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## Roles of manganese in plants at physiological and biochemical perspectives

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### Abstract

Manganese, being an essential micronutrient plays crucial roles in physiological and biochemical processes in plants. The essentiality of available oxidised Manganese ( $Mn^{2+}$ ) in most acid soils (toxic) at low pH (<5.5) is recognised in plant processes. In contrast,  $Mn^{2+}$  is insufficient at higher soil pH (up to 8.0) in alkaline soils. The present review includes manganese dynamics in soil, absorption by rhizosphere, physical transport mechanisms,  $Mn^{2+}$  transporters in plants,  $Mn^{2+}$  functioning at the level of organelles, and its uptake by leaf cells. Besides, metabolic roles of manganese as cofactors of several enzymes that involve in carbon assimilation, nitrogen assimilation, mediation of growth regulation through hormones, are discussed. The physiological and biochemical indices manifested plausibly by  $Mn^{2+}$  deficiency and toxicity in plants are presented for practical importance. The mechanisms of tolerance and susceptibility of plants to  $Mn^{2+}$  at cellular level in terms of synthesis of certain organic molecules, anti-oxidant systems, sequestration of manganese internally, ionic interaction etc. have been discussed. Evidences on plant growth, morphology and yield & yield components of crop plants modulated by Mn distribution in plants are portrayed. Physical environmental factors related to manganese availability to plants occupy a fair discussion in the chapter. Finally, influences of manganese on pest and diseases infestation in plants are exemplified in the paper.

**Keywords:** Acis soil, manganese, dynamics, transport, soil pH, rhizosphere, crops

### Introduction

Manganese (Mn) is one of the essential micronutrients for growth and development of plants, and it imparts metabolic roles within different plant cell compartments (Alejandro *et al.*, 2020)<sup>[9]</sup> measured in terms of some physiological and biochemical indices in plants (Yomso and Baharli, 2021)<sup>[207]</sup>. For instance, in photosynthesis process, it is an essential cofactor for the oxygen-evolving complex (OEC) as it catalyses the water-splitting reaction in photosystem II (PSII). The sub cellular Mn segregation helps to maintain Mn-dependent metabolic processes like glycosylation, ROS scavenging, photosynthesis etc. mediated by transport proteins. However, Mn beyond a critical limit interfere physiological processes, and Mn becomes toxic to all susceptible plants on poorly drained and acid soils. In contrast, Mn deficiency stands as a severe nutritional disorder in dry, well-aerated and calcareous soils, and in soils containing high amounts of organic matter. The effects of Mn on various aspects of plants especially growth and development, Physio-biochemical aberrations due to toxicity and deficiency of  $Mn^{2+}$ , effects of environmental factors on fate of Mn in plants etc. and mechanism of plants to cope with these situations have been reviewed.

### Source of Manganese for plants

Manganese is included in the category of the most plentiful and extensively dispersed metals in nature. It consists of about 0.1% of the Earth's crust (Emsley, 2003)<sup>[43]</sup>. The element is found in combining with oxygen, sulfur, carbon, silicon, and chlorine (Turekian and Wedepohl, 1961)<sup>[191]</sup>. Manganese is available in soil in 11 oxidation states, ranging from -3 to 7+ viz.,  $Mn^{2+}$ ,  $Mn^{3+}$  (e.g.,  $Mn_2O_3$ ),  $Mn^{4+}$  (e.g.,  $MnO_2$ ); but it's abundant in biological systems as  $Mn^{2+}$ ,  $Mn^{3+}$ ,  $Mn^{4+}$ . So, availability of Mn to plants depends on its oxidation state.  $Mn^{2+}$  is the most soluble species, and  $Mn^{2+}$  can be readily transported into root cells and transported to the shoot. The oxidized species,  $Mn^{3+}$  and  $Mn^{4+}$  form insoluble oxides that form sediment rapidly (Stumm and Morgan, 1996)<sup>[182]</sup>. Therefore, dynamics of Mn in soils are recognized by a balance between soluble  $Mn^{2+}$  and insoluble Mn oxides ( $MnO_x$ ).

The solubility of  $Mn^{3+}$  and  $Mn^{4+}$  are very low in acid soil condition (Guest *et al.*, 2002)<sup>[66]</sup>. Both pH and redox conditions determine Mn bioavailability in soils (Marschner, 1995; Porter

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*et al.*, 2004)<sup>[119]</sup>. In most acid soils at low pH (<5.5) and at an increased redox potential of Mn, oxides can be easily reduced in the soil exchange sites (Kogelmann and Sharpe, 2006)<sup>[98]</sup>, increasing the concentration of soluble Mn<sup>2+</sup> (Watmough *et al.*, 2007)<sup>[197]</sup>. At higher soil pH (up to pH 8), Mn<sup>2+</sup> auto-oxidation forms MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>3</sub>O<sub>4</sub> and even Mn<sub>2</sub>O<sub>7</sub>, which are not normally accessible to plants (Ducic and Polle, 2005; Humpries *et al.*, 2007)<sup>[40]</sup>. At higher soil pH, Mn is adsorbed into soil particles, and it becomes unavailable to plants (Fageria *et al.*, 2002)<sup>[44]</sup>. Mn insufficiency in plants is mainly prevalent in alkaline soils, where oxidization of Mn<sup>2+</sup> to unavailable MnO<sub>x</sub> is preferred. The geographical distribution of such soils is in the northern part of Europe, the UK, USA, China, and in southern Australia commonly (Husted *et al.*, 2009; George *et al.*, 2014)<sup>[87, 54]</sup>. Besides level of pH, the oxygen status (pO<sub>2</sub>) in soil and soil microorganisms too, decide Mn dynamics in soils. Plant root exudates can alter the Mn accessibility in the rhizosphere. The Mn redox potential in soils occupies chiefly the competent soluble highly mobile oxidants (molecular O<sub>2</sub>), and soluble reducing organic molecules, emerged from soil organic matter and biological sources. In aerobic soils, Mn oxidation is favored rather than reduction of MnO<sub>x</sub> by microorganisms because of the high mobility and redox potential of O<sub>2</sub> (Lovely, 1995)<sup>[113]</sup>. By contrast, water logging causes a reduction of MnO<sub>x</sub> most likely by decreasing the O<sub>2</sub> concentration, leading to an increase of plant-available Mn<sup>2+</sup> in soil solution up to toxic levels (Khabaz-Saberi *et al.*, 2006)<sup>[95]</sup>. El-Jaoual and Cox (1998)<sup>[42]</sup> also reported that an excess of water with water logged condition or applications of organic material favors a reducing environment. The role of various organic molecules is to dissolve unavailable Mn from Mn oxides, and transform them into an available form of Mn for plants through a reduction process (Laha and Luthy, 1990)<sup>[100]</sup>.

