1. General introduction

Manganese is an essential element to act as activator to many essential enzymes of the tricarboxylic acid cycle (Burnell *et al.,* 1988) and also has a key role in the water splitting enzyme involved in photosynthetic oxygen evolution and also it is essential for many plant functions. Some of them are: i. the assimilation of carbon dioxide in photosynthesis, ii. it aids in the synthesis of chlorophyll and in nitrate assimilation, iii. Manganese activates fat forming enzymes, iv. it functions in the formation of riboflavin, ascorbic acid, and carotene, v. it functions in electron transport during photosynthesis (Gerretsen 1949; Linus *et al.,* 1949; Ducic and Polle 2005; Kimimura and Katoh 1972).

The stability of the chloroplast lamellar system may be affected by severe Mn deficiency (Burnell 1988), hence the photosynthesis and carbohydrate production is reduced in the leaves. The studies on the enzyme activation indicate that Mn act as a cofactor (Graham 1988 and Marschner 1995) and affects the synthesis of proteins (Lerer *et al.,* 1976) and carbohydrates (Burnell *et al.,* 1988).

Manganese deficiency in field crops has been reported worldwide, which often limits crop growth and results in decreased yield. The increasing occurrence of Mn deficiency in wheat crop make it necessary to undertake studies to understand the underlying reasons and which may lead to evolve techniques for the efficient management of this nutritional disorder (Nayyar 1999). The alleviation of Mn deficiency can not be easily accomplished in soils of high pH, and with foliar sprays it may requir multiple applications of fertilizer. In recent years in some parts of Germany have seen an increase in Mn deficiency problems due to application of lime which has resulted in an increase in soil pH. In this condition, the availability of Mn to plant declines (White and Zasoski 1999) and Mn deficiency is becoming a major plant

nutritional problem. In Mn-deficient soils with high amount of free $CaCO_3$, most of the Mn fertilizers are immobilized during a week of application and Mn uptake is decreased. However, Manganese deficiency continues in spite of recommended rates of Mn fertilizer.

Over the last decade, Mn deficiency in crop plants and identification of crops and their genotypes that grow and yield well in Mn deficient soils (Mn efficient) has been subject of numerous publications. It had also been observed that certain genotypes of cereals grown in India yielded markedly better on low plant available Mn soils than others and were, therefore, likely to be Mn efficient (Nayyar 1999). Ascher-Ellis *et al.*, (2001) defined that Mn efficiency is the ability of a genotype to produce high yield in a soil which is of limiting Mn content for a standard genotype. Genotypes may differ in the mechanism used to acquire nutrients from environments with low nutrient availability, thus avoiding nutrient deficiency stress. Plants may change the morphology of their root system, change physiology and biochemistry of nutrient uptake; modify the chemistry of the rhizosphere to increase the availability of nutrients (Rengel 1999). Genotypic differences in susceptibility to the Mn deficiency are related to the proportion of Mn-oxidizing bacteria in the rhizosphere (Timonin 1946).

Some factors which have been proposed to contribute to differential Mn efficiency include: Mn content of seed; improved translocation of Mn to the shoots; mobilizing or immobilizing Mn in the rhizosphere by root exudates or rhizosphere microorganisms; Mn uptake kinetics; Mn requirement; differential root growth at low Mn supply and the population of Mn oxidizing and reducing microorganisms in the rhizosphere; (Godo and Reisenauer 1980; Graham 1988; Graham and Rengel 1993; Marschner *et al.*, 2003; Huang *et al.,* 1994; Pedas *et al.*, 2005; Sadana *et al.*, 2002).

In this investigation a few relevant factors have been reviewed under the following headings:

1.1 Manganese in soil and its availability to plants

Manganese occurs in soils mainly in the form of compounds of Mn^{2+} and as oxide-Mn (Sanders, 1983; Merckx *et al.,* 1986). Three oxidation (II, III & IV) states occur in soil but plants are only capable of absorbing Mn^{2+}. The soil solution component, generally a very small proportion of total soil Mn, exists in equilibrium with mineral forms and with organically complexed and exchangeable Mn. Manganese availability to plants is controlled by its concentration in soil solution which is dependent both on the chemistry of manganese and of the soil matrix (Uren 1989). Concentrations of Mn were depressed in leaf tissue of plants (wheat) from limed soils and also in high P soils because of depressed soil solution Mn concentrations resulting from elevated pH (Neilsen *et al.*, 1992). High pH reduces the availability of Mn, while low pH increases availability. At high pH (above 7.5), there is little plant-available Mn and may not cover the needs of the plants. Soils with high pH and a high content of organic mater contain only small amounts of plant available Mn. Increasing the pH results in the formation of complexes between divalent Mn ions and organic material, thus reducing the amount of Mn that is available for plant growth. Although, McBride (1982) found that Mn tends to form weak coordination complexes with organic matter.

