

Availability of Mn, Zn and Fe in the rhizosphere

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Abstract

This review paper critically assesses the literature on soil-microbe-plant interactions influencing availability of micronutrients in the rhizosphere. The emphasis is placed on Zn and Mn, but Fe is also covered to some extent.

Micronutrient availability in the rhizosphere is controlled by soil and plant properties, and interactions of roots with microorganisms and the surrounding soil. Plants exude a variety of organic compounds (carboxylate anions, phenolics, carbohydrates, amino acids, enzymes, etc.) and inorganic ions (protons, phosphate, etc.) to change chemistry and biology of the rhizosphere and increase micronutrient availability. Increased availability may result from solubilization and mobilization by short-chain organic acid anions, amino acids and other low-molecular-weight organic compounds. Acidification of the rhizosphere soil increases mobilization of micronutrients (eg. for Zn, 100-fold increase in solubility for each unit of pH decrease).

For diffusion-supplied micronutrients, the uptake rate is governed by the soil nutrient supply. Fertilisation with micronutrients (more so in case of Zn than Fe) can be effective in increasing the concentration of micronutrients at the soil-root interface. In addition, micronutrient-efficient crops and genotypes can increase an available nutrient fraction and hence increase micronutrient uptake.

Our understanding of the physiological processes governing exudation and the soil-plant-microbe interactions in the rhizosphere is currently inadequate, especially in terms of spatial and temporal variability in root exudation as well as the fate and effectiveness of organic and inorganic compounds in increasing availability of soil micronutrients and undesirable trace elements. The interactions between microorganisms and plants at the soil-root interface are particularly important as well obscure.

Keywords: Exudation, manganese, microflora, micronutrients, rhizosphere, zinc

1. Introduction

Micronutrient-deficient soils are widespread; many millions of hectares of arable land worldwide are deficient in one or more micronutrient elements. This fact has been brought into sharp focus in the

last decade because of a large proportion of people being deficient in micronutrients (particularly Fe and Zn). Biofortification (Olsen and Palmgren, 2014; Vaz Patto *et al.*, 2015) via agronomic means

is becoming widespread (especially in case of Zn, Olsen and Palmgren, 2014; Tan *et al.*, 2015) and is dependent on the interactions of numerous soil and plant factors, some of which will be covered in this paper.

Plants suffer nutrient deficiency stress when availability of soil nutrients, and/or the amount of nutrients taken up, is below that required for sustaining metabolic processes in a particular growth stage. This may result from an inherently low nutrient status of soil, low mobility of nutrients within soil, poor solubility of the given chemical form of the nutrient, or the soil-microbe-plant interactions (eg. Rengel, 2002a; Marschner *et al.*, 2011).

Low-Zn soils may have low total Zn content (e.g., some leached acidic soils in tropics) or may have relatively large total Zn content, but a plant-available fraction is low because of soil chemistry favoring formation of sparingly soluble Zn complexes (Rengel, 2002a). Soils with low plant-available Zn (incorrectly called Zn-deficient soils because only living organisms can be Zn-deficient) are common in tropical and temperate climates, but are most widespread in regions with the Mediterranean type of climate (Sillanpää and Vlek, 1985). Low plant-available Zn was reported for soils of various characteristics: high and low pH, high and low organic matter, calcareous, sodic, sandy, wetland or ill-drained, limed acid soils, etc. In rice, Zn deficiency is common on neutral to alkaline pH soils containing more than 10 g organic matter/kg as well as on calcareous soils used for upland rice production (Rehman *et al.*, 2012).

Even though Mn is not considered in biofortification, there are important soil-plant and plant-microbe interactions that govern Mn availability in soil, justifying inclusion of Mn in this review. Manganese is the eleventh most common element in earth's crust, with an average concentration of total Mn of 900 mg/kg (Barber, 1995). Soils known to cause

Mn deficiency in susceptible crops are usually impoverished siliceous and calcareous sandy soils of neutral or alkaline pH that favour chemical and microbial oxidation and immobilization of plant-available Mn^{2+} . Even these soils, however, contain large reserves of total Mn relative to the amounts removed in crop harvests. Therefore, resulting Mn deficiency of susceptible crops is due to insufficient availability of soil Mn to plants rather than an absolute shortage of soil Mn (Rengel, 2000).

