



Manganese as a Micronutrient in Agriculture: Crop Requirement and Management

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Abstract

Manganese (Mn) as an essential plant micronutrient affects plant development, when at deficient or toxic levels. Manganese is used in several biological processes as an important contributor in plant growth and development. Manganese uptake depends on forms of Mn in soil solution, crop characteristics including growth rate, and interactions with other environmental factors. Its distribution in soils and requirement for crops vary from location to location, depending on soil type and reactions. Despite the metabolic roles of Mn in different plant cell compartments, the importance of Mn requirement in plants, distribution in soils and application to crops has been understated. As a micronutrient, judicious Mn management requires to critically evaluating its concentration in soils, biochemical functions, critical levels, soil availability and interactions with other nutrient elements is essential. This review has critically analysed the existing body of knowledge on Mn distribution in soils, dynamics, functions and management towards better crop production and safe environment.

Key words: Critical limit, Crops, Manganese, Micronutrient, Soils

Introduction

The production of crops is often restricted by the low phytoavailability of essential elements and/or the presence in the soil solution of too many potentially toxic mineral elements (White and Brown, 2010). Micronutrients are essential nutrient elements that are found in trace amounts in plant tissue, but play a critical function in plant growth and development. Manganese (Mn) is a distinctly favourable micronutrient that plants essential for optimum growth. Manganese plays an important role in many physiological processes such as photosynthesis and acts as an activator or cofactor in at least 35 enzymes and is involved in metabolic processes (Diedrick, 2010). It is a constitutional element of the photosystem-II water oxidizing system and donates in chlorophyll production. Manganese and zinc (Zn) are closely related due to their participation in enzyme systems (Millaleo et al., 2010). Manganese ion (Mn^{2+}) is transformed to Mn^{3+} or Mn^{4+} easily where Mn plays a vital role in oxidation and reduction processes by electron transport in photosynthesis. An important anti-oxidant such as SOD (superoxide dismutase) is the structural part of Mn that inhibits the formation of free radicals in plant cells, which destroys plant tissue. Involvement of Mn in protecting plants against pathogens is reported by Brady and Weil (2012). As a mineral element, it is nutritionally required while at the same time can be toxic. The need for micronutrients as Mn for plants was first found in 1922 (Mulder and Gerretsen, 1952).

Manganese is of critical concerns in both plant and soil by two ways with its deficiency on the one hand and its toxicity on the other. In both cases there is a reduction in the yield and growth of the crop and a negative affect

on the biochemical processes of the soil. The amount of Mn varies from soil to soil. The total amount of Mn in the soils fluctuates between 20 to 3000 ppm and on average it is 600 ppm (Schulte and Kelling, 1999). It participates in many complex and uneven reactions in the soil such as oxidation reduction (redox), ion exchange, specific adsorption and solubility equilibria etc. (Norvell, 1988). The amount of available Mn in the soil is affected by soil pH, organic matter, moisture and soil aeration (Michael et al., 2001). As the pH of the soil decreases, the availability of Mn increases in the soil. Lack of Mn in alkaline soils is very common which limits the growth and yield of plants. Manganese deficiency is widespread but calcareous soils, soils with high pH and low ventilation are mainly Mn deficient (Behera and Shukla, 2014). Lack of Mn in human body is rare. However, due to the toxicity of Mn, hepatic cirrhosis, polycythemia, dystonia, and Parkinsons disease are often seen (Li and Yang, 2018).

The concentration of Mn in plant tissues ranges from 50 to 150 ppm (Schulte and Kelling, 1999). The critical level of Mn varies depending on the cultivar, crop species and environmental conditions and its range from 10 to 50 $\mu g g^{-1}$ dry matters (Michael et al., 2001). Low levels of Mn as an essential micro nutrient are necessary for normal nutrition and growth of plants. The content of Mn in the leaves of the crop species varies from 30 to 500 $mg kg^{-1}$ (Clarkson, 1988). If excessive amounts of Mn are present, it is extremely toxic to the plant cells (Migocka and Klobus, 2007). Manganese usually accumulates in the peripheral cells of the leaf petiole and palisade and spongy parenchymatous cells. Toxicity of Mn in acidic soils is an important feature that inhibits plant growth. Plant growth and photosynthesis are

reduced if the soil contains high levels of Mn. Mn toxicity usually starts when the soil pH is 5.5 or lower but it is seen when the soil pH is less than 6.0.

Crop species such as wheat, soybean, mustard and common beans are very sensitive to Mn deficiency and they respond positively to the application of Mn fertilizer. Lack of Mn in the above mentioned crops results in reduced dry matter production and yield, weakens the immune system against pathogens and decreases heat and drought resistance. However, very little attention has been paid to Mn and its role in plant and soil. Therefore, the effect of Mn fertilizer on these crops is necessary to be identified. Intensive cropping, cultivation of high yielding crop varieties, imbalanced fertilization without micronutrients, little or no use of organic manures have resulted in depletion of micronutrients in Bangladesh soil. Critical limit of a nutrient in soils refers to a level below which the crops will readily respond to its application. For all crops and varieties under varying soils and environmental conditions, one important critical limit may not be used. Information on the use of Mn fertilizer come from soil testing laboratories should be based on the critical limits of extractable Mn for different crops and soils. This will also save different amount of fertilizers being wasted by the farmers while growing the crops. The threshold value of Mn in soil and plant assumes greater importance in monitoring the sustainability related to soil Mn reserve.

This review article focuses on Mn as a micronutrient mentioning its biochemical functions, critical levels, distribution and chemistry in soil, deficiency and toxicity in plant and soil, interactions with other nutrient elements and recommendation for application in order to highlight the significance of Mn in agriculture for better crop production.

