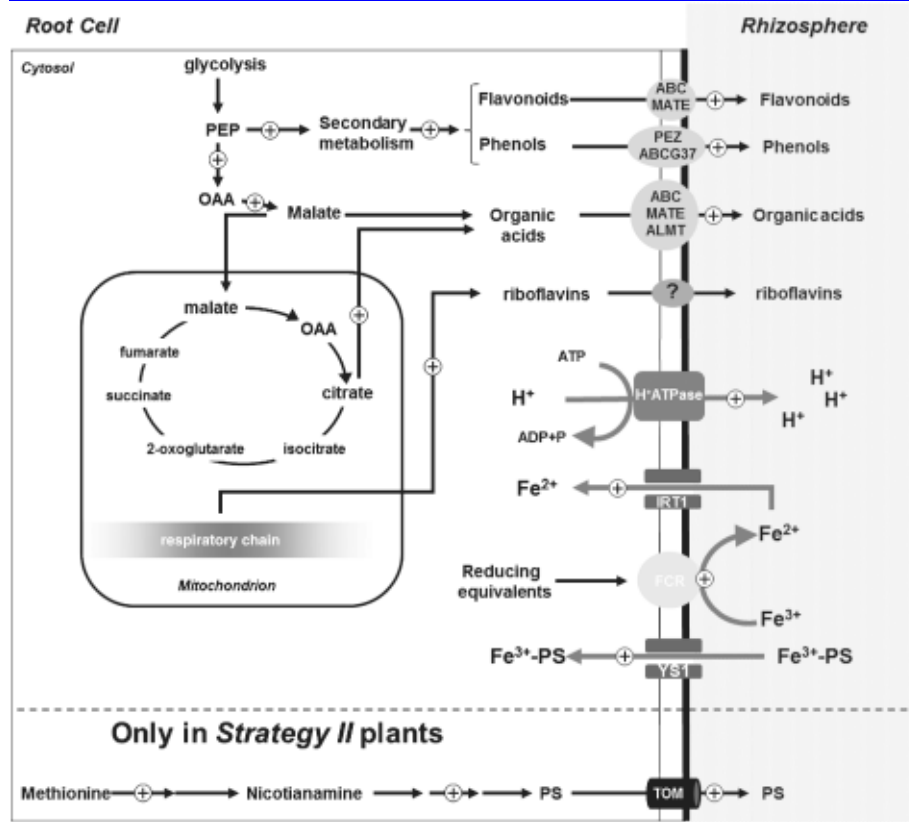


Figure 3.

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Schematic representation of the root exudation and main metabolic changes occurring in plants under Fe deficiency. The Fe shortage determines a strong mitochondrial alteration characterized by a reduction in the activity of the respiratory chain as well as an increase of organic acid biosynthesis (mainly citrate and malate). To support energetically the mechanism of Fe acquisition the activity of glycolysis is strongly induced. There is an increase of secondary metabolism pathways leading to an accumulation of phenolic compounds. The phenols, together with the organic acids and the unused riboflavins, are released from the root (see text for more details). Below the dashed line the pathway of synthesis and exudation of phytosiderophores occurring only in Strategy II plants grown under Fe-deficiency is also summarized.

Phenols act as antioxidant compounds and as Fe-ligands in plant tissues and can play a critical role in facilitating the reutilization of apoplastic Fe in roots (Jin *et al.*, 2007). Moreover, these compounds can be increased or synthesized *de novo*, not only under Fe deficient conditions, but also as a response to other nutrient deficiencies. Under these stressed conditions carbohydrates can be diverted into secondary metabolism to produce phenols (Donnini *et al.*, 2012; Vigani *et al.*, 2012; Tato *et al.*, 2013). The activation of such processes allows the production and accumulation of phenols in plants and, in turn, their release into the rhizosphere.