When grown on soils with low micronutrient availability due to either chemical or biological fixation, or spatial or temporal unavailability, micronutrient-efficient genotypes have a greater yield in comparison with inefficient ones, even when fertilized with smaller amounts or less frequently (Rengel and Marschner, 2005). The literature on differential micronutrient efficiency is voluminous, and will not be covered here; readers are referred to other reviews (eg. Rengel, 2001; Sadeghzadeh and Rengel, 2011; Rehman *et al.*, 2012).

Arbuscular mycorrhiza undoubtedly can increase accumulation of many nutrients, including Zn (for recent reviews see Rehman *et al.*, 2012; Srinivasagam *et al.*, 2013), but their practical importance varies in dependence on fertilization practices, soil and crop properties and management, etc. This paper will not cover mycorrhiza; instead readers are referred to recent review papers (eg. Casieri *et al.*, 2013; Recorbet *et al.*, 2013).

2. Soil pH – the master variable influencing nutrient availability

The soil pH represents measure of H^+ activity in the soil solution that is in a dynamic equilibrium with a negatively charged solid phase (Rengel, 2011). The H^+ ions are strongly attracted to these negative sites and can replace other cations from them. An unstirred

diffuse layer in a vicinity of a negatively charged surface has higher H^+ activity than the bulk soil solution (Rengel, 2002b). However, the pH value most relevant to soil and plant biogeochemical processes is the pH of the soil solution. For example, the pH of the soil solution is a better predictor of maize yields than the soil pH measured in soil/extractant mixtures (Moody *et al.*, 1998).

Soil pH is a dynamic parameter, with significant spatial (Behera and Shukla, 2015) and temporal differences (Kariuki *et al.*, 2010). Diurnal fluctuations of as much as one pH unit may occur, as well as season-to-season variations (Rengel, 2011). During seasons with low to moderate rainfall (whereby evapotranspiration exceeds precipitation), salts are not being removed by deep percolation; increased salt concentration tends to decrease pH by forcing exchangeable H^+ ions into the soil solution. Conversely, during wet seasons, salts are diluted/removed from the topsoil and pH increases (Rengel, 2002b). This season-to-season fluctuation in the total salt content should not be confused with long-term effects occurring over decades and centuries when increased rainfall leaches basic cations from soil causing acidification (Tang and Rengel, 2003).

High-pH soils range from calcareous (around pH 7) to alkaline saline and sodic soils (pH 8 and higher) (Qadir *et al.*, 2007). Such soils have major nutritional constraints (deficiency of cationic micronutrients and P) and/or toxicity of Na coupled with excess HCO_3^- , water deficiency (such soils frequently occur in arid areas), mechanical impedance and poor aeration (Clark and Baligar, 2000).

On the other side of the pH spectrum, close to 4 billion hectares (about 30% of the ice-free soils) in the world are acidic (Sumner and Noble, 2003). The worst situation is in the south-east and Pacific Asia and South America, with well over 50% of the total land in these areas having low pH. Almost 2/3 of all acidic soils in the world are Ultisols, Entisols and

Oxisols. In terms of use of acidic soils, they are mostly under forests (about 66%) and pastures (about 11%), with a relatively small proportion (5%) supporting crops (Sumner and Noble, 2003). In Australia alone, 33 million ha of agric land are highly acidic and further 55 million ha are at risk. Soil acidity has been identified as the most serious land degradation issue for Australia, with an estimated \$1 billion in lost production per year (CSIRO, 2004).

Soil pH has a dominant effect on solubility and therefore availability and potential phytotoxicity of ions (nutrients as well as toxic elements) (Clark and Baligar, 2000). Whereas low pH shifts the equilibrium toward free metal cations and protonated anions, higher pH favours carbonate or hydroxyl complexes. Therefore, availability of the micronutrient and toxic ions present in soil solution as cations (e.g. Al^{3+} , Mn^{2+} and Fe^{2+}) increases with increasing soil acidity (Porter *et al.*, 2004; Khabaz-Saberi and Rengel, 2010), whereas availability of those present as anions [MoO_4^{2-} , CrO_4^{2-} , SeO_4^- , SeO_3^- and $B(OH)_4^-$] increases with increasing pH (Rengel, 2002b; 2011).