The oxidation of Mn<sup>2+</sup> in environments with abundant O<sub>2</sub> is slow if either biological catalysts or microorganisms are absent for the oxidation process (Sparrow and Uren, 2014)<sup>[175]</sup>. In fact, microorganisms have the ability to catalyze Mn<sup>2+</sup> oxidation 103 times faster than an abiotic oxidation (Morgan, 2005)<sup>[125]</sup>. The enzymes produced by some microorganisms oxidize Mn<sup>2+</sup> directly or generate extracellular superoxide to produce insoluble MnO<sub>x</sub> (Hansel *et al.*, 2012; Zhang *et al.*, 2014; Marschner, 1995)<sup>[69, 208, 153]</sup>. Instead, some other microorganisms reduce MnO<sub>x</sub> and thereby augment Mn accessibility for plant uptake (Rengel, 2015). Meteorological indices such as temperature, humidity affect soil Mn availability by modulating the activity of Mn-oxidizing microorganisms (Sparrow and Uren, 2014)<sup>[175]</sup>. Therefore, a considerable population of Mn-oxidizing and Mn reducing microorganisms is important key factor in the availability of soil Mn for plant uptake.

The soil types determine the total Mn content in it. There is ambiguity regarding Mn contents in soil. Because, in some instances, total Mn contents in soils may vary from 20 to 10,000 mg kg<sup>-1</sup> soil (Sparks, 1995)<sup>[174]</sup> or 450 - 4,000 mg Mn kg<sup>-1</sup> soil (Adriano, 2001)<sup>[3]</sup>. It's also reported that the total Mn contents in acid soils without liming (pH about 4.4) are 15 to 17 mg kg<sup>-1</sup> (Hue and Mai, 2002)<sup>[85]</sup>. In practice, lime application beyond a requirement value decreases soluble Mn in acid soils, and it accelerates soil pH (Hue and Mai, 2002)<sup>[85]</sup>. The mobilization of Mn<sup>2+</sup> around the root rhizosphere is also under the control of the acidification caused by the release of H<sup>+</sup> or low molecular weight organic acids from

plants (Rengel and Marschner, 2005)<sup>[153]</sup>. Because, in acidic condition, anionic organic acids such as arabinose, citric acid and malic acid form complexes with Mn<sup>2+</sup> as these can dissolve MnO<sub>x</sub> (Ryan *et al.*, 2001; Neumann and Romheld, 2001; Tsuji *et al.*, 2006)<sup>[160, 132, 190]</sup>. Mn content in soil is also determined by environmental conditions. For instance, soluble and exchangeable Mn are higher under warm waterlogged conditions in acid soils following hot, dry summers due to the limitation of Mn-oxidizing organisms. Instead, there is reduction of Mn oxides in these soils (Sparrow and Uren, 1987; Conyers *et al.*, 1997)<sup>[176]</sup>.

Based on the soil condition, if the rhizosphere is acidic due to root excretion of H<sup>+</sup> and aerated, there is reduction of MnO<sub>x</sub> by microorganisms. But, in aerated and calcareous soils or in poorly aerated or submerged soils, Mn availability is decreased by the Mn-oxidizing bacteria. Besides, negatively charged organic matter forms Mn complexes leading to lessening of the amount of exchangeable Mn. Of course, the Mn present in organic matter exchanges with the H<sup>+</sup> released from the roots (Bradl, 2004)<sup>[17]</sup>.

The exudation of protons (H<sup>+</sup>), carboxylates, and enzymes by plant roots becomes an important factor of Mn dynamics in soil. Proton exchanges with immobilized Mn in the rhizosphere. Organic matter, clay minerals (negatively charged) and also alkaline soils immobilize Mn to make it available for the exchange process (Rengel, 2015). Strong rhizosphere acidification in some Mn-hyperaccumulators (e.g. *Phytolacca* species) facilitates Mn uptake (Lambers *et al.*, 2015)<sup>[101]</sup>. Noteworthy, Even carboxylate exuded from roots chelates with Mn and reduces Mn<sup>4+</sup> to Mn<sup>2+</sup> in either acidic or alkaline soils for its availability and uptake (Jauregui and Reisenauer, 1982; Gherardi and Rengel, 2004)<sup>[91]</sup>.

The dominant organic P in soils i.e. Phytate (inositol hexaphosphate) has the potential to complex Mn<sup>2+</sup>. Phytases catalyze the degradation of phytate and increases the Mn availability by releasing Mn<sup>2+</sup> (George *et al.*, 2014)<sup>[54]</sup>. The release of carboxylates into the rhizosphere is a mechanism for the acquisition of Mn alike with P (Nuruzzaman *et al.*, 2006). But, Mn<sup>2+</sup> acquisition is decreased by elevated levels of soil-P by the reduction of carboxylate and phytase exudation (Lambers *et al.*, 2015; Giles *et al.*, 2017)<sup>[101, 57]</sup>. However, a competition between Mn<sup>2+</sup> and P may decrease in Mn uptake under elevated P supply rather than formation of a Mn-P complex (Pedas *et al.*, 2011)<sup>[142]</sup>.

### 3. Absorption and translocation Mn in plants

Plants absorb Mn<sup>2+</sup> from the rhizosphere initially by passive process where Mn<sup>2+</sup> is exchanged freely along with Ca<sup>2+</sup> or other cations in the rhizosphere which is facilitated by the negatively charged cell wall constituents of the root-cell apoplastic spaces (Humphries *et al.*, 2007; Clarkson, 1988)<sup>[86]</sup>. It's followed by an active mechanism in epidermal root cells for transport it into the plants (Marschner, 1995; Gherardi and Rengel, 2003; Pittman, 2005)<sup>[153]</sup>. The uptake of Mn<sup>2+</sup> into the symplast is controlled by plant metabolism (Humphries *et al.*, 2007)<sup>[86]</sup>. Plasma membrane Ca<sup>2+</sup> channels are generally permeable to Mn<sup>2+</sup> and allow uptake of Mn<sup>2+</sup> (Wymer *et al.*, 1997; White *et al.*, 2002)<sup>[204]</sup>.

Manganese ion transportation is caused by the high capacity of ion carriers and channels through the plasma membrane (Humphries *et al.*, 2007)<sup>[86]</sup>. This Mn<sup>2+</sup> uptake pathway is limited by its competition with Ca<sup>2+</sup> as Mn<sup>2+</sup> concentration in soil usually far less abundant than Ca<sup>2+</sup> (Broadley *et al.*, 2012)<sup>[19]</sup>. The transpiration stream preferably is involved in

the Xylem transport of the ion from roots to the above-ground parts of plants (Rengel, 2001). The transport of ion within the phloem is selective, and driven by the concentration gradient from sources to sinks (Marschner, 1995) <sup>[153]</sup>. Since Mn has lower mobility in the phloem, its transport and redistribution varies with plant species and developmental stages (Herren and Feller, 1994; Li *et al.*, 2017) <sup>[78]</sup>.