Manganese is more mobile in the reduced state, so its availability changes rapidly depending on the redox condition in the soil. For example, the reduction of β-MnO_2 may be written as: $\beta\text{-}MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$, with log k = 41.89 (Norvell 1988). The most insoluble oxide of Mn appears to be pyrolusite, β-MnO_2 (Schwab and Lindsay 1983). Manganese availability to plant is controlled by redox potential and soil pH (Norvell 1988; Schwad and Lindsay 1983; Uren 1989; Sims and Patrick 1978; Neilsen *et al.,* 1992; McBride 1982). Patrick and Fontenot (1963) found that decrease in redox potential of a soil under

flooding condition had little effect on Mn uptake by rice. In contrast Clark *et al.*, (1957) found that Mn solubility and its availability to rice plants greatly increased under flooding a soil.

1.2 Uptake of Mn from soil by plants

Manganese is one of the transition elements essential for plant growth (Marschner 1995). Manganese uptake, at a given soil Mn availability, will depend on plant properties like the size of the root system and those properties that affect the Mn influx.

1.2.1 Root system size

The amount of nutrient a plant takes up from the soil depends on the size of the root system. The root system size may also be described by the root-shoot ratio, i.e. the amount of roots to feed a unit of shoot. Sadana *et al.*, (2005) found that root growth of some wheat cultivars was reduced under Mn deficiency conditions in soil. Under low Mn supply conditions root growth was more strongly inhibited than shoot growth by the reduction of the root length-dry matter yield ratio (RL/DMY ratio). This effect was most pronounced in inefficient durum wheat cultivar PDW 233. The low Mn efficiency of durum wheat cultivar was related to the strong decrease of its root growth under low soil Mn supply. Lombnaes and Singh (2003) found that under Mn deficiency RL-DMY ratio decreased for barley and oat grown in chelator-buffered nutrient solution. A possible function of Mn for root growth is in auxin metabolism and the synthesis of phenols and lignin. Manganese deficiency results in lower concentration of these compounds in wheat roots (Brown *et al.,* 1984). Auxin is required for cell elongation and thus root growth. Lignin is needed for cell-wall thickening, cell-wall strength, and lignifications of cell wall. In contrast of Mn, it has been shown that phosphorus (P) shortage may increase root length (Anuradha and Narayanan 1991), root-

shoot ratio (Föhse *et al.*, 1988) and increase root hair density and length (Föhse and Jungk 1983).

1.2.2 Factors that influence the Mn Influx

Influx is the rate of entry of nutrients into the root which may be expressed per unit of root length (mol cm^{-1} s^{-1}) or per unit of surface area (mol cm^{-2} s^{-1}). Influx of a nutrient per unit of root is equal to the flux from soil (Claassen and Barber 1976; Claassen *et al.*, 1986). This can be illustrated by Figure 1.1, relating the flux of a nutrient into a unit of root as a function of concentration in the ambient soil solution and the progress of soil solution depletion under the influence of the respective flux out of the soil. The Mn influx at a given Mn availability is dependent on morphological and physiological root properties and their interaction with soil.

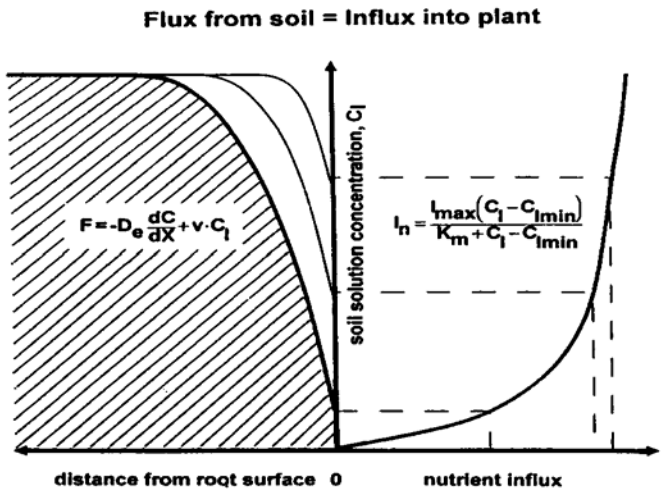

Figure 1.1 Schematic representation of the Barber-Claassen model relating nutrient uptake kinetics of roots to nutrient depletion of soil (Waisel *et al.,* 1996).