At pH 5.5, Mn oxides solubilize and release Mn^{2+} into soil solution (Rengel, 2000; Porter *et al.*, 2004). At pH <3.8 Fe^{2+} becomes the dominant ion. At pH <3.2, H^+ and Fe^{2+} ions are the main exchangeable ions (Rengel, 2002b).

Solubility of Fe compounds in soils is relatively low. Consequently, toxicity of Fe may occur only in very acidic soils (pH<3.2) or soils contaminated with Fe-containing waste materials or under anaerobic conditions (Fageria *et al.*, 2008; Khabaz-Saberi *et al.*, 2010). Reduced conditions as well as lowering of pH favour conversion of non-available (non-toxic) Fe^{3+} into plant-available Fe^{2+} ions (Genon *et al.*, 1994) that is toxic if present at high ionic activity (Rengel, 2002b; Khabaz-Saberi and Rengel, 2010).

Manganese toxicity occurs when pH is 5.5 if sufficient total Mn is present in soil, and also at

higher pH in poorly drained soils where reducing conditions prevail (Rengel, 2000; Porter *et al.*, 2004; Khabaz-Saberi and Rengel, 2010). In case of Mn toxicity, redox potential is more important than just pH (Rengel, 2000). The expression of (pE+pH) (pE=-log of free-electron activity) is frequently used to characterize the soil with respect to solubilization of Mn compounds (values around 16 are associated with relatively high solubility of Mn^{2+} , the reverse applies to (pE+pH) values around 20) (Sumner *et al.*, 1991).

3. Rhizosphere

The rhizosphere is defined as the soil-root interface consisting of a soil layer varying in thickness between 0.1 and up to a few millimetres depending on the length of root hairs. Availability of nutrients in the rhizosphere is controlled by the combined effects of soil properties, plant characteristics, and the interactions of plant roots with microorganisms and the surrounding soil (eg. Dotaniya and Meena, 2015). The rhizosphere is characterised by relatively high concentration of easily degradable compounds exuded from roots (Vranova *et al.*, 2013), especially at the root tip (eg. Kaiser *et al.*, 2015).

Chemical conditions in the rhizosphere, including pH, are usually quite different from those in the bulk soil farther away from roots (Rengel, 2002b; Dotaniya and Meena, 2015). Root-induced changes in the rhizosphere pH are a result of the balance between H^+ and HCO_3^- (OH^-) excretion, the release of CO_2 by respiration and the excretion and decomposition of various organic compounds exuded by roots (Hinsinger *et al.*, 2003).

The balance between excretion of H^+ and HCO_3^- (OH^-) by plant roots depends on the cation/anion uptake ratio (Tang and Rengel, 2003; Jing *et al.*, 2012; Ma *et al.*, 2014). Greater net excretion of H^+ that accompanies greater absorption of cations than anions

results in rhizosphere acidification; the reverse occurs when uptake of anions exceeds that of cations, and therefore net excretion of HCO_3^- exceeds that of H^+ (Rengel, 2002b; Tang and Rengel, 2003). The form of nitrogen is the most influential one in determining the cation/anion ratio: ammonium-fed plants take up more cations than anions, and they usually have the more acidic rhizosphere than the bulk soil, whereas nitrate-fed plants take up more anions than cations and show the opposite relationship between rhizosphere and the bulk soil pH (Tang *et al.*, 2000; Tang and Rengel, 2003; Jing *et al.*, 2012; Ma *et al.*, 2014). It should be borne in mind, however, that the effects on rhizosphere pH are also dependent on plant species as well as the genotype of the particular species (Rengel and Marschner, 2005; Tanikawa *et al.*, 2014).

4. Manganese

4.1. Availability of Mn in the rhizosphere

Availability of Mn to plants depends on its oxidation state: the oxidized form (Mn^{4+}) is not available to plants, whereas the reduced form (Mn^{2+}) is. Generally, oxidation reactions are mostly biological, but reduction may be either biological or chemical in nature (Rengel, 2000). When oxygen is depleted from the growing medium, changes in the redox potential occur; in such a case, NO_3^- , Mn, and Fe serve as alternative electron acceptors for microbial respiration, and are transformed into reduced ionic species. This process increases the solubility and availability of Mn and Fe.