Biochemical functions of Mn

Manganese plays a vital role in biological systems because it exists in a type of oxidation states and is concerned in activation of multiple enzyme systems (Mukhopadhyaya and Sharma, 1991). It is analogous to metallic element as magnesium (Mg^{2+}) as each ion

connects adenosine triphosphate with complexes of enzymes like phosphotransferase and phosphokinase. Dehydrogenase and decarboxylase in the Krebs cycle and ribonucleic acid polymerase are also activated by Mn^{2+} (Marschner, 1995; Burnell, 1988). Manganese plays an effective role of nitrate reduction; nitrate accumulates in the leaves which cause Mn deficiency. Lack of Mn causes lignin deficiency in plant and it takes on a deadly shape at the roots of the plant, reducing its resistance to attack fungi infection (Marschner, 1995). The role of Mn in lipid metabolism is not clear though (Ness and Woolhouse, 1980). Hydrogen peroxide is produced with the help of peroxidase enzyme, which is another Mn-dependent enzyme that helps prevent pathogen. Hydrogen peroxide is not only associated with cell wall stability but is also toxic to pathogens (Heine *et al.*, 2011) and acts as a fungicide (Graham and Webb, 1991).

Due to the deficiency of Mn the plant height, dry matter yield and the amount of chlorophyll decreases (Polle *et al.*, 1992). Excess magnesium supplementation alleviates the effects of high Mn level by increasing the biomass, the concentration of the chlorophyll, deoxyribonucleic acid, Hill reaction activity, and the activity of peroxidase (Heenan and Campbell, 1981). If broad bean (*Vicia faba* L.) seeds are treated with Mn, they affect total chlorophyll content, growth, Mn accumulation in root and shoot, proline content and peroxidase activity. Roots and shoots of broad bean are increased positively in response to increasing Mn level which is more in the roots than in the shoots. The application of Mn increases the amount of total chlorophyll (Arya and Roy, 2011). Application of $MnSO_4$ with $FeSO_4$ and $ZnSO_4$ increased the chlorophyll content and photosynthesis in plant which in turn increases the biological yield, seed weight and seed yield of soybean (Sharma and Misra, 1997; Bhanavase *et al.*, 1995).

Manganese requirement in crops

Manganese is an essential micronutrient that, relative to iron, is required by plants in the second largest quantity. Crops can be divided into three major groups on the basis of the Mn requirement, such as high Mn responsive, medium Mn responsive and low Mn responsive (Brouder *et al.*, 2003).

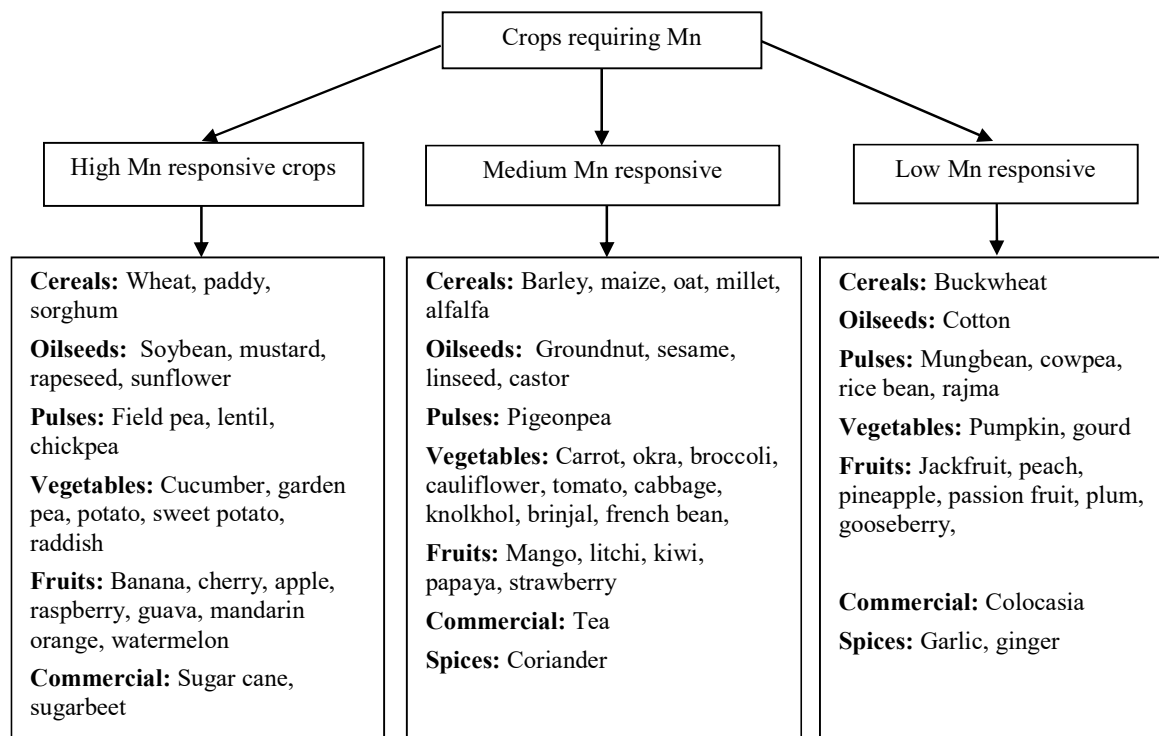


Fig. 1. Diagram showing Mn responsiveness in plants (modified from Ray *et al.*, 2015)

On the low-Mn soils, crop species and cultivars differ drastically in their ability to grow. Nevertheless, the critical tissue Mn requirement lies between 10-20 mg Mn kg⁻¹ for most plant species. Soybean, for example, is a high Mn-requiring plant and its root nodule bacteroids use nicotinamide-adenine dinucleotide (NAD)-malic enzyme activated by Mn to obtain energy from the plant. In order to release fixed nitrogen from root nodules into leaves and growing pods, Mn-dependent enzymes are needed (Winkler *et al.*, 1985). The concentration of Mn in rice stems and leaves increased with the rise in Mn levels (Alam, 1985). The application of Mn substantially increased the consumption of Mn in wheat plants, suggesting that the requirement of Mn for wheat is higher than for other crops (Fageria and Baligar, 1997). Research results indicate that for optimal growth and photosynthesis, the C4-NAD malic enzyme species have a 10-30 fold greater tissue requirement for Mn (Kering *et al.*, 2009).