In plants, Manganese accumulate predominantly in the shoots than in the roots (Page and Feller, 2005; Page *et al.*, 2006) <sup>[137, 138]</sup>. The transport proteins with a broad specificity such as Fe<sup>2+</sup> and Ca<sup>2+</sup> transporters has the ability to transport and maintain adequate Mn concentrations in the cytoplasm (Pittman, 2005). Alternatively, Mn<sup>2+</sup> transporters in plants can transport other divalent cations, such as Fe<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Ca<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>. If Fe transport activity is inhibited in different Fe-binding domains by modifications of specificity, Mn<sup>2+</sup> transport capability is unaffected (Chu *et al.*, 2017; Dubeaux *et al.*, 2018) <sup>[39]</sup>. So, in the case of Mn-deficient conditions, *AtNRAMP1* is moderately up-regulated, and plants accumulate less Mn in shoots under Mn deficiency. So, the protein *AtNRAMP1* functions as a high-affinity Mn<sup>2+</sup> uptake transporter (Cailliatte *et al.*, 2010) <sup>[24]</sup>. The major Fe uptake ZIP transporter AtIRT1 of dicots may help to carry the active Mn<sup>2+</sup> uptake also (Castaings *et al.*, 2016) <sup>[25]</sup>. In rice, transporters involved in uptake, xylem loading and root-to-shoot translocation of Mn has been studied well (Shao *et al.*, 2017) <sup>[169]</sup>. The first Mn 2+ transporter found in rice roots was OsNRAMP5 (Sasaki *et al.*, 2012) <sup>[163]</sup>. Mn<sup>2+</sup> uptake and translocation into the stele facilitated by transporters, is localized to the plasma membrane of the proximal side of these cell layers (Ueno *et al.*, 2015) <sup>[192]</sup>.

In rice, Mn<sup>2+</sup> is transported by OsNRAMP3 from the xylem to the phloem at the basal node, followed by its distribution to young leaves, panicles and root tips. At high Mn availability, Mn is circulated to mature tissues (Yamaji *et al.*, 2013).

Manganese distribution in plants is facilitated by importers and exporters. Importers transfer Mn from the extracellular and intercellular spaces into the cytosol. The glaring example of importers are the 'Natural Resistance Associated Macrophage Protein' (NRAMP) family, the 'Zinc-Regulated Transporter/Iron-Regulated Transporter' (ZRT/IRT)- related Protein (ZIP) family, and the 'Yellow Stripe-Like' (YSL) family. Exporters exclude Mn from cytosol into intracellular spaces or into the apoplast *viz.*, Cation Diffusion Facilitator/Metal Transport Protein (CDF/MTP) family, the Vacuolar Iron Transporter (VIT) family, the Ca<sup>2+</sup>/Cation Antiporter (CaCA) super family, the Bivalent Cation Transporter (BICAT) family, and the P<sub>2A</sub>-type ATPase family (Xia *et al.*, 2010; Li *et al.*, 2014; Tiwari *et al.*, 2014) <sup>[189]</sup>. A Cd/H antiporter is also involved in Mn accumulation in vacuoles to avoid Mn toxicity in cell (Shigaki *et al.*, 2003) <sup>[172]</sup>. Some of the Mn<sup>2+</sup> uptake transporters found in the plasma membrane are: AtIRT1, Nramp, AtYSL (Ducic and Polle, 2005; Pittman, 2005) <sup>[40]</sup> and PHO84 (Ducic and Polle, 2005) <sup>[40]</sup>. Nramp transports protein also, and is localized in the vacuolar membrane tonoplast but not in the plasma membranes (Thomine *et al.*, 2003) <sup>[185]</sup>. Mn 2+ transport and vacuolar localization was found in rice, where. *OsMTP8.1* was highly expressed in older leaves, and it was induced and repressed by high and low Mn<sup>2+</sup> levels, respectively (Chen *et al.*, 2013).

Manganese plays a significant role in chloroplast function, as it is essential for photosynthesis process. There is a high requirement for Mn for the configuration of the Mn<sub>4</sub>Ca-

cluster in the OEC of PSII, leading to water splitting. To facilitate Mn for chloroplast function, two members of the BICAT family, which are related to the GDT1 protein in yeast (Demagde *et al.*, 2013) <sup>[35]</sup> and the Mn<sub>x</sub> protein in the *Cyanobacterium Synechocystis* (Brandenburg *et al.*, 2017) <sup>[18]</sup>, are identified for Mn loading of the chloroplast and the distribution within this organelle. AtBICAT1 (Mn-sensitive phenotype of the *pmr1* yeast mutant) involves in Mn<sup>2+</sup> and Ca<sup>2+</sup> flux into thylakoids for assembly of the Mn<sub>4</sub>Ca-cluster, and also in the homeostasis of stromal Ca<sup>2+</sup>, for regulating processes in chloroplasts (Sello *et al.*, 2018) <sup>[167]</sup>. Disruption of *AtBICAT2* (Mn-sensitive phenotype of the the *pmr1* and *pmr1gdt1* yeast mutants) produced severe chlorosis, impaired plant growth, defective thylakoid stacking, and harsh reduction of PS II complexes, reduced photosynthetic activity (Eisenhut *et al.*, 2018; Frank *et al.*, 2019) <sup>[52, 41]</sup>. Manganese is also effluxes into the mitochondria (Ducic and Polle, 2005 Pittman, 2005) <sup>[40]</sup>, chloroplasts and Golgi (Lanquar *et al.*, 2010) <sup>[102]</sup>. Ca- ATPase transports Mn<sup>2+</sup> into Golgi apparatus (Mills *et al.*, 2008) <sup>[123]</sup>. BICAT proteins act as Mn<sup>2+</sup> and Ca<sup>2+</sup> transporters (Hoecker *et al.*, 2017; Frank *et al.*, 2019) <sup>[79, 52]</sup>. The Cation/Ca<sup>2+</sup> exchanger (CCX) and the H<sup>+</sup>/Cation exchanger (CAX) families are both members of the CaCA super family present within all plants. In plant, between the two P-type Ca<sup>2+</sup>-ATPases (2A & 2B), P<sub>2A</sub>-type Ca<sup>2+</sup>-ATPases have a role in Mn<sup>2+</sup> transport as it has not auto-inhibitory domain (Johnson *et al.*, 2009) <sup>[93]</sup>. In Arabidopsis, six mitochondrial Ca<sup>2+</sup> uniporter (MCU) isoforms are predicted to be localized in mitochondria (Stael *et al.*, 2012) <sup>[177]</sup>. The cMCU protein mediates Ca<sup>2+</sup> fluxes across the chloroplast envelope, not in mitochondria (Teardo *et al.*, 2019) <sup>[184]</sup>. In peroxisomes, Mn acts as an important cofactor of the peroxisomal MnSOD. This enzyme is prevalent in some plant species e.g. pea, cucumber, and pepper (Corpas *et al.*, 2017) <sup>[33]</sup>.

