CHAPTER -II

REVIEW OF LITERATURE

2.1. Zinc in soils

Zinc occurs in soils in primary minerals and clays. It exists as free and complexed ions in soil solution, as adsorbed ions occluded mainly in soil carbonates and hydrous oxides, biological residues and living organisms and in the lattice structure in soils (McLaren and Crawford, 1973; Iyengar et al., 1981; Nielsen et al., 1986; Liang et al., 1991). The distribution of Zn in these forms varies widely in soils as a result of differences in mineralogy, parent materials and organic matter content (Iyengar et al., 1981; Hajra et al., 1987; Baker, 1990; Liang et al., 1991). Zinc remains adsorbed on organic matter and clays, and it precipitates as hydroxide, phosphate, carbonate and silicate at slightly acid to alkaline pH. The average Zn content in soil ranges from 17-160 mg/kg. Generally, data on total Zn have been of little value in indicating the occurrence of Zn deficiency or the need for Zn fertilization (Iyengar et al., 1981; Kabata-Pendias and Pendias, 1992). Zinc is present in the ferro magnesium minerals, augite, hornblende and biotite. Soils derived from more siliceous acid rocks like, gneiss and sandstone are poorer in Zn, whereas those from the basic igneous rocks are richer in Zn. In addition, Zn forms a number of salts in soils such as; ZnO, ZnCO$_3$, (ZnFe)S, ZnSiO$_3$, Zn$_2$SiO$_4$, ZnS etc. Besides, Zn present in the soil is associated with the exchange sites of clays and organic matter and on the surface of calcium carbonate, sesquioxides etc., in the adsorbed state. The element may be adsorbed as Zn$^{2+}$, ZnOH$^+$ or ZnCl$^+$. Zinc retained on exchange sites and chemisorbed by organic matter and hydrous oxides is believed to be readily available to plants (Soon, 1994).
2.2. Content, forms, distribution and transformation of zinc in soils

Total Zn content in the normal soils of the world range from 10 - 300 ppm. In Indian soils total Zn ranges from a few ppm to about 1000 ppm. It ranges from 7 ppm in coarse textured alluvial soils (Entisols) to 284 ppm in fine textured vertisols (Ganjir et al., 1973). Highly weathered coarse textured laterite and red soils were found to be poor in total Zn. The less weathered calcareous heavy textured soils were richer in total Zn. The clayey fractions contained 164 to 429 ppm Zn against 14 to 94 ppm in sand fractions.

Zinc in soils exists in several forms such as water soluble + exchangeable, complex, organically bound, acid soluble etc. Availability of applied Zn is largely influenced by its rate of transformation in soils. Generally, added Zn is transformed into water soluble, exchangeable, complex, oxides, carbonates and residual forms. Zinc present in water soluble, exchangeable and complex form is readily available to plants, whereas Zn associated with oxides and other primary/secondary minerals is relatively unavailable (Mandal and Mandal, 1986).

The release of complexing agents by organic matter causes Zn to redistribute into different fractions. Soils rich in organic matter releases complex Zn or provides chelating agents which reduces adsorption and precipitation (Singh and Abrol, 1986). Under submerged conditions, application of organic matter caused a substantial increase in water soluble plus exchangeable, organic, complex and amorphous sesquioxides bound fractions of native or applied Zn (Mandal et al., 1988).

Raychaudhuri and Biswas (1964) reported that sand stone, lime stone, shale and igneous rocks contain 16, 24, 47 and 51 ppm of Zn respectively. Randhawa and Kanwar (1964) found positive significant relationship between silt + clay and Zn content of Punjab soils. Some highly leached acid soils are very poor in Zn with total values of 10-
30 ppm. Available Zn content in Indian soils ranges from 0.08 to 20.5 ppm. On an average, it is around 0.6 ppm. Critical limits for available Zn was suggested by Takkar and Mann (1975). According to Takkar et al. (1989) 43 per cent of the soils in India are deficient in Zn. The total concentration of Zn, Cu, Mn an Fe varied widely from 40 to 280 mg kg$^{-1}$, 27 to 210 mg kg$^{-1}$, 23.7 to 1872 mg kg$^{-1}$ and 2.00 to 5.6 per cet, respectively and content was comparatively high in the 20 – 40 cm depth except for Fe. Almost similar results were reported by Avasthe and Avasthe (1995) for agricultural soils of Sikkim, out of the 200 soil samples, 46 per cent were deficient(<0.6 ppm), 41 per cent were marginal (0.6-1.2 ppm) and 13 per cent were sufficient (>1.2 ppm) in Zn.