Critical levels of Mn in soil

In plants, every essential nutrient has a particular role to play and its existence in the above critical concentration is a must for a plant to complete its life cycle. Not only for soil and crop species, but also for different varieties of a given species, the critical limits or levels can differ (Singh and Agrawal, 2007). Soils, crops and methods of extraction are essential factors in deciding the critical limit of nutrient. For balanced fertilization to obtain optimum crop yields, evaluation of the critical limit of

Mn is important. In order to divide the soil of a specific region into deficient and non-deficient classes, essential levels of Mn are needed, either in soil or in plant. It helps fix the application dose of Mn to achieve the expected crop yield. Using the diethylene triamine-penta acetic acid (DTPA) extraction process, the critical limit for Mn in Bangladesh soil (Esatern Gangetic Plain) was fixed 1.0 ppm in few decades back but continued to be used till to date (FRG, 2018). The critical level of Mn in ustochrepts soil of India is 2.9 mg kg⁻¹ for green gram (Bansal and Nayyar, 1989). As per the statistical tool R-project and scatter diagram, 5.85 mg Mn kg⁻¹ soil is fixed as the critical limit of Mn for wheat under goradu soil of India (Bairwa, 2015). In another study, the critical level of Mn is 3.3 mg kg⁻¹ by using both graphical and statistical models for soybean (Bansal and Nayyar, 1990). Critical Mn deficiency level in recently matured terminal leaflet blade at V₆ growth stage (before flowering) in soybean plant is 22.0 µg g⁻¹ (Keisling and Mullinix, 1979). In Shirpur Tahsil Khandesh region of Maharashtra, the critical limit of Mn is 2.4 mg kg⁻¹ for Mn deficient soil (Mahashabde *et al.*, 2012). By the same method, the critical limits of Mn in different Egyptian sandy and calcareous soils are 1.4 and 1.2 µg g⁻¹, respectively (Elgala *et al.*, 2008). In calcareous soils of Iran, the critical Mn level is 4.3 mg kg⁻¹ for wheat (Ziaeian and Malakouti, 2000) whereas in some selected soils of Mazandaran province of Iran is 4.10 mg kg⁻¹ with Cate-Nelson method for soybean (Asadi *et al.*, 2004). Dryland wheat requires more Mn

than other micronutrients. Soil Mn critical limit for dryland wheat is greater than irrigated wheat. Critical levels of Mn for irrigated and dryland wheat are 5.0 and 5.5 mg kg⁻¹, respectively (Lindsay and Norvell, 1978; Agrawal, 1992; Feiziasl *et al.*, 2009). Balali *et al.* (2000) reported that in Kermanshah province of Northwestern Iran, which had a maximum Mn critical level of 4.6 mg kg⁻¹, calculated Mn critical value as 4.3 mg kg⁻¹ by Cate-Nelson graphical method for irrigated wheat. Different extractable methods rely on the critical level of Mn. Four extractable methods, such as Double Acid- 2.6 ppm, DTPA-0.22 ppm, Mehlich (NH₄Cl-NH₄F)-1.8 ppm and AB-DTPA (NH₄HCO₃-DTPA)-0.4 ppm in soybean sandy soil are used to assess essential deficiency levels using the Cate-Nelson process (Shuman *et al.*, 1980).

Manganese toxicity in plant and soil

The signs of Mn toxicity differ widely as the most common symptoms among plant species with chlorotic leaves and necrotic spots (Millaleo *et al.*, 2010). The concentration of toxic Mn is highly dependent on plant species and genotypes (Broadley *et al.*, 2012; Fernando and Lynch, 2015). Excess Mn may be stored in vacuoles (Dou *et al.*, 2009), cell walls (Fuhrs *et al.*, 2010), and distributed to various leaf tissues (Fernando *et al.*, 2006). Amao and Ohashi (2008) suggested that high concentrations of Mn in spinach leave inhibit oxygen activity resulting from the PS-II complex. Similarly, excessive Mn at the molecular level can prevent the absorption and translocation of other essential elements such as Ca, Mg, Fe, and P (Blamey *et al.*, 2015; Leskova *et al.*, 2017). Therefore, plants that are deficient in iron, calcium, magnesium, phosphorus or silicon may exhibit Mn toxicity (El-Jaoual and Cox, 1998). Manganese toxicity causes necrotic or brown spots to display on the older leaves (Figure 2). Manganese toxicity also frequently causes chlorosis (pale or yellow colour), most extreme on the younger leaves, due to an induced iron deficiency (Millaleo *et al.*, 2010). Either one or both of these symptoms can be observed in crops affected by Mn toxicity. These symptoms are occurred less in up light intensity compared with less light intensity. Manganese toxicity begins with chlorosis in the older leaves and spreads to younger leaves (Reichman, 2002; Wissemeyer and Horst, 1992). Excess Mn or Mn toxicity decreases the rate of CO₂ assimilation and stomatal conductance, resulting in decreased shoot biomass in turn. The activity of antioxidant enzymes such as peroxidase (POD), superoxide dismutase (SOD) and catalase (CAT) is increased at Mn doses (Santos *et al.*, 2017). The activities of POD and SOD in the presence of high Mn divide in the roots are the main physiological responses of soybean plants. Mn toxicity can be removed by using a high amount of magnesium (Terry *et al.*, 1975).