#### 4. Manganese uptake by leaf cells

The distinctiveness of Mn<sup>2+</sup> transporters in the plasma membrane of leaf cells is largely difficult to understand. OsNRAMP6 functions as Fe and Mn<sup>2+</sup> transporter when expressed in yeast (Peris-Peris *et al.*, 2017) <sup>[143]</sup>. Its expression in shoots is localized at the plasma membrane. A second transporter for Mn uptake into leaf cells of rice is OsYSL6 which transports Mn<sup>2+</sup>-NA complexes from the leaf apoplast to the symplast (Sasaki *et al.*, 2011) <sup>[162]</sup>. It is localized in the plasma membrane of older leaves, and has ability of OsYSL6 to increase Mn<sup>2+</sup> influx. The expression level of OsYSL6 does not change irrespective of Mn deficiency or excess. So, OsYSL6 acts as a constitutive Mn importer in leaf cells.

#### 5. Role of Mn in plant metabolism

Manganese plays a pivotal role in the water-splitting process of photosystem II (PSII). Here, electrons are generated and transported through electron transport chain of chloroplast. Finally, assimilatory powers (ATPs and NADPHs) are produced through the process of Cyclic and Non-cyclic photophosphorylation. The main mechanism of photolysis of water is carried out in presence of a cluster of four Mn atoms coupled with the oxygen evolving complex (OEC), and combined to the reaction center protein (D1) of systemf PSII (Goussias *et al.*, 2002) <sup>[63]</sup>. Then, four positive charges oxidize two water molecules, releasing one O<sub>2</sub> molecule and four protons. Therefore, Mn cluster is a catalyst in water oxidation (Zouni *et al.*, 2001) <sup>[209]</sup>.



In C<sub>3</sub> photosynthesis, RuBP carboxylase reaction and ATP synthesis (Pfeffer *et al.*, 1986) [144] is also catalysed by Mn (Houtz *et al.*, 1988) [83]. The biosynthesis processes of fatty acids, acyl lipids and proteins involve Mn (Ness and Woolhouse, 1980) [131]. Besides, Mn is an activation and cofactor of many enzymes (e.g. Mn SOD, Mn catalase, Pyruvate dismutase, Pyruvate carboxylase, and PEP carboxylase) in plants (Burnell, 1988; Ducic and Polle, 2005) [22, 40]. Mn is essential for biosynthesis of chlorophyll molecule, aromatic amino acids (e.g. tyrosine), secondary products, like lignin and flavonoids, isoprenoids (Lidon *et al.*, 2004) and assimilation of nitrate (Ducic and Polle, 2005) [40]. Therefore, Mn controls metabolic processes such as photosynthesis, respiration, synthesis of amino acids and Indol acetic acid activation throughout the IAA-oxidases (Burnell, 1988) [23].

## 6. Manganese and Physiological disorders

A low level of Mn is essential for normal growth and development of plants. In plant leaves, Mn is variably present in between 30-500mg Kg<sup>-1</sup> dry mass (Clarkson, 1988) [29]. But supra optimal concentration of Mn is toxic to plants (Migocka and Klobus, 2007) [122], where its effects are dose responsive to produce toxicity symptoms proportionately with an exceptional inter and intra specific differences in Mn concentration to exhibit symptoms (Foy *et al.*, 1988) [50]. The common symptoms of Mn aberration in plants are both interveinal and marginal leaf chlorosis, necrotic leaf spots, and ultimate reduction in growth rate due to physiological halt. These were previously reported elsewhere for canola (Moroni *et al.*, 2003) [127], clover (Rosas *et al.*, 2007) [157], ryegrass (Mora *et al.*, 2009), barley and cowpea (Demirevska-Kepova *et al.*, 2004; Fuhrs *et al.*, 2008) [36]. The most reliable indicator of Mn toxicity in plants is the appearance of necrotic brown spots and chlorotic leaves (Wissemeier and Horst, 1991). Sometimes, Mn toxicity symptom is confused with the similar interveinal chlorosis due to Fe deficiency (Sarkar *et al.*, 2004) [161]. The deficiency of other elements *viz.*, Ca, Mg, K, Fe and Si etc aggravates the Mn toxicity in plants (Abou *et al.*, 2002) [2]. In rice (*Oryza sativa* cv. Safari) receiving excess Mn in a nutrient solution, leaves accumulate more Mn in comparison to its accumulation in roots (Lidon, 2001).

Mn in excess reduces the rate of photosynthesis, both Chlorophyll-*a* and Chlorophyll-*b* contents, and carotenoids in plants (Macfie and Taylor, 1992; Hauck *et al.*, 2003) [116]. Rice plants supplied with varying concentrations of Mn (2.3 to 583 μM), had the lowest chlorophyll *a* content at the highest Mn concentration. Accumulation of Mn in thylakoid interferes its stacking, and decreases net photosynthesis (Lidon and Teixeira, 2000a) [108]. Similarly, an early inhibition of photosynthesis was observed by Nable *et al.*, (1988) [83] while *Nicotiana tabacum* was aqua cultured with a Mn excess (1,000 μM). Lidon *et al.*, (2004) also observed a decline in net photosynthesis (μmol CO<sub>2</sub> m<sup>-2</sup>s<sup>-1</sup>) and photosynthetic capacity (μmol O<sub>2</sub> m<sup>-2</sup>s<sup>-1</sup>) in rice plants by Mn (9.1 and 36.4 μM) respectively.

## 7. Manganese and Oxidative stress in plants

Mn in excess causes oxidative stress in plant cells. At high concentration, Mn damages macromolecule leading to disruption of the cell homeostasis (Polle, 2001) [146]. Mn toxicity in plants generates reactive oxygen species (ROS), mainly OH<sup>•</sup>, which are harmful species in cells (Lynch and St. Clair, 2004; Lidon and Henriques, 1993) [110]. Higher

concentration of Mn disorganises chloroplast. For instance, in rice, an increase in Mn in the thylakoid lamellae (McCain and Markley, 1989) [121] inhibits the non-cyclic photophosphorylation process, accelerates in ROS formation that causes injury to the thylakoid peroxidase system (Lidon and Teixeira, 2000b) [111].

Plants (*Cucumis sativus*) fed with excess Mn under optimum light intensity condition increased Mn content in the tissues which inhibited plant growth (Shi *et al.*, 2006). In mature leaves of *Phaseolus vulgaris*, lipid peroxidation is not induced by Mn (Gonzalez *et al.*, 1998), but lipid peroxidation was detected in isolated chloroplast of wheat (Panda *et al.*, 1986) [139].