Both the oxidative pentose phosphate pathway and Calvin cycle can provide a carbon skeleton in the form of erythrose-4-, which, with phosphoenolpyruvate (PEP) formed from glycolysis, can be used as a precursor for phenylpropanoid metabolism *via* the shikimic acid pathway (Herrmann, 1995). These pathways convert carbohydrates into aromatic amino acids (such as phenylalanine), which is the first substrate for the phenylpropanoid pathway and thus a precursor for the synthesis of various phenolic compounds (Herrmann, 1995). Some enzymes belonging to the shikimate pathway, such as phenylalanine ammonia lyase (PAL), shikimate kinase (SK) and shikimate dehydrogenase (SDH), increased their activities under Fe deficiency in different plants (Vigani *et al.*, 2012).

In addition, the accumulation and the extrusion into rhizosphere of some flavin compounds such as riboflavins (Rbfl) have been observed (Cesco *et al.*, 2010; Rellán-Álvarez *et al.*, 2010). The exact role of accumulating flavins under Fe deficiency is still unknown and it has been hypothesized that flavin accumulation in the roots may be an integral part

of the Fe-reducing system of Strategy I plants (FCR is a flavin-containing protein). It has been observed that flavin accumulation and Fe reduction are localized in the sub-apical zone of roots (López-Millán *et al.*, 2000). These compounds can also be released into the soil and mediate the extracellular electron transfer between FCR and Fe deposits in the soil (Jin *et al.*, 2007). The accumulation of flavins in roots of Fe-deficient plants is supported by the strong induction of 6,7-dimethyl-8-ribityllumazine (DMRL) synthase activity, which catalyzes the fourth step of Rbfl biosynthesis (Rellán-Álvarez *et al.*, 2010). Riboflavin is a precursor of some compounds such as flavin adenine dinucleotide (FAD) and mononucleotide (FMN), which are cofactors of important enzymes whose activities are affected by Fe deficiency. Flavin adenine dinucleotide is a cofactor for the root plasma membrane FCR and for ferredoxin-NADP<sup>+</sup> reductase (FNR) of PET, while FMN groups are cofactors of complexes I and II of RET. It has been postulated that by affecting RET complexes Fe deficiency might allow the unused Rbfl to be transported outside the mitochondria and thereby also extruded from the roots (Higa *et al.*, 2010; Vigani, 2012).

All these findings suggest that root exudates are synthesized by cellular metabolism both as a specific response to mobilize Fe outside the cell and as unused/accumulating compounds in the cell, which result from metabolism influenced by Fe deficiency.

#### *Processes involved in exudate release from roots*

Root cells can produce and release exudates quickly in response to mainly abiotic or biotic stresses, particularly with Fe deficiency; however, the processes involved in their release and regulation are still poorly known (Mathesius & Watt, 2011).

The release of ROCs, mainly amino acids, PSs, phenolics and organic acids that act as complexing and reducing (in the case of phenolic compounds) agents of Fe<sup>III</sup>, is critical in the Fe acquisition strategy of plants. It was shown over 30 years ago that caffeic acid was the main organic compound released by roots of Fe-deficient tomato and peanut plants (Römheld & Marschner, 1983). It is still unknown which proteins are involved in the release of these phenolic compounds. Two proteins, PEZ1 and PEZ2 (Phenolics Efflux Zero 1 and 2), have been characterized as caffeic and protocatechuic acid transporters in rice and onion (Ishimaru *et al.*, 2011). There are strong indications that these proteins, as well as loading into the xylem sap, are also able to release phenolic compounds into the apoplast, where they help to dissolve precipitated apoplastic Fe.

ATP-binding cassette (ABC) transporters are a large and ubiquitous family of proteins that transport a wide spectrum of solutes (metals, lipids, xenobiotics, terpenoids, carboxylates, auxin and other organic compounds). They are primary active transporters that use the energy from nucleotide triphosphate hydrolysis. It can be hypothesized that many proteins in this family are involved directly in the release of root exudates, but up to now only one has been shown to be directly involved in the Fe-deficiency response by catalyzing the release of phenolic compounds (Rodríguez-Celma *et al.*, 2013).