Fig. 2. Mn toxicity in soybean and wheat crops

One of the main threats to plant growth on acid soils is toxicity from Mn. Manganese toxicity is normally associated with soils of pH 5.5 or lower, but can occur if the pH of the soil is lower than 6.0. Plants fertilized with acid-forming fertilizers such as superphosphate, nitrate, etc are likely to be harmful to Mn. (El-Jaoual and Cox, 1998). Poor drainage, waterlogging, or soil compaction leading to Mn toxicity can result in insufficient soil aeration, even in slightly acidic soils. Again in strongly acidic soils, Mn toxicity can occur in combination with aluminium (Al) toxicity (Mahoney *et al.*, 1981). However, at a soil pH which is too high for Al toxicity to impact plant growth, it is possible to have Mn toxicity.

Mn deficiency in plant and soil

Nutrient deficiencies are subjective and excessive amounts of another element are indicated by a deficiency of one element. Thus, as a consequence of nutrient deficiency or imbalance, plants exhibit external signs of intense hunger. Manganese deficiency is found in plants without strong visual signs. Generally, the essential concentration for plant Mn deficiency is below

10 mg kg⁻¹ dry weight (Broadley *et al.*, 2012). Pale mottled leaves and interveinal chlorosis are the most visible symptoms of Mn disorder (Schmidt *et al.*, 2016) (Figure 3).



Fig. 3. Mn deficiency in soybean and wheat crops

Typical symptoms of Mn deficiency first occur in younger leaves because of the low phloem mobility of Mn (Li *et al.*, 2017), which vary with Mg deficiency in plants that manifest mainly in older leaves. (Longnecker *et al.*, 1991). Under extreme Mn deficiency, leaves can also develop gray speck symptoms, which are marked by brownish or necrotic spots (Broadley *et al.*, 2012). Manganese deficiencies are sometimes recognized in dicot plants with small yellow spots on leaves, while signs of Mn deficiency occur as tape and gray-green spots on the base of leaves in monocot plants. Necrotic spots have been suggested to be the result of an increase in free oxygen radicals in damaged chloroplasts and a decrease in MnSOD activity (Hajiboland, 2012).

In roots, an increase in the frequency of root hairs can be observed under Mn deficiency (Yang *et al.*, 2008). If the deficiency becomes more severe, root tips can develop serious necrosis (Yamaji *et al.*, 2013). Manganese deficiency causes lignin concentrations to decrease, particularly in plant roots (Rengel *et al.*,

1993). The Mn-deficient plants are more prone to fungal diseases like take-all caused by the fungus *Gaeumannomyces graminis* and weed infestation with less biomass production. Manganese deficiencies in plant tissues is caused by impairment in fatty acid production, which can adversely affect the cuticular wax deposition, as wax synthesis starts with fatty acid synthesis in plastids. Since the wax layer is responsible for limiting the loss of non-stomatal water and reducing the heat load on the leaves, weakening of this layer may lead to an increase in crop sensitivity to both drought and heat stress due to Mn deficiency. Latent Mn deficiency in barley, for example, is found to significantly reduce the wax content (up to 40 percent), resulting in increased transpirational water loss and lower efficiency of water usage (Hebberner *et al.*, 2009). Manganese deficiency has very severe effects, in particular on non-structural carbohydrates and root carbohydrates. Due to Mn deficiency, crop quality and quantity decrease, and this is due to low pollen fertility and low carbohydrates during grain filling. Plant growth may also be reduced and stunted (Marschner, 1995). The key indication of deficiency is a decrease in the efficacy of photosynthesis, leading to a general decrease in the productivity and yield of dry matter. Therefore, Mn deficiency has adverse effects on the photosynthetic apparatus, such as damage to the chloroplast structure and reduction in the amount of chlorophyll and net photosynthesis, due to reduced photosynthetic electron transport and oxidative stress (Ndakidemi *et al.*, 2011; Schmidt *et al.*, 2016).

The frequency and severity of Mn deficiency depend on seasonal conditions, as Mn deficiency in the cold and wet seasons is more extreme due to decreased metabolic activity of the roots in Mn uptake (Bately, 1971). In coarse-textured soil with high pH, Mn leaching is the key pathway for Mn loss, while excessive Mn absorption is the primary pathway for Mn loss in clay-textured and acid soil (Lu *et al.*, 2004; Mousavi *et al.*, 2011). Soils rich in organic matter are deficient in Mn (more than 6%). As the volume of organic matter increases in the soil, due to higher organic matter formation and Mn complexes, the amount of exchangeable Mn decreases. In addition, certain soils, especially as a result of huge amount of fertilizer and lime applications, can cause Mn deficiency.

Mn distribution in Bangladesh soil

With advancement of time, soil micronutrient deficiency has arisen in floodplain soils of Bangladesh like macronutrients. Sarker *et al.* (2018) reported that available Mn level of top soil (0-15 cm depth) in AEZ 19 (Old Meghna Estuarine Floodplain) during the year 2011-2012 varied from 3.0-141.2 mg kg⁻¹ (mean 24.8 mg kg⁻¹) whereas previous Mn status of that soil (1997-2002) ranged from 4.0-148 mg kg⁻¹ (mean 41.2 mg kg⁻¹). These results reflect an indication of declining Mn status in the Old Meghna Estuarine Floodplain soils.