## 8. Mechanisms of tolerance to Mn toxicity

Plants can follow avoidance and/or tolerance mechanisms to Mn toxicity. In case of avoidance, plant cell does not allow Mn ions to enter into the cytoplasm (Blamey *et al.*, 1986; Marschner, 1991) [15, 119]. The tolerance strategy detoxifies Mn ions while Mn crosses the plasma membrane or internal organelle bio-membranes (Macfie *et al.*, 1994) [115]. In *Vigna unguiculata*, tolerance to Mn excess is brought about by the reduction of Mn<sup>2+</sup> activity in the apoplast, through complex by organic acids (Horst *et al.*, 1999) [81]; production of phenolic compounds in the cell walls (Wissemeier and Horst, 1992) [201]. The instances of Mn avoidance mechanisms are: Mn<sup>2+</sup> oxidation by peroxidases in the cell walls of roots (Marschner, 1991) [119]; the accumulation and secretion of Mn<sup>2+</sup> in and around the trichomes of *Helianthus annuus* (Blamey *et al.*, 1986) [16]. Plants can discharge excess Mn by its efflux from cell via secretors, vesicles to the cell surface (Ducic and Polle, 2005) [40].

In plants, the sequestration of Mn by organic compounds takes place mainly into vacuole (Pittman, 2005) [40]. For instance, there is an increase in phenolic compounds in the hydrophyte (*Trapa natans*) leaves exposed to high Mn levels, 130 μM (Baldisserotto *et al.*, 2004) [12]. The phenolic compounds capture Mn inside the vacuole, and reduce the damage to the protoplasm (Davis *et al.*, 2001) [34]. Similarly, oxalic acid combines with Mn and stores it in vacuoles of hyper accumulator plants (*Phytolacca americana*) (Dou *et al.*, 2008) [38]. A deposition of Mn oxides or an increase in polyphenol oxidase activity in *Citrus volkameriana* plants is a tolerance mechanism (Papadakis *et al.*, 2007) [140]. Rice plants can tolerate Mn toxicity (Lidon, 2001) due to the capacity of the leaf tissues to accumulate 5 to 10 times more Mn as compared to other grasses (Foy *et al.*, 1978) [49]. The apoplastic influx from the cortex toward the steel is inhibited, and holds symplastic Mn assimilation in the shoot protoplast (Lidon, 2001). There is variation of quantum Mn localisation in both roots and shoots according to plant species and genotype (Andrew and Hegarty, 1969) [10]. Manganese translocation is possible to the tops of the plant easily because of its low electro-negativity (Chino, 1981) [27]. Chloroplast proteins are important for CO<sub>2</sub> fixation, and photosynthesis become limiting upon Mn-induced stress (Fuhrs *et al.*, 2008).

An antioxidant system plays an important role in tolerance mechanism to metal (eg. Mn) toxicity. The antioxidant systems consist of antioxidant enzyme which scavenges oxy radicals. The most important of these are superoxide dismutase (SOD), catalase (CAT), peroxidases (phenol peroxidase, POX, ascorbate peroxidase, APX, guaiacol peroxidase, GPX). There are also non-enzymatic antioxidant molecules *viz.*, ascorbate, α-tocopherol, carotenoids,

flavonoids and glutathione (Foyer and Noctor, 2003; Apel and Hirt, 2004) <sup>[51]</sup>. Antioxidant enzymes become reactive while Mn is excess in woody plants (Lei *et al.*, 2007) <sup>[103]</sup>, in herbs like white clover (*Trifolium repens.*), in ryegrass (*Lolium perenne*) (Rosas *et al.*, 2007; Mora *et al.*, 2009) <sup>[157]</sup>. A tolerant plant uptakes lower amount of Mn, and conducted to other organs (Hall, 2002) <sup>[67]</sup>. Manganese toxicity may be reduced by the release of organic acid anions (e.g. oxalate and citrate in ryegrass) by roots around rhizosphere (Gonzalez and Lynch, 1999; Mora *et al.*, 2009) <sup>[124]</sup>.

Other nutrients may also involve in minimizing the Mn toxicity. For instance, silica (Si) application retards lipid peroxidation due to Mn toxicity (Iwasaki *et al.*, 2002; Shi *et al.*, 2005) <sup>[90]</sup>. In barley plants (*Hordeum vulgare*), Ca content is decreased by excess Mn, (Alam *et al.*, 2001) <sup>[7]</sup>. Calcium inhibits Mn translocation from roots to shoots despite uninterrupted absorption of calcium (Alam *et al.*, 2006) <sup>[8]</sup>. High K contents in plants may also prevent both the absorption and the translocation of Mn (Alam *et al.*, 2005) <sup>[5]</sup>.

### 9. Mn deficiency: impacts on photosynthesis and other physiological processes

Like Mn toxicity, Mn deficiency also depresses rate of photosynthesis in plants due to reduction of the number of PSII units per unit leaf area (Henriques, 2003) <sup>[76]</sup>. Photosynthesis is the driver of plant growth and productivity governed by the acclimation to the changing environmental conditions (Tikkanen and Aro 2012; Schottler and Toth, 2014). Nutrient deficiency disrupts the photo assimilation and thereby growth and yield development of plants (Whitcomb *et al.*, 2014; White *et al.*, 2012). As Mn is a catalytic enzyme (Nouet *et al.*, 2011) <sup>[133]</sup>, plants depend on Mn essentially for its indispensable role in the OEC of PSII (Ono *et al.*, 1992; Umena, *et al.*, 2011) <sup>[136]</sup>. So, Mn deficiency reduces photosynthetic electron transport and causes oxidative stress, and retards photo assimilation.

Interveinal chlorosis appears in plants deficient in Mn when plant growth is depressed severely (Hannam and Ohki, 1988) <sup>[22]</sup>. As Mn has low phloem mobility in plants, Mn is not remobilized from older to younger leaves, and its deficiency is generally found in younger leaves (Loneragan, J.F., 1988) <sup>[112]</sup>. The critical concentration of Mn in young fully expanded leaves ranges from 15–20 mg Mn g<sup>-1</sup> dry weight. Leaf necrosis (brown spots between the veins) may develop on leaves while plants suffer from Mn deficiency for long period of time due to accumulation of reactive oxygen species (ROS) within the chloroplasts (Hannam and Ohki, 1988) <sup>[23]</sup>.

A redox shuttle mediates the addition of monolignols to existing phenolic groups in the cell wall to biosynthesize the lignin polymerization (Onnerud *et al.*, 2002; Barros *et al.*, 2015) <sup>[135]</sup>. A plant deficient in Mn has reductions in lignin concentrations particularly in roots (Rengel *et al.*, 1993). Mn deficiency makes plants more prone to fungal diseases (e.g., take-all caused by the fungus *Gaeumannomyces graminis*), which reduces biomass production leading to weak weed competitor. Mn deficient plants have low water use efficiency (WUE) as the cuticular wax layer is ruined, and transpiration rate is increased, and plants become less tolerant towards drought stress (Hebber, C.A. *et al.*, 2009) <sup>[72]</sup>. Moreover, Mn deficiency reduces suberin wax deposition on the endodermal cell walls in roots, put through the abscisic acid and ethylene signaling pathways (Barberon *et al.*, 2016) <sup>[13]</sup>.