Other types of proteins are able to transport phenolic compounds and carboxylates such as MATE (multi-drug and toxic compound extrusion) transporters. MATEs can export a wide array of solutes by a secondary active mechanism, generally using a sodium or proton gradient, and are mainly known to be involved in the resistance to aluminium (Al) toxicity by releasing citrate that complexes Al in soils (Magalhaes *et al.*, 2007). Another MATE protein is involved in the xylem loading of citrate, which is fundamental for Fe translocation within plants (FRD3; Durrett *et al.*, 2007). Another family of transporters is the Al-activated malate transporter (ALMT), which generally facilitates the diffusion of solutes from or to the cytosol in Al-contaminated soil. Some ALMTs have been related to mineral nutrition, although not specifically to Fe-deficiency, in maize roots and seem to be related to inorganic anion transport (ALMT1) or malate exudation (ALMT2; Ligaba *et al.*, 2012).

Recently the transporter involved in the release of PSs has been isolated and characterized in rice and barley (Nozoye *et al.*, 2011). The protein named TOM1 catalyzes the release of DMA from these plant species. It is a component of the major facilitator superfamily (MFS), which is a large family of membrane proteins that act as uniporters, cotransporters or antiporters. They are proteins that either facilitate the diffusion for uniporters or are secondary active transporters that need a positive electrochemical gradient of, generally, protons to move a solute through the membrane. It can be hypothesized that many other uniporters, channels or pores in the plasma membrane might be involved in the release of exudates from roots. However, because of their overlapping activities and the difficulty in characterizing these membrane proteins, there is a lack of evidence confirming this suggestion.

Finally, other transport systems might be involved in the exudate release from roots of Fe-deficient plants, and highly lipophilic compounds might be able to diffuse across the lipid bilayer; however, most root exudates are too polar to simply diffuse through membranes, especially when it is considered that they are often glycosylated, acylated or hydroxylated (Weston *et al.*, 2012). Further, some volatiles such as ethylene and NO might be directly released by roots, but it has been hypothesized that even in this case some specific transport system might be involved (Dudareva *et al.*, 2004). The exocytosis of compounds *via* a subcellular vesicle transport system is often proposed in response to

stress or for the release of mucilage from the root cap, but clear evidence confirming the presence of vesicular root exudation is still missing (see Badri & Vivanco, 2009).

### Effects of agrochemicals

In modern agriculture, agrochemicals are largely employed to control pests (target organisms) and to guarantee yield. The extensive use of agrochemicals has led to some concerns for the environment: most of these are associated with the long persistence of their residues, which can sometimes be found in the water-soil system after long periods (Chaudhry *et al.*, 2001). In addition, weed control practices can leave unwanted herbicide residues such as glyphosate (Ozturk *et al.*, 2008) in soil, which could represent a risk for non-target crops in the following management.

Plants possess detoxificative systems for the removing of agrochemicals made by a multiphase metabolism (Del Buono & Ioli, 2011). Rhizosphere processes can be affected directly by these toxic compounds. Root exudates such as ROCs, when secreted by stressed plants, may participate in the external transformation/biodegradation of pollutants, through activation of abiotic oxidants by exuded organic acids and through oxidation of pollutants by extracellular enzymes from the roots (Muratova *et al.*, 2009).

There are very few studies to determine how these chemicals can regulate or interfere with root exudation. This is surprising when herbicides such as PET inhibitors are considered. These herbicides inhibit the photosynthesis at the level of photosystem II, binding themselves to the protein D-1 at the site for plastoquinone (Del Buono *et al.*, 2011). Other herbicides disturb the photosynthesis by targeting enzymes involved in chlorophyll and pigment biosynthesis (Del Buono *et al.*, 2011). As a consequence of such interference, variations in the amount and type of compounds released by roots can be assumed. Nonetheless, increases in the release of carbohydrates and amino acids by roots of plants treated with *glyphosate*, a non-PET interfering and non-selective broad spectrum herbicide, have been described (Kremer *et al.*, 2005). In these plants a considerable amount of glyphosate, translocated from shoot to roots, is also released into the rhizosphere (Kremer *et al.*, 2005). Increases in nitrogen exudation have been described in *Brachiaria decumbens* Stapf. treated with glyphosate, glufosinate-ammonium and paraquat (Damin *et al.*, 2010). This is consistent with the larger ammonium accumulations found in weeds treated with glyphosate and glufosinate (Manderscheid *et al.*, 2005).