The chemistry of Mn in high-pH soils where poor availability of Mn may occur is not completely understood (eg. Clark and Baligar, 2000; Pan *et al.*, 2014). In aerated soils, Mn^{2+} concentration in soil solution should theoretically decrease 100-fold for every unit of pH increase (Barber, 1995). However, with

various organic compounds capable of complexing Mn and changing solubility equilibria, a decrease in Mn^{2+} concentration with an increase in pH is not that severe (eg. 5- to 10-fold decrease for a 0.5-unit pH increase, Neilsen *et al.*, 1992). The complexity of the relationship between Mn concentration in soil solution and pH was illustrated by Rule and Graham (1976) solubilisation, availability, uptake, soil solution</keyword></keywords><dates><year>1976</year></dates><urls></urls></record></Cite></EndNote> who used ^{54}Mn to determine soil Mn pools. With an increase in pH, soil Mn pools under *Trifolium repens* actually increased, whereas pools in soils planted to *Festuca elatior* decreased. So, soil supply of Mn is a complex variable that depends not only on soil chemistry but also on plant responses as well as activity of microorganisms.

Exudation of H^+ can lower the pH of alkaline soils and thus increase micronutrient availability (Rengel, 2000). Because availability of Mn is low at neutral to alkaline pH, acidification of rhizosphere has an important role in mobilising soil Mn (Clark and Baligar, 2000; Rengel, 2000). The pH changes in rhizosphere depend on the buffering capacity of soils, bulk soil pH, nitrogen sources, and other factors (eg. Tong *et al.*, 1997).

The nature and activity of root exudate components that might be involved in mobilization of Mn are unclear (Gherardi and Rengel, 2004; Mora *et al.*, 2009; George *et al.*, 2014). Both root and microbial cells exude low-molecular-weight substances that either mobilize Mn in the rhizosphere and/or facilitate transport across the root-cell plasma membrane (Rengel, 2001). The importance of organic acid anions (eg. malate and citrate) (eg. Mora *et al.*, 2009) remains unclear because their effectiveness in forming stable complexes with micronutrients is low at high pH (Rengel, 2000), where Mn deficiency usually occurs. Exudation of phytase might be important in

Mn acquisition from high-pH soils (eg. in landraces of oats and barley), but might need to be linked to some other plant traits to influence Mn uptake (George *et al.*, 2014). Further research on root exudates effective in mobilizing Mn from the high-pH substrates is warranted.

Oxalate, tartarate, L-malate, lactate, malonate, maleate, citrate and succinate were detected and quantified in exudates of *Medicago sativa* under a range of Mn supplies (Gherardi and Rengel, 2004). Exudation increased with plant age, but amounts of individual carboxylates remained constant in proportion to the total amount exuded. A significant increase in exudation of all carboxylates other than malonate and maleate was caused by deficient Mn supply (Gherardi and Rengel, 2004).

4.2. Microflora influencing Mn availability

Microorganisms that oxidize Mn decrease its availability to plants (Rengel, 2000). Indeed, up to 10-fold greater numbers of Mn-oxidizing bacteria (and fewer Mn reducers) have been found on roots of *Glycine max* in Mn-deficient patches of the crop than on plants outside these patches (Huber and McCay-Buis, 1993). Ratio between Mn-oxidizing and Mn-reducing bacteria may determine availability of soil Mn to plants. Altering that ratio by inoculating wheat roots with Mn-reducing bacteria might increase Mn uptake and improve growth in soil with low Mn availability (Marschner *et al.*, 1991). Inoculation of a low-Mn soil with the Mn-reducing fluorescent pseudomonad strain 2-79 increased Mn uptake by *Triticum aestivum* and *Glycine max* (see Rengel, 2000). Production of root exudates that are toxic to Mn-oxidizing microorganisms in the rhizosphere also increased Mn availability (Timonin, 1946).