Again, the topsoil (0-15 cm) Mn status (ranging from 3.0-141.2 mg kg⁻¹ and average 24.8 mg kg⁻¹) was higher compared to subsoil (15-30 cm) Mn status (3.95-100 mg kg⁻¹ and average 20 mg kg⁻¹). Generally, intensive crop cultivation, imbalanced use of fertilizers, leaching loss etc. are the vital factors of Mn decline in soil. It is expected that Mn level might be low in calcareous soil of Bangladesh with high pH. According to upazila nirdeshika of SRDI (Soil Resource Development Institute), Mn deficient soils are rare in Bangladesh. Previously, according to the reports of SRDI (LSRUG 1997; 2013), the amount of available Mn has a decreasing trend in calcareous alluvium of Ramgoti upazila under Laxmipur district (AEZ 18) with time. The previous (1995) Mn statuses in Ramgoti, Nilkomol and Hatiya series of Ramgoti upazila were 21.1, 21.5 and 26 ppm, respectively whereas the present (2013) Mn statuses are 6.97, 8.67 and 10 ppm, respectively (Figure 4).

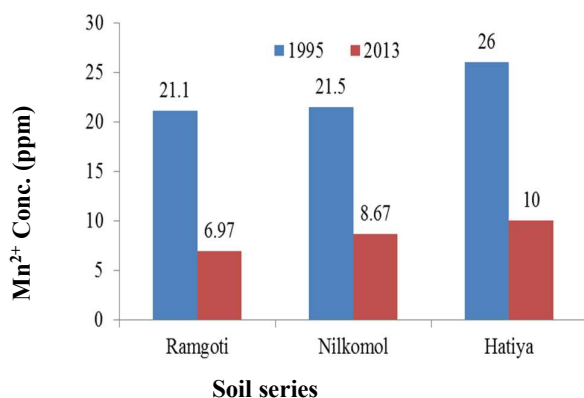


Fig. 4. Comparative study of soil Mn status in different series of Ramgoti upazilla (LSRUG, 1997; 2013)

A different scenario was observed for piedmont soils of Bangladesh. Recently, Sarker *et al.* (2020) reported that the available Mn status of soils in AEZ 22 (Northern and Eastern Piedmont plain) was categorized as very high in both previous (1996-2003) and present status (2011-2012) ranging from 4.0 to 171 (average 44.6 µg g⁻¹) and 17 to 91 µg g⁻¹ (average 45.1 µg g⁻¹), respectively. Again, the Mn content ranged from 9.6 to 67.4 µg g⁻¹ (average 28.8 µg g⁻¹) in the sub-surface soil which was comparatively lower than surface soil. Research is needed to evaluate the present Mn status of soils in different AEZs and to develop Mn map of Bangladesh.

Manganese transformation in soil

Water logging causes a reduction of MnOx by decreasing the O₂ concentration leading to an increase of Mn²⁺ in soil solution up to toxic levels (Khabaz-Saberietal, 2006). Manganese is one of nature's most plentiful and widely dispersed metals and constitutes

about 0.1 percent of the crust of the earth (Emsley, 2003). Manganese can exist in 11 oxidation states, ranging from -3 to +7, but in soils, Mn is mainly present as +2 (e.g. Mn²⁺), +3 (e.g. Mn₂O₃) and +4 (e.g. MnO₂). Availability of Mn to plants depends on its oxidation state; Mn²⁺ is the only plant-available form which can be readily transported into root cells and translocated to the shoot, whereas the oxidized species Mn (III) and Mn (IV) form insoluble oxides that rapidly form sediments (Stumm and Morgan, 1996). Mn²⁺ is the most soluble form of manganese. Mn⁴⁺ is soil-insoluble and should not be used by plants. Unless environmental factors turn it into Mn²⁺, plants can not transform and use it. The prevalence of Mn⁴⁺ is typically encouraged by factors such as good soil aeration and acidic or alkaline pH. However, Mn⁴⁺ is reduced to Mn²⁺ when the soil is humid or waterlogged and soil oxygen is low (Rengel, 2015). When oxygen is depleted from the growing medium, changes in the redox potential occur; in such a case, NO₃⁻, 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 soils with high pH where poor availability of Mn may occur is not completely understood (Clark and Baligar, 2000; Pan *et al.*, 2014). Manganese concentration in soil solution could theoretically decrease 100-fold with each unit of pH rise in aerated soils (Barber, 1995). Manganese exists in a number of forms in the soil, including soil solution Mn²⁺, exchangeable Mn²⁺, organic compounds, various minerals, and as other ions (Fageria *et al.*, 1990). The relative water content, xylem exudation, leaf water potential of soybean plants are sharply decreased at 75 mM NaCl salt combined with water shortage environment (Shawquat *et al.*, 2015). Soil microorganisms also appear to reduce the availability of Mn by oxidizing Mn to less-available forms and competing with crops for available Mn. Poor soil aeration, or reduced oxygen level, usually is caused by excess moisture along with high microbial activity. High microbial activity, when soil temperatures and organic carbon sources are favorable, absorbs oxygen. Manganese oxide is converted to soluble Mn (Mn²⁺) as a consequence. Soluble Mn leaches out of the soil after a long period of waterlogged conditions. Manganese and iron deposits may plug tile lines as drainage water carrying these elements contacts air in the tile. Short-term waterlogged conditions lead to the toxicity of Mn, but prolonged wet conditions can result in Mn deficiency, as in a marsh (Patiram *et al.*, 2000; Chaudari *et al.*, 2012).