As well as their impact on the rhizosphere and environment, herbicides may have severe consequences for crops (non-target plants), influencing their development, growth inhibition, delayed development, yield reduction, germination decrease or necrosis (Magne *et al.*, 2006). Research on the effects of chlorsulfuron and diclofop-methyl on wheat showed that these chemicals reduced the uptake of P, K, N, S and Ca, and that of the micronutrients Zn, Cu, Mn and Fe (Osborne *et al.*, 1993). The uptake of nutrients that move principally to plant roots by diffusion was decreased by the herbicides more than that of nutrients that move principally by mass flow. Herbicides modified the ability of roots to explore soil rather than decreasing absorption at the root surface (Osborne *et al.*, 1993). Another study on the effect with wheat showed that chlorsulfuron reduced the uptake of Cu, Mn and Zn (Rengel & Wheal, 1997).

It is well known that the acquisition of Fe by plants is linked to S availability: S deficiency decreases the efficiency of PSs release in Strategy II plants and reduces the activity of root FCR in Strategy I plants (Astolfi *et al.*, 2006; Iacuzzo *et al.*, 2012). Herbicide metabolism in plants is S-consuming: plants often detoxify agrochemicals by conjugating them with glutathione (Del Buono & Ioli, 2011). In addition, herbicidal action determines oxidative stress, and the plants consume thiols and mainly glutathione to overcome this (Del Buono *et al.*, 2011). This suggests that herbicide detoxification in plants, because of the large amount of S in the form of reduced glutathione, can interfere with the Fe-acquisition process. There have been few studies to ascertain the effect of agrochemicals on Fe acquisition. However, it has been shown that these chemicals can have negative effects on Fe deficiency and also accelerate its expression, and exacerbate problems of Fe chlorosis (Franzen *et al.*, 2003). In sugar cane, the herbicides ametryn, trifloxysulfuron-sodium and 2,4-D reduced significantly the Fe content in plants, with an additive effect when the treatment was conducted in combination with the first two chemicals together (Reis *et al.*, 2008). Iron deficiency is also becoming prevalent in cropping systems receiving frequent applications of glyphosate. Its usage is increasing with the widespread use of glyphosate-resistant transgenic crops and the adoption of no-tillage cropping systems (Cerdeira & Duke, 2006). For soybean treated with glyphosate, field studies indicated that the chemical significantly decreased the Fe concentrations in plants; some greenhouse experiments also showed that Fe acquisition in leaves of certain sensitive cultivars was inhibited by glyphosate. These findings were explained on the basis of the inhibiting effect of the herbicide on the activity of FCR in roots (Bellaloui *et al.*, 2009). In addition, hydroponic experiments showed that 1.3–6% of the recommended dose of glyphosate caused a significant decrease in root uptake and translocation to shoots of radio-labelled Fe (Bellaloui *et al.*, 2009). Impairment of Fe nutrition seems to be an adverse effect of glyphosate application: other findings suggest that the chemical decreases root uptake and root to shoot transport of Fe in sunflowers. In this case the interference was also explained on the basis of an inhibiting effect of the herbicide on FCR; some experiments conducted on sunflowers demonstrated that glyphosate reduced the enzyme activity by

50% within 6 hours after the treatment and more severely at 12 and 24 hours after the treatment. The decrease in FCR activity was dose dependent and the inhibitory effect occurred at very small concentrations of glyphosate (Ozturk *et al.*, 2008).

#### **Open questions, concluding remarks and perspectives**

The role of ROCs in the soil–microbe–plant system involved in Fe acquisition processes (including their synthesis within plants and their release into the rhizosphere) has been widely studied as outlined in this review. However, from our present knowledge more as yet undefined functions of ROCs with regard to nutrient acquisition, need to be better understood and studied in more detail in the future for a better management of rhizospheric soil aimed at increasing Fe acquisition efficiency by crops.