2.3. Zinc species in soil solution

Forms of Zn dominant in soil solution are Zn$^{2+}$ and ZnOH$^+$. The specific forms present are determined largely by the Soil pH. The simple cation dominates under acid conditions and more complex hydroxy metal cation form predominates as the soil pH is increased. Among inorganic species Zn$^{2+}$ is the major ionic species below pH 7.7. The hydrolyzed species Zn(OH)$^+$ and Zn(OH)$_2$ are formed only above pH 7.7 and 9.1, respectively. Other complex species such as Zinc-ammonia complexes Zn(NH$_3$)$_4^{2+}$, Zn(OH)(NH$_3$)$_3^+$ and Zn HPO$_4$ become significant only at alkaline pH. Formation of ZnSO$_4$ may also occur which result in high solubility and movement in soil. The concentration of Zn in soil solution is very low, only in parts per billion range. About 60 per cent of soluble Zn is associated with soluble organic acids and amino acids (Stevenson and Ardakani, 1972; Hodgson et al., 1966). Zinc interacts with soil organic matter and both soluble and insoluble Zn organic complexes are formed. Soluble Zn organic complexes are mainly associated in the fulvic acids and insoluble organic complexes are associated with the humic acids.
The solubility of Zn and the mechanism that control Zn solubility may vary with soil properties, such as pH, organic matter and clay content (Kathryn et al., 2002). Gupta et al. (1987) suggested that at high pH, precipitation reactions control Zn solubility, whereas at neutral to acidic pH, specifically adsorbed Zn may control the Zn solubility. Singh and Abrol (1985) found that precipitation of Willemite (Zn2SiO4) was likely at pH greater than 7.9 and that adsorption may occur below pH 6. Jeffery and Uren (1983) concluded that at neutral to alkaline pH, specific adsorption of hydrolyzed form of Zn (Zn(OH)\(^+\)) may account for low soluble Zn concentration. Zinc may bind to Fe, Mn, and Al oxides, clays, or organic matter in soils. Iron, Mn and Al oxides contain surface hydroxyl functional groups that may strongly bind metals, with increased adsorption at high pH (Sposito, 1984). Adsorption of Zn by these oxides has been suggested by several studies (Dang et al., 1996). McBride and Blasiak (1979) suggested that adsorption to oxide surfaces, which have a high affinity for Zn, may be important in controlling Zn solubility. Zinc adsorption by clays has been shown to be pH dependent (Baeyens and Bradbury, 1997; Kurdi and Doner, 1983). Brigatti et al. (1996) reported that Zn solubility is influenced by the cation exchange capacity of the soil. According to McBride et al. (1997), it is difficult to distinguish the effects of organic matter because it is often related to pH and organic matter composition tends to vary across soils. Some studies indicate that total soluble Zn is not affected by organic matter (Mc Bride et al., 1997). Zinc concentration in soil solution, and hence its availability to plants is regulated by its adsorption on the surface of soil colloids and also by precipitation resulting from its interaction with other ions in soil (Swift and Mc Laren, 1991).

2.4. Factors affecting Zn retention and availability

Zinc is available at acidic pH and becomes less available at alkaline pH as the mineral and organic form has low solubility. High solubility of Zn is maintained in acid
soils of pH 5 or below and Zn deficiency may occur because of the leaching of Zn from root zone. The solubility of soil Zn decreases 100 fold with a unit increase in soil pH (Lindsay, 1991). Liming of acid soil (Cottenie and Kickens, 1974) and high soil sodicity (Mehrotra et al., 1986) are