Manganese dynamics in soil

Manganese is the eleventh abundant element in the world which forms the crust of the earth after iron (Fe) (Malakouti and Tehrani, 1999). It is important to calculate both the total and usable Mn in the soil. The distribution mechanism of Mn in various fractions helps

to understand its soil retention and plant release (Shuman, 1979). Soil Mn release patterns in various cropping systems vary from soil to soil (Narender *et al.*, 2017). The total soil Mn distributed in various pools is shown in Figure 5.

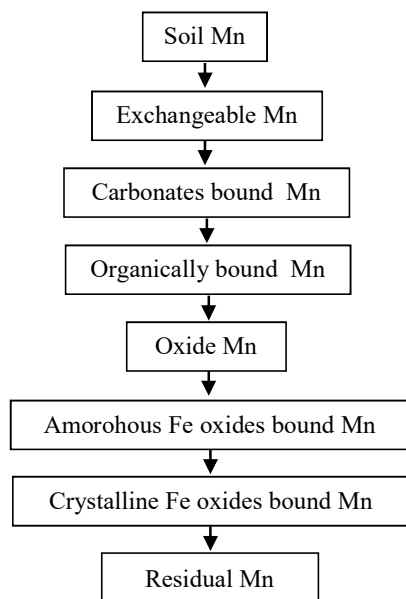


Fig. 5. Seven steps of sequential fractionation for partitioning Mn (Tessier *et al.*, 1979)

As the amount of Mn application increased, the content of Mn in all fractions increased (Yadava and Malik, 2018). The form of Mn feeding is the most important to determine nutrient uptake and growth under various soil conditions. Narender *et al.* (2016) showed that in reaction to changing soil properties, the distribution of Mn among different chemical forms varied. In all the fractions, the content of Mn in soils decreased with increasing soil depth. Mn occurs in the soil as an exchangeable manganese, manganese oxide, organic manganese and ferro-manganese silicate minerals. The manganese ion (Mn^{2+}) is comparable to magnesium (Mg^{2+}) and ferrous iron (Fe^{2+}) and can substitute silicate minerals and iron oxides for these components (Schulte and Kelling, 1999).

The Mn forms do not exhibit any consistent distribution pattern. Their content is higher in fine textured soils compared to coarse textured soils, regardless of the different fractions of Mn. The soil solution plus exchangeable Mn retained onto organic site and oxide surface (amorphous) and increased with increase in organic carbon, silt and clay contents. With an increase in silt and clay content, Mn adsorbed onto the inorganic site (crystalline) is increased. With an increase in organic carbon content, DTPA-Mn rises, whereas Mn is adsorbed on oxide surfaces. Total Mn is closely

associated with soil organic carbon, silt, and clay material (Sharma *et al.*, 2016). The proportion of Mn fractions collected from the soil is as follows: adsorbed to oxide surfaces > adsorbed to inorganic surfaces > organically bound > DTPA > soil solution + exchangeable (Sharma *et al.*, 2011). Total and extractable Mn varied widely with extractants and soil series of different states of India. In the most urbanized region of India, the usable and total status of soil Mn is 205-2800 and 2737-10,122 $mg\ kg^{-1}$, with mean values of 1178 and 2274 $mg\ kg^{-1}$, respectively (Khageshwar *et al.*, 2015). Mn available for Rajasthan soil ranges from 2.05 to 12 ppm. Usable Mn decreases significantly in some of the large soil groups with calcium carbonate (Mehra and Baser, 1991). Singh (2009) noted that Mn deficiency in wheat exists in many parts of the globe, where soils, such as loamy sand soils, have very low available Mn status.

Use of Mn fertilizers

The use of chemical fertilizers is very imbalanced which is not dependent on plants requirement in most regions of the globe. Each element in proper plant nutrition should be adequately accessible to plants, and balanced nutrient fertilization is essential (Alloway, 2008). Micronutrient deficiencies such as Zn, B and Mo in many soils in Bangladesh have recently been identified (FRG, 2018). As Mn deficiency in our soil still remains uncertain, the application of Mn as fertilizer is not well practiced in Bangladesh. Due to the conversion of the applied Mn from inaccessible forms, the recovery of the applied Mn in all soils is poor. For the better yield and quality of certain crops in many regions, the soil or foliar application of Mn is crucial.

Up to 10 ppm of Mn alone increased rice's dry matter yield, while yield decreased with a further increase in Mn levels (Alam, 1985). With Mn foliar application, crop yield increased due to increasing photosynthesis efficiency and carbohydrate synthesis such as starch (Diedrick, 2010). Soil application of 20 $mg\ Mn\ kg^{-1}$ soil substantially improved green gram yields (Bansal and Nayyar, 1989). Brennan and Bolland (2003) demonstrated that the use of Mn fertilizer ($MnSO_4$ and MnO) doubled the yield of lentils grown on Australia's Mn-deficient alkaline soils. The application of manganese sulphate to irrigated wheat improved its yield and quality significantly. Soil application of $MnSO_4 \cdot 4H_2O$ has been shown to be 1.5 and 10 times more efficient than Mn-frits and MnO_2 , respectively, in rising wheat grain yields in sandy soils of Punjab (Bansal and Khurana, 2007). By microbial or chemical mobilization, Mn solubility is increased. Some wheat cultivars' low Mn efficiency is due to their reduced root growth and plant height at low soil Mn supply (Khan *et al.*, 2008; Sadana *et al.*, 2002). With foliar application of Mn, potato yield and quality are increased and dry matter storage is improved by the combined use of Mn and zinc (Mousavi *et al.*, 2007).