In particular, most of the studies reported in the literature are based on hydroponic plant cultures, which can be compared with field conditions only to some extent. The main drawbacks of studying the spatial and temporal dynamics of nutrient availability within the rhizosphere in real conditions are the small soil volume and the available methods. Most of the methods are destructive and *ex-situ*, thereby biasing the results, especially information on fast interactions of ROCs with microorganisms and the soil matrix. For instance, Fe mobilization from soil minerals usually involves small amounts of material and therefore bulk mineralogical analyses such as XRD may not be sensitive enough in detecting variations in soil mineral composition. For this purpose micro-analytical methods should be adopted. As well as more traditional electron microscopy techniques (SEM, TEM and EPMA), micro X-ray diffraction or micro X-ray absorption spectroscopy with synchrotron light sources could provide rhizosphere research with new, powerful and non-destructive tools to understand the mechanisms of nutrient mobilization from soil minerals. Soils and especially the rhizosphere are extremely complex environments with a large degree of heterogeneity down to the nanometre scale. It is at the sub-micrometre scale that the interactions between soil constituents, plant roots and microorganisms take place and therefore it is at this scale (or even smaller) that future research should aim to investigate processes occurring in the rhizosphere.

In addition, because of the broad and heterogeneous chemical nature and concentration of ROCs, synergistic effects are not fully understood. Such effects could explain why certain compounds, for which a specific role in Fe mobilization has not been yet identified, are exuded in combination with substances that have well-established mobilizing properties. Synergistic effects may render low concentration of ROCs already efficient for a significant nutrient mobilization thus allowing plants to save C resources limiting their root exudation. Moreover, the actual concentration of the ROCs and their related turnover is a major issue that should be more carefully addressed. In particular, combined thermodynamic and kinetic studies involving Fe mobilization from soil constituents in relation to ROC exudation rates, sorption onto soil particles, microbial degradation activity and uptake by plants and microorganisms could define better the role of ROCs in promoting Fe solubility in soil up to concentrations suitable for plant growth. For this purpose, extraction methods as well as *in-situ* methods to study the fate of ROCs in soil need to be implemented.

A major effort is also needed to identify the transporters involved in the release of ROCs and to characterize their transport affinity and specificity. The ROC synthesis inside plants is also not completely clear and this topic needs to be studied in more detail, and there is very little knowledge on the regulation of both synthesis and release of ROCs in response to Fe deficiency. The information gained could be very important in determining the possibility, by breeding or biotechnologies, to increase plant synthesis and release ROCs with a positive impact on the acquisition process of Fe from naturally-present sources in soil. The enhanced release of specific root exudates could play an important role, having an impact on microbes interacting with Fe availability. A more detailed characterization of rhizospheric microbial communities will contribute to understanding the role of soil microbiota in plant-microbe interactions. The complete identification of very complex microbial communities, such as those inhabiting the rhizosphere, will be achieved by means of metagenomics and other molecular biology approaches. Very recently, with direct and high-throughput sequencing technologies, metagenomic approaches have tried to understand the genomic potential of the entire microbial community by determining the identities of all microorganisms. Analogously, metatranscriptomics are the direct analyses of transcribed material by gene expression. Unfortunately, the complete coverage of a complex microbial community, such as that inhabiting rhizosphere soil, consisting of few numerically predominant populations within huge numbers of low abundance ones, remains largely unattained (Morales & Holben, 2011).

These powerful methods, despite the limits and the technical challenges that will be probably overcome in the future, still remain the way to link specific functions to bacterial populations and species. It is likely, in fact, that a multispecies approach such as metatranscriptomics will lead to the identification of unknown plant-microbe relationships and as yet unidentified beneficial microbes. In particular, multi-approach future research will provide the knowledge to assess field conditions and even create new 'designed' plants to achieve the best plant-microbe-soil interactions. The identification of beneficial microbial species might encourage their use in the field to improve mineral plant nutrition and thus more sustainable food production. This kind of agricultural system requires the

reduction of agrochemicals including herbicides, which might interfere with ROC activities, Fe availability and microbial activity. For these reasons, it seems important to further our knowledge on the behaviour of agrochemicals in the soil-microbe-plant system, paying attention to what occurs in the Fe acquisition process of non-target plants. This might be one starting point to set up sustainable agronomical practices that encourage the use of natural resources already present in soil.

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Ancillary

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