Mn deficiency in plant cell decreases in chloroplast number (Henriques, 2003; Henriques, (2004) <sup>[76, 77]</sup>, and reduces

number of functional PSII centers greatly within the grana stacks (Simpson and Robinson, 1984) <sup>[173]</sup>. Mn deficiency changes chloroplast ultrastructure greatly (Papadakis *et al.*, 2007) <sup>[140]</sup>. There is dislocation of thylakoid membrane system of chloroplast. Chloroplast length decreases, but the diameter of the grana thylakoids increases (Possingham *et al.*, 1964) <sup>[148]</sup>. This reconfiguration of chloroplast repairs the PSII processes by enriching proteases and proteins to the damaged PSII (Kirchhoff, 2014) <sup>[96]</sup>.

### 10. Effects of Manganese on growth and morphology of plants

Kobraee (2019) <sup>[97]</sup> conducted a field experiment on chickpea cultivars to determine the effects of zinc (Zn) and manganese (Mn) foliar fertilization in the forms of ZnSO<sub>4</sub> and MnSO<sub>4</sub> on yield, dry matter accumulation, Zn and Mn concentrations in leaf and seed of chickpea. The result indicated that spraying treatments had a significant effect on dry weight of stems, leaves, pods, seeds and total plant.

Wang *et al.*, (2015) <sup>[196]</sup> conducted an experiment with 11 d old rice seedlings of Wuyunjung 7, an Al- tolerant cultivar of rice which were grown in kimura B nutrient solution containing 6.7, 200, 500, 1000µM Mn in the presence or absence of 200µM Al for 24 hr or 3 weeks. AlCl<sub>3</sub> and MnCl<sub>3</sub> were supplied and P<sup>H</sup> of each solution was adjusted to 4.5. The results indicated that rice growth was inhibited by high Mn concentration and caused wilting in older leaves. Shoot height significantly decreased with increasing Mn concentration in absence of Al but addition of Al improved growth of rice at 500 and 1000µM. It showed that Al alleviates Mn toxicity in rice. Ibrahim *et al.*, (2018) <sup>[88]</sup> carried out a pot experiment to determine the effect of manganese fertilizer on the growth and yield of rice. Manganese was applied in form of MnSO<sub>4</sub> at five different levels of manganese (0, 5, 10, 15 and 20 kg ha<sup>-1</sup>) with a soil pH of 6.29 and low manganese content (0.70 mg kg<sup>-1</sup>). The results suggested that the tallest plant and higher number of tillers were obtained with 10 kg ha<sup>-1</sup>. Manganese at the rate of 10 kg ha<sup>-1</sup> gave the highest grain yield and highest dry matter weight.

Timotiwi and Dewi (2014) <sup>[141]</sup> conducted an experiment to test the effects of manganese application on rice growth and yield. Two concentrations of Mn: 0 ppm (Mn<sub>0</sub>) and 5 ppm (Mn<sub>1</sub>) were applied on Mekongga variety of rice. Mn was applied three times starting on day 21 after the planting with four intervals. The data were analysed using orthogonal contrast and polynomial and the entire test was done at level of  $\alpha$  of 5% and 1%. The result showed that Mn was relatively immobile and accumulated in the leaf tissue of the rice plants, and the addition of 5ppm Mn increased the green leaves of rice as compared to those without Mn addition. Mn application on the rice plants was evident from the increase number of productive tillers and dry weight.

Fageria *et al.*, (2008) <sup>[45]</sup> stated that Mn deficiency occurred in upland rice which was grown on highly weathered Oxisols, amended with liming. They conducted a greenhouse experiment on upland rice genotypes, and evaluated Mn-use efficiency (MnUE). The soil was an Oxisol where 0 mg Mn kg<sup>-1</sup> (natural soil Mn level) and 20 mg Mn kg<sup>-1</sup> of soil were applied as manganese sulfate. There were significant variations of grain yield, panicle number, and grain harvest index (GHI) and shoot dry weight between the treatments. The treatments also affected the Mn uptake in the shoot and in the grain of the genotypes. MnUE (mg grain weight/mg Mn

accumulated in shoot and grain) varied significantly among the genotypes. So, the genotypes were categorized as efficient and responsive (ER): Carisma, CNA8540, and IR42); efficient and nonresponsive (ENR): CNA8557 and Maravilha; non efficient and responsive (NER): Bonanca, Canastra, Caraja, and Guarani; and non efficient and non responsive (NENR): Caipo. The genotypes producing higher grain yield at a low level of Mn and respond well to Mn additions were the most efficient. These genotypes could possess higher yield potential in a varied range of Mn availability.

### 11. Effects of Manganese on biochemical parameters

Alam *et al.*, (2000) [6] reported that owing to excess manganese (11 mg Mn), old leaves of rice developed brown spots and mild interveinal chlorosis in addition to depression in growth. Both deficiency and excess of manganese resulted in low concentration of Chlorophyll a and Chlorophyll b as well as reduced Hill reaction activity in leaves. Lidon *et al.*, (2004) carried out an experiment on 21- day old plant to gain fundamentals insights into adaptation to Mn excess, and also the characterisation of photosynthetic apparatus in Mn-treated rice. The result showed that there were 17 and 11- fold increases in Mn in the leaf tissue and thylakoid respectively when the plants were grown in nutrient solution hydroponically with Mn concentration between 0.125 and 32 mg L<sup>-1</sup>. There was decrease in the net photosynthetic and photosynthetic capacity after the 0.5 and 2 mg L<sup>-1</sup> Mn treatment respectively. Rezai and Farboodnia (2008) conducted an experiment on pea plants which were grown in different concentration of manganese (0, 25, 50, 100 and 200 ppm) to study the effects of manganese on chlorophyll content and antioxidant enzymes. The result showed that the low concentration of manganese below 25ppm induced decrease in chlorophyll content, and above 50 ppm inhibited chlorophyll synthesis. The content of Chlorophyll a was higher than Chlorophyll b in pea leaves. The pea plants grown in 25ppm manganese concentration, contained higher content of chlorophyll to compared of other treatments.

Narender and Malik (2016) conducted a pot experiment to evaluate the effect of nitrate and manganese application on Mn pools in soils and also its uptake in wheat. The experiment comprising of three levels of Mn (0, 25, 50 mg kg<sup>-1</sup>) as manganese sulphate and four levels of NO<sub>3</sub><sup>-</sup> (0, 30, 60, 90 mg kg<sup>-1</sup>) applied through ammonium nitrate was laid out in factorial completely randomized design (CRD). The soil used was slightly alkaline in nature with pH 8-10. Result showed that the highest yields of grain and straw were recorded with 25 mg Mn kg<sup>-1</sup> and 90 mg NO<sub>3</sub><sup>-</sup> kg<sup>-1</sup> soil application.