The spectrum of adequacy of Mn and its responsiveness differ from crop to crop. The soybean adequacy range for Mn is 20-100 ppm, which is high. Also, wheat responsiveness is high when the sufficiency range of Mn is 20-200 ppm (Brouder *et al.*, 2003). Parker *et al.* (1981) reported that in five of the eight soybean cultivars, the addition of 11.2-22.4 kg ha⁻¹ Mn to the soil increased leaf Mn in all cultivars and seed Mn content and seed yields (about 27 percent higher compared to control). In another analysis, 25 kg ha⁻¹ Fe, 40 kg ha⁻¹ Zn and 40 kg ha⁻¹ Mn recorded the highest production of soybean seeds and biomass (Vahid Ghasemian *et al.*, 2010). Foliar application of Mn on 10 cultivars of soybean increased the economic and biological yield, dry matter, Mn concentration and uptake by soybean plants (Bansal and Nayer, 1994). Ozbahce and Zengin (2014) reported that the form of Mn fertilizer, its doses and methods of application can have a major impact on dwarf bean yield and net revenue. Table 1 represents some fertilizer sources of Mn and the suitable Mn fertilizers for soil and foliar application are manganese sulfate (MnSO₄.H₂O) and chelated manganese (MnEDTA) as suggested by Schulte and Kelling (1999).

Table 1. Fertilizer sources of Mn with chemical formula and % Mn content

Manganese source with chemical formula	% Mn content
Manganese carbontes (MnCO ₃)	31
Manganese chelate (MnEDTA)	12
Manganese chloride (MnCl ₂)	17
Manganese dioxide (MnO ₂)	63
Manganese oxide (MnO)	41-68
Manganese sulfate (MnSO ₄ .H ₂ O)	36

The beneficial aspects of nano-enabled fertilizers can become a highly valued tool for addressing the problem of global food security through better understanding and management. Nano Mn on wheat in near-neutral soils, for example, showed no evidence of apparent crop toxicity (Raliya *et al.*, 2018). In this respect, the lack of stronger impact may be due to the original level of soil Mn being above the critical level for wheat and also the effects on vegetative and reproductive yields. There are major differences due to nano Mn on wheat as greater shooting (37%) and grain (12%) and the application of nano Mn as a foliar treatment will allow greater control over plant responses (Dimkpa *et al.*, 2018).

Application method

a) Broadcast application

Soil applications are short-term and costly at best, but can lead to significantly higher crop production. Manganese transmission along with other chemical fertilizers can in some cases, increase the level of soil testing or prevent Mn deficiency. However, broadcast applications of Mn fertilizer or attempts to build soil test

Mn levels are not recommended particularly on high pH and high organic matter containing soils because of their capacity to fix Mn rapidly. The methods of broadcasting Mn application was found to be inefficient and in most cases ineffective since large quantities of fertilizers are needed to have some impact and the conditions in the soil quickly become inaccessible (Murdock *et al.*, 1977). According to Moosavi and Ronaghi (2011), soil application of Mn is not a successful method in preventing induced Mn reduction in soybean by Fe applications in calcareous soils.

b) Band/row application

The application of Mn fertilizers in bands or rows is more efficient than the broadcast application. After application, most of the fertilizers create an acid environment in the soil and if Mn is added into the band, this environment can help prevent it from being bound up and inaccessible (Murdock *et al.*, 1977). Mixing Mn in a fertilizer band with ammonium nitrogen increases its availability. Although the use of Mn fertilizer alongside the line is better than broadcasting, in many cases it is still an improper practice.

c) Foliar application

By minimizing interaction with soil particles, foliar application of Mn decreases chemical fixation. Foliar application of Mn in soybeans remains an important and economically sound choice to prevent yield loss and nutrient imbalance in calcareous soils, as proposed by Moosavi and Ronaghi (2011). Crown root initiation, tillering and joining stages of wheat are important stages to apply MnSO₄ in sandy soils (Dhaliwal and Manchanda, 2008; Sutradhar *et al.*, 2017). The number of seeds plant⁻¹ and seed yield of safflower grown in black clay soil in the South-East Australia are increased through foliar application of 500 g ha⁻¹ Mn (Lewis and Mcfarlane, 1986).

While foliar application is an effective procedure, when micronutrients are applied at high concentrations, it can cause leaf burning and occasional toxicity (Rehman *et al.*, 2014). With foliar Mn applications, for optimum response, two or three applications are often required. Although foliar Mn application can supply sufficient Mn to overcome Mn deficiency, this strategy is expensive and often impractical for farmers on marginal lands. Moreover, foliar Mn sprays are only effective for a limited time period since Mn is very little mobile in the plant and does not remobilize from older leaves to Mn deficient young leaves (Li *et al.*, 2017).

d) Seed treatment

Seed treatment (seed coating and priming) is pragmatic and cost-effective method of micronutrient application (Farook *et al.*, 2012). Recently, Ullah *et al.* (2017) demonstrated that Mn application in rice as seed treatment (seed coating or seed priming) was better and more economical than soil or foliar application as this

method improved the yield-related traits, rice yield, water productivity and grain Mn contents of fine grain aromatic rice grown in both conventional and conservation production systems.