1.2.2.1 Root morphology

Nutrient fluxes in the rhizosphere are also influenced by the morphological root properties such as diameter and formation of root hairs. Root hairs increase surface area per

unit root length (Föhse *et al.*, 1991) this was shown important for P uptake (Hendriks *et al.,* 1981; Föhse *et al.*, 1991). Root systems consisting of thin and long roots can therefore be regarded to be more efficient in exploiting the soil of nutrients than those with thick and short roots. Root hairs are even more efficient in this regard. Dong *et al.*, (1995) showed that a bread wheat cultivar (Zn-efficient) improved longer and thinner roots than a bread wheat of less Zn-efficient and a Zn-inefficient durum. The growth of root hairs has been shown to increase under nutrient deficiencies such as P, Fe, and nitrate (Foehse and Junk 1983; Muller and Schmidt 2004), while Ca deficiency can inhibit root hair growth (Tanaka and Woods 1973). Mantai and Newton (1981) reported that the increase of root growth in Myriophyllum spicatum L. showed a highly significant linear relationship with decreasing nitrate and phosphate concentrations. Konno *et al.,* (2003) found that Mn deficiency increased root hair formation at pH 6 and suppressed main root growth slightly. In contrast, increasing the Mn concentration suppressed low-pH-induced root hair formation. However, very little is known about whether root hair growth is affected by plant Mn status or Mn concentrations at the root surface.

1.2.2.2 Uptake kinetics and root absorbing power

The uptake kinetics describes the relationship between the influx (I_n) of an ion (uptake per unit root and unit time, e.g., mol cm^{-1} s^{-1}) and its concentration in solution at the root surface (C_{Lo}). For a concentration range, as found in the soil solution, it usually follows a saturation curve that can be described by the Michaelis-Menten equation, described by the parameters maximum net influx (I_{max}) and the Michaelis constant (K_m), the same that define enzyme activity (Epstein and Hagen 1952). Nielsen (1972) modified this equation to account

for the fact that plants do not deplete the concentration to nil, but only to a certain minimum concentration, C_{Lmin}, where influx equals efflux and net influx is zero:

$$I_n = \frac{I_{\max}(C_L - C_{L\min})}{K_m + C_L - C_{L\min}}$$

Where I_n is the net influx, I_{max} is the maximum net influx, K_m is the Michaelis constant, equal to the substrate ion concentration that gives half of the maximum net influx; the lower this constant, the higher the affinity between the carrier sites and ions. C_{Lmin} is the concentration at which net uptake of ions ceases (Marschner 1995). C_{Lmin} differs considerably among plant species and nutrients. For potassium, C_{Lmin} values of approximately 1 µmol L^{-1} have been found (Claassen and Barber 1974), and for phosphate values below 0.1 µmol L^{-1} are common (Drew *et al.,* 1984; Jungk *et al.,* 1990). For Mn the C_{Lmin} is close to zero, because the plants can reduce Mn concentration to near zero. Hence the I_n is given:

$$I_n = \frac{I_{\max} \cdot C_L}{K_m + C_L}$$

The parameters of ion uptake kinetics are not constant. Influx may vary widely among species (Loneragan and Asher 1967; Brewster and Tinker 1972; Caradus and Snaydon 1986; Fist 1987; Föhse et al 1988), among varieties (Nielsen and Barber 1978; Schenk and Barber 1980), along the roots (Bhat and Nye 1974; Häussling *et al.*, 1988), and with age and nutritional status (Mengel and Barber 1974; Jungk and Barber 1975; Bhat *et al.*, 1979). Drew *et al.*, (1984) found that K starvation of barley caused a decrease in K_m value from 53 to 11 µmol L^{-1}, without alteration of I_{max}.

For maximum growth, though, the influx is far below I_{max}, so the concentrations below K_m are sufficient (for P around 1 µM, K 1 to 5 µM and Mn around 0.2 to 0.5 µM), and the