### 12. Mn content in shoot and grain

Marcar and Graham (1987) [117] grew two wheat cultivars Bodallin and Bayonet under Mn deficient soil to determine the importance of seed manganese content for the seedling growth. The seed used were obtained from different field site (giving a Mn content range of 0.1 to 6.4 µg Mn seed<sup>-1</sup>) as well as from soaking seed in MnSO<sub>4</sub> before sowing. The result revealed the strong dependence of wheat seedlings on seed Mn supply for optimal growth on severely Mn deficient soil. Tanaka and Navasero (1996) [183] conducted an experiment under water culture conditions in rice plants and observe that a level of 0.01 ppm Mn in the solution is low enough to produce manganese deficiency and 25 ppm is high enough to produce toxicity symptoms, although other factors, such as pH, nitrogen source, etc., interact with the critical level.

Fernando C. Lidon (2001) investigated the tolerance of rice to excess Mn in the early stages of vegetative growth over 15, 21 and 28-days period in nutrient solutions containing Mn concentration varying between 0.125 and 32mg/l. The electric conductivity and the root acidification decreased about 50% until the 32mg/l Mn treatment. Root and shoot showed increasing Mn concentration from the 0.125 mg/l Mn treatment of 15, 21, 28 days old plants. The number of stomata cells remained unchanged but the transpiration rate decreased considerably in each treatment.

### 13. Effects of Manganese on yield and yield components

Rout *et al.*, (2001) conducted an experiment on Mung bean (*Vigna radiata* L.) and rice (*Oryza sativa* L.) cultivars to test their tolerance to different levels of manganese (Mn<sup>+2</sup>) 2.0 µM (control), 71, 142, 284, 568 and 1136 µM in nutrient solution of pH 6.8. The experiment was conducted to investigate the effect of manganese toxicity on the standard growth parameters such as shoot length, root length, root/shoot dry biomass and root/shoot tolerance index. The result based on the growth parameters, eight cultivars of mung bean and six cultivars of rice were ranked in respect of their tolerance to manganese: TARM-21 > PDM-116 > TARM-1 > K-851 > LGG-407 > TARM-22 > Dhauli > TARM-26 and Khahdagiri > Subhadra > Rudra > Nilgiri > Annapurna > Sankar respectively. Manganese toxicity was correlated with increased peroxidase activity and decreased catalase activity in different cultivars of mung bean and rice.

Jhanji *et al.*, (2014) reported that Manganese efficiency depends upon uptake of each root segment i.e. the influx which in turn depends on depletion of Mn in the rhizosphere during vegetative phase and higher utilization efficiency of acquired Mn during reproductive phase that governs the ultimate grain yield. Abbas *et al.*, (2011) conducted an experiment on under irrigated condition to evaluate the wheat response to five different levels (0, 4, 8, 12 and 16 kg/ha) of manganese along with 150-100-60 kg NPK/ ha application Mn in the form of manganese sulphate (30% Mn) was applied on BK-2002 variety of wheat. AB- DTPA extractable Mn was measured on Atomic absorption spectrophotometer. All P, K and Mn were applied at sowing time while nitrogen fertilizer was applied in three equal splits (1<sup>st</sup> at sowing time, 2<sup>nd</sup> at first irrigation and 3<sup>rd</sup> at third irrigation). The wheat grain yield was significantly increased by the application of manganese with NPK over NPK alone. The highest grain yield was recorded with the application of 16kg Mn/ha. The uptake of N was significantly increased with different levels of Mn over NPK alone except 4kg Mn/ha, and the highest N uptake was recorded with 16 kg Mn/ha. The N uptake ranged from 105.87 to 116.23 kg/ha, P uptake was not significantly increased with various levels of Mn over NPK alone, K uptake ranged from 138.67 to 149.33 kg/ha, the highest in 16 kg Mn/ha, while the lowest from NPK alone. Mn addition had significantly synergistic effect on the uptake of N, P, K and manganese. However, Mn had antagonistic effect on uptake of P in wheat plants.

Kumar *et al.*, (2016) conducted an experiment comprising 3 levels of manganese concentration 0, 5, and 10 kg ha<sup>-1</sup> using rice variety HUBR2- 1. The treatment applied as manganese 5 kg ha<sup>-1</sup> showed the maximum growth attributes and yield of rice. Li *et al.*, (2016) conducted an experiment with two rice cultivars Meixiangzhan and Nongxiang 18. MnSO<sub>4</sub> at four different levels 100 mg, 150mg, 200mg, 250mg pot<sup>-1</sup> in sandy loam soil with 15.34% Mn content and P<sup>H</sup> 6.54. The result



showed that 250 mg  $\text{MnSO}_4 \text{ pot}^{-1}$  recorded 20.83% and 12.96% higher panicle number  $\text{pot}^{-1}$  and 1000 grain weight for Meixiangzhan while for Nongxiang 18, higher panicle number  $\text{pot}^{-1}$  and 1000 grain weight which were 43.04% and 5.86% at 200 mg  $\text{MnSO}_4 \text{ pot}^{-1}$ . Ullah *et al.*, (2018) examined the role of Mn applied through various methods on fine grain aromatic rice to evaluate its role in improving the productivity and grain bio-fortification. The experiment was conducted at two locations with experimental soil pH 7.7 and 7.9. Manganese was delivered as soil application (SA) ( $0.5 \text{ kg ha}^{-1}$ ), foliar spray (FA) (0.02 M Mn), seed priming (SP) (0.1 M Mn) and also seed coating (SC) ( $2 \text{ g Mn kg}^{-1}$  seed). Result showed that Mn application through either method, improved the grain yield and grain Mn contents of fine grain aromatic rice. Mn applied as SC and FA was the most beneficial and cost effective.

Timotiwu *et al.*, (2017) conducted an experiment on irrigated rice field to investigate the effect of Mn and Si application and their response on growth and yield of rice. Mn was applied at two different concentrations 0 and 5 ppm and five concentration of Si (0, 50, 100, 150, and 200 ppm). Foliar application of Si was in the form of  $\text{SiO}_2$  and Mn in form of  $\text{MnSO}_4$ . The result showed that application of 5 ppm Mn increased plant growth and yield except for plant height in all variables. While the application of 200 ppm Si increased plant height, dry weight, number of productive tillers, filled grain weight, 1000 grain and grain yield. The best application of 5 ppm of Mn with 50 ppm of Si showed the best result of rice on the filled grain weight and grain yield. Shahi and Srivastav (2018) conducted experiment on green gram to determine the effect of micronutrient manganese on the physiological performance under saline condition. The result showed that foliar application of Mn (0.15%) as manganese chloride ( $\text{MnCl}_2$ ) improved the physiological parameters in green gram at higher salinity level (200 and 300 mM NaCl), and were considerably useful in alleviating effects of NaCl.