Manganese interactions with other nutrients

Nutrient interaction in crop plants is a very important factor affecting crop yields. Interaction may be positive, negative or neutral (Fageria, 2001). The main variables for interaction are soil, plant and climatic conditions. Interactions occur on the root surface that allows ions to form chemical bonds and complexes to precipitate (Fageria *et al.*, 2002). Another form of interaction

occurs between ions whose chemical properties are sufficiently similar and they compete for site of absorption, transport, and function on plant root surface or within plant tissues. Such interactions are more prevalent between nutrients of comparable size and charge (Wilkinson *et al.*, 2000). The abundance of micronutrients in the soil not only increases the intake of the same micronutrients, but also influences the absorption of other micro and macro nutrients in the soil (Graham and Webb, 1991). Again, even in case of the same nutrient element, Mn interaction may be synergistic for one crop but antagonistic for another crop (Table 2).

Table 2. Interaction effects of Mn with other nutrient elements in various crop species

Nutrient element	Interaction	Crop species	Effects on plants	References
N	Antagonistic	Barley	limited plant growth	Husted <i>et al.</i> (2005)
P	Synergistic	Potato, Rice, Soybean, Wheat,	inhibited stem streak necrosis	Sarker <i>et al.</i> (2004), Shahandeh <i>et al.</i> (2003), Shuman and Anderson (1976), Sharma and Bapat (2000).
	Antagonistic	Barley, Tomato	decreased plant growth	Pedas <i>et al.</i> (2011), Gunes <i>et al.</i> (1998)
K	Antagonistic	Barley	phytotoxicity	Alam <i>et al.</i> (2003)
S	Synergistic	Broccoli	increased shoot fresh yield	Akay and Uzun (2017)
	Antagonistic			
Ca	Antagonistic	<i>Epibolium hirsutum L.</i> , Bean, Tomato, Soybean, Wheat	small seedlings with small pale green leaves, crinkle leaf in the shoot apices and reduction in transpiration rate	Islam (1986), Horst and Marschner (1978), Gunes <i>et al.</i> (1998), Shuman and Anderson (1976)
Mg	Synergistic	Soybean	increased shoot dry weight and seed yield	Kuwano <i>et al.</i> (2016), Moreira <i>et al.</i> (2003)
Cu	Antagonistic	Barley	limited plant growth	Lombnaes and Singh (2003)
Fe	Antagonistic	Tomato, Potato, Soybean,	roots, stems and individual leaves affected	Tanaka and Navasero (1966), Lee (1972), Kovacevic <i>et al.</i> (2004). Heenan and Campbell (1983), Adiloglu (2006), De Varennes <i>et al.</i> (2001)
Zn	Antagonistic	Maize, Annual Medics	decreased dry matter, decreased plant growth	Soltangheisi <i>et al.</i> (2014), Kobraee and Shamsi (2015), Mahbobeh <i>et al.</i> (2011). Ishizuka and Ando (1968).
	Synergistic	Sweet corn, Soybean, Bean, Rice	enhanced roots and shoots, enhanced shoot dry weight, increased kernel weight, shilling% and harvest index	Zakikhani <i>et al.</i> (2014)
Mo	Synergistic	Rice	enhanced Mn uptake of shoot	Zakikhani <i>et al.</i> (2014)
Si	Synergistic	Maize, Lettuce, Pea, Carrot, Wheat	promoted Mn translocation to the shoot	Greger <i>et al.</i> (2018)

Manganese recommendation for crops

Balanced and timely nutrient management practices applied for crop plants contribute to sustainable growth, yield and quality of crops, affect plant health, minimize environmental risks, assists in integrated pest management and support higher income for the farmers (Hellal and Abdelhamid, 2013). The recommendation of Mn fertilizer depends on Mn deficiency. Before

applying a Mn fertilizer, it is important to determine whether sample soils or plants need this element. As suggested by Lacerda *et al.* (2017), the most important aspect when applying micronutrients in the soil, topdressing or seed furrow, foliar or seed treatment, is the application time and dosage of micronutrients to provide the nutrients in adequate amounts the plant requires. In many areas of the world Mn as foliar

application is recommended in calcareous soils. Research is needed to elucidate the consequences after Mn fertilizer application in soil (comperatively low Mn status). Table 3 shows some recommended doses of Mn for different crops as suggested by some researchers.

Table 3. Mn recommendation in various crops for yield maximization

Crop	Recommended dose with method	References
Soybean	14.57 kg ha ⁻¹ (broadcasting)	Vahid Ghasemian <i>et al.</i> (2010)
Wheat	16 kg ha ⁻¹ , (broadcasting), 0.5% (foliar)	Abbas <i>et al.</i> (2011), Pahlavan-Rad <i>et al.</i> (2009)
Corn	1.5 mg kg ⁻¹ (foliar)	Nozulaidi <i>et al.</i> (2016)
Potato	4 ppt (foliar)	Mousavi <i>et al.</i> (2007)
Bean	6-12 mg kg ⁻¹ (foliar)	Ozbahce and Zengin (2014)
Sesame	3 kg ha ⁻¹ (broadcasting)	Habimana <i>et al.</i> (2016)

Conclusions

Manganese increases the photosynthetic efficiency and development of dry matter in plants as an important micronutrient for plant metabolic processes. By increasing plant tolerance to diverse diseases, it offers resistance to biotic stress. Both toxicity and Mn deficiency change cell-level physiological, biochemical and molecular processes. For the purpose of soil and plant interaction management, it is crucial to know the limitations of the soils, especially in relation to the deficiency and toxicity of Mn. Initial indication of potential Mn deficiency and toxicity will be provided by the soil test level and pH. In order to determine the optimum Mn fertilization for a crop, the identification of the critical limit of Mn in different soils is important. A crop's growing conditions, including soil type, organic matter, and past history, can help provide a more comprehensive image of Mn status of a cropping system. Thus, to improve crop production in our country, the knowledge on Mn requirement, uptake, dynamics, accumulation, and application is of paramount importance for efficient fertilizer management.

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