The ribosomal intergenetic spacer (RISA) banding patterns of bacterial communities in the wheat

rhizosphere changed markedly with increasing soil Mn (Marschner *et al.*, 2003). The bacterial community structure in the wheat rhizosphere was significantly correlated with concentration of DPTA-extractable Mn in the rhizosphere, fertilizer Mn rate, shoot dry matter and total shoot Mn uptake (Marschner *et al.*, 2003), indicating significant soil-plant-microbe interactions governing Mn availability and uptake. The changes in community structure with increasing soil Mn concentration suggested that the competitive ability of bacterial species varied with dynamics of Mn availability (Marschner *et al.*, 2003).

Many of the organisms promoted as potential biological controls of soil-borne pathogens can reduce Mn in the rhizosphere and thereby increase Mn availability for plant uptake (Huber and McCay-Buis, 1993; Guest *et al.*, 2002). Seed bacterization with Mn-reducing organisms decreased fungal disease take-all and increased grain yield (Huber and McCay-Buis, 1993). In contrast, the mode of action of take-all fungus (*Gaeumannomyces graminis*) is oxidation of Mn in the infection court (at the hyphal tips) (Rengel, 1997a; Guest *et al.*, 2002), thus depriving the host root of Mn, weakening root cell walls, and making roots susceptible to infection (Rengel *et al.*, 1996).

4.3. Mn toxicity

Soils with excess Mn causing toxicity to plants are widespread; after Al, excess Mn is the most growth-limiting factor in acid soils worldwide (see Rengel, 2000). High concentrations of Mn in soil (attributed to mild acidification) are a widespread nutritional problem in southeastern Australia (eg. Weir, 1988). In addition, high concentrations of Mn in the soil solution also occur in poorly drained and reduced environments (Sparrow and Uren, 1987) associated with waterlogged soils.

Waterlogging is a complex constraint, causing numerous changes not only in plants, but also in soil (Khabaz-Saberi *et al.*, 2006; Khabaz-Saberi and Rengel, 2010; Shabala, 2011; Huang *et al.*, 2015). In soil, waterlogging causes reduction of oxidized compounds, eg. Fe^{3+} and Mn^{4+} (Dufey *et al.*, 2009), leading to an increase in concentration of Mn^{2+} (as well as Fe^{2+}) in soil solution beyond the plant nutritional requirements. High to toxic concentrations of Mn were observed in shoot tissues of wheat after waterlogging on acidic soil (Khabaz-Saberi *et al.*, 2006).

4.4. Zinc

Zinc is usually added to soil as an inorganic fertilizer (Rengel, 2002b; Rehman *et al.*, 2012; Singh *et al.*, 2014). The most common form is Zn sulphate (ZnSO_4) (23-55% Zn, depending on the water content), whereas other forms (percentage of Zn indicated in parentheses) include the Zn-ammonia complex (10%), Zn nitrate (22%), Zn oxide (50-80%), Zn oxysulphate (40-55%), Zn carbonate (52-56%), Zn chloride (48-50%), and organics, such as lignosulphonate (5-8%) and synthetic chelates (with EDTA, 14% Zn; with HEDTA and NTA, 9% Zn) (Shuman, 1998).

Most Zn fertilizers dissolve relatively slowly in soil, which in some cases may be too slow to supply adequate amounts required for the vigorous plant growth (Rengel, 2002a; Rehman *et al.*, 2012). Even when soluble salts (such as Zn sulphate) are used, soil equilibria result in conversion of released Zn into less soluble forms (generally carbonates, oxides and various hydroxides). Also, the movement of Zn from fertilizers down the soil profile is relatively poor, unless chelated forms are used (Alloway, 2009).

Increasing soil pH, especially above 6.5, results in decreased extractability and plant availability of soil Zn. Soil Zn is usually more available in soils with

greater organic matter content (Iratkar *et al.*, 2014) and a relatively higher proportion of clay (Rengel, 2002a; Alloway, 2009). In contrast, Zn extractability from soil is negatively related to phosphate (Yang *et al.*, 2011) and calcium carbonate content in soil (Iratkar *et al.*, 2014). Therefore, low plant availability of Zn can be expected in calcareous soils.