Barros *et al.*, (2015) carried out an experiment to evaluate effect of different manganese sources and levels in irrigated rice production. The manganese treatment supplementation was applied as foliar spray in five levels (0.5, 1.0, 1.5, 2.0 and  $2.5 \text{ kg ha}^{-1}$ ). The sources of manganese used were Mn- nitrate, Mn- Chloride, Mn- Chelate and Mn- Carbonate at two different density A:  $1.827 \text{ g dm}^{-3}$ , B:  $1.86 \text{ g cm}^{-3}$ . Two cultivars of upland rice were used Canastra and Confianca. Result showed that the source Mn Carbonate at density  $1.86 \text{ g cm}^{-3}$  at the dose of  $1.5 \text{ kg ha}^{-1}$  provided highest grain yield with  $7,375 \text{ kg ha}^{-1}$ , and an application of 1.0 to  $1.5 \text{ kg ha}^{-1}$  of Mn gave the highest values.

#### 14. Environmental factors and Manganese in plants

Soil environmental factors *viz.*, dry, acidic, or waterlogged soils affect Mn availability and its impacts on physiology of plants. A change in global climatic variables (IPCC, 2014) <sup>[89]</sup> modulates Mn phytotoxicity (Fernando and Lynch, 2015). For instance, elevated atmospheric temperature due to rising in green house gases e.g.  $\text{CO}_2$  and ozone levels, is related to frequent occurrence of flood, drought, more exposure of plants to solar radiation, and plants encounter consequences from times to time elsewhere (Bromfield *et al.*, 1983; Dias, 2009; Fernando *et al.*, 2009; Hayes *et al.*, 2012; Heenan and Carter, 1977; Lynch and St Clair, 2004; Rufty *et al.*, 1979; Scott *et al.*, 1987; StClair and Lynch, 2010).

A loosely-bound soluble  $\text{Mn}^{2+}$  in the soil solution is bio-available to plants (Clarkson, 1988; Gilkes and McKenzie,

1988) <sup>[29]</sup>. Acidification, high temperatures, extreme wetting and drying cycles, continuous water logging; favour the release of  $\text{Mn}^{2+}$  in soil on overexposed plants (Grasmanis and Leeper, 1966; Hayes *et al.*, 2012). Plants may not show apparent physiological aberrations along with stress when Mn concentrations frequently set off beyond usual nutritional requirements. (Foulds, 2003; Marschner, 2002). Mn tolerance in crop species might be imparted even in a situation of over accumulation of foliar Mn (Fernando and Lynch, 2015). However, symplastic Mn in excess can become phytotoxic while it interacts with environmental factors like solar radiation and atmospheric ozone (Gonzalez and Lynch, 1999b; Gonzalez *et al.*, 1998; StClair *et al.*, 2005; StClair and Lynch, 2004). The hyper accumulated symplastic Mn causes physiological photo-bleaching under solar radiation. Plant Mn toxicity in the symplast is controlled via reactive oxygen species (ROS) damage, and photo-bleaching leads to leaf chlorosis (Fernando and Lynch, 2015; Horiguchi, 1988). The metal co-factors integral to stress-mitigating enzyme (e.g. SOD) activities are antagonised by oxidative stress due to Mn (Fernando and Lynch, 2015; Gonzalez *et al.*, 1998; Horiguchi, 1988; StClair *et al.*, 2005).

Higher accumulation of Mn in foliage affects many crops like Wheat (*Triticum aestivum* L.), soybean (*Glycine max* Merr.), and canola (*Brassica napus* L.) (Burke *et al.*, 1990; Heenan and Campbell, 1980, 1990; Moroni *et al.*, 2012; Reddy *et al.*, 1991; Scott and Wratten, 1997) <sup>[128]</sup>. Mn toxicity crop (e.g. *Phaseolus vulgaris* L.) is usually mitigated by soil liming, but a moderate to hot ambient field condition often hurdles it due to its free radical damage (StClair and Lynch, 2004; StClair *et al.*, 2005; Gonzalez *et al.*, 1998). However, in a variety tolerant to Mn toxicity, excess Mn is disposed into vacuoles of dermal cells (Gonzalez and Lynch, 1999a) <sup>[60]</sup>. Appearance of dark foliar spots is a manifestation of higher Mn oxides and phenols due to the rapid oxidation of  $\text{Mn}^{2+}$  restricted in excess of it (Horst and Marschner, 1978; Wissemeyer and Horst, 1987) <sup>[82]</sup>.

The contribution of environmental changes creates conditions that aggravate the solubilisation of Mn in soil, and plant inheritance characteristics underline the plant responses to available excess Mn. For instance, foliar Mn concentrations in wheat and soybean increased with Mn feeding, and it was amplified by heat. There are phenotypic variations due to spatial distribution pattern of Mn deposited in leaf cells, environmental parameters contribute to Mn accumulation and stress, which is linked inextricably where apoplastic and symplastic Mn toxicity phenomena may run in plants. Manganese deficiency in plants is of greater concern to the orientation of chloroplast in terms of its structural changes, PSII activities leading photosynthesis, growth and yield of crops under a set of soil and environmental conditions.

#### 15. Role of Manganese against diseases in plants

When a plant is infected by a pathogen, its physiology is impaired, and especially nutrient uptake, assimilation, translocation from the root to the shoot and also utilization (Marschner, 1995) <sup>[153]</sup>. There are pathogens that can immobilize nutrients in the rhizosphere, the soil surrounding plant roots, or utilization efficiency and can cause nutrient deficiency. One of the most common symptoms of many soil borne pathogens is root infection, which reduces the ability of roots to provide the plant with water and nutrients. The effect is more serious when the levels of nutrients are marginal and also for immobile nutrients (Huber and Graham, 1999) <sup>[66]</sup>.

Soil is the major source of plant nutrients which are responsible for growth and development of plants as well as plant associated microorganisms. Soil applications of manganese fertilizers are found to reduce common scab of potato (Keinathand Loria, 1996) <sup>[94]</sup>, infections in cotton and squash (Graham and Webb, 1991; Agrios, 2005) <sup>[4]</sup>. Manganese has also been observed beneficial in the control of the diseases like potato common scab, Rice Blast, Rice leaf spot, Wheat Mildew, Cotton Wilt, Avacado Root rot etc. Manganese controls lignin and suberin biosynthesis (Vidhyasekaran, 1977) through activation of several enzymes of the shikimic acid and phenyl propanoid pathways (Marschner, 1995) <sup>[153]</sup>. Both lignin and suberin are important biochemical barriers to fungal pathogen invasion, since they are used in plant disease control due to secretion of some chitinase enzyme as a strong factor involves in biological control (Vidhyasekaran, 1977; Morid and Zafari, 2013) <sup>[126]</sup>. So, applications of micronutrient fertilizers can impact on biological control efficacy of microorganisms.

### Conclusion

Manganese being one of the essential micronutrients plays multifaceted roles in plants. Soil pH is the predominant factor impinging the toxicity or deficiency aberrations in higher plants. Plant follows its own physiological and biochemical features (e.g. Mn homeostasis, Ca<sup>2+</sup> signalling, enzymatic and non enzymatic defence mechanisms, etc.) imparting tolerance to manganese toxicity, and accelerating Manganese use efficiency and productivity of crops in acid soil conditions.

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