4.5. Exudation of organic compounds into the rhizosphere

When subjected to Zn deficiency, plants exude a range of organic acid anions and aminoacids (Hajiboland *et al.*, 2005; Rasouli-Sadaghiani *et al.*, 2011; Soltani *et al.*, 2014), whereas exudation of phytosiderophores was observed in many plant species (eg. Gries *et al.*, 1998; Tolay *et al.*, 2001), but not always consistently (Pedler *et al.*, 2000). Zn-efficient genotypes of wheat (Daneshbakhsh *et al.*, 2013) and rice (Widodo *et al.*, 2010) released greater amounts of phytosiderophores and also took up more Zn than Zn-inefficient genotypes (Erenoglu *et al.*, 1999). However, a positive correlation between phytosiderophore exudation and Zn efficiency was not always found in wheat genotypes (Cakmak *et al.*, 1998), indicating a complexity of the Zn efficiency syndrome in wheat. Similar differential responses were observed among wild grasses adapted to neutral or alkaline calcareous soils likely to be low in available Zn: even though *Hordeum murinum* and *Agropyron orientale* exuded large amounts of phytosiderophores under Zn deficiency stress (Cakmak *et al.*, 1996), *Hordelymus europaeus* did not exude appreciable amounts of phytosiderophores when Zn deficient, but was clearly capable of exuding them under Fe and Cu deficiency (Gries *et al.*, 1998).

A range of organic acid anions (malate, maleate, fumarate and *cis*-aconitate) and amino acids (alanine, valine, proline, aspartic acid and glutamic acid) were

exuded by barley genotypes at low Zn supply, at least partially explaining genotypic differences in Zn efficiency (Rasouli-Sadaghiani *et al.*, 2011). In wheat, various amino acids were released into the rhizosphere influencing Zn availability and uptake (Soltani *et al.*, 2014). In rice, greater exudation of malate was associated with increased Zn efficiency (Hajiboland *et al.*, 2005). However, whether exudation of citrate enhances Zn mobilization appears to be soil dependent (Duffner *et al.*, 2012), even though more soils would need to be tested to ascertain this phenomenon.

4.6. Rhizosphere microflora

Soil Zn availability and the plant Zn status influence the composition and abundance of microbial communities in the rhizosphere (Rengel, 1997b; Dotaniya and Meena, 2015). Some microbial species may be instrumental in increasing Zn availability in the rhizosphere (see Muhammad *et al.*, 2014) because soil microflora was not Zn-deficient in low-Zn soil (Khan and Joergensen, 2010). Wheat genotypes differing in Zn efficiency may differentially influence microbial populations in the rhizosphere (Rengel *et al.*, 1998). Zinc deficiency increased abundance of fluorescent pseudomonads in the rhizosphere of all wheat genotypes tested so far, but the effect was particularly obvious for Zn-efficient genotypes (Rengel, 1997b). Further work on a possible causal relationship between composition and abundance of rhizosphere bacteria and an increased capacity of crop genotypes to acquire Zn under deficient conditions is warranted.

Diazotrophs isolated from the rice rhizosphere solubilized Zn-containing compounds (Sarathambal *et al.*, 2015). Moreover, bacteria isolated from Zn-hyperaccumulator *Sedum alfredii* increased DTPA-extractable Zn in the rice rhizosphere and enhanced Zn uptake and biofortification of rice grain (Wang

et al., 2014). Hence, using specific bacterial strains may be helpful in enhancing soil Zn availability as well as plant uptake and accumulation in grain (biofortification) (for a recent review see Muhammad *et al.*, 2014) in a range of crops, including wheat and soybean (Aketi *et al.*, 2014).

5. Conclusions

Micronutrient availability in the rhizosphere is influenced by the complex microbe-plant-micronutrient interactions. Comprehensive studies of these interactions will improve our understanding of the rhizosphere effects influencing growth and nutrition of plants in the environments with low availability of Zn, Mn and other micronutrients. This knowledge will allow integration of abiotic (soil chemistry, water, etc.) and biotic factors (plants, microorganisms, etc.) into dynamic agricultural ecosystems that will underpin production of crops with improved micronutrient nutrition as a cornerstone of sustainable agriculture and biofortification for nutrition of susceptible human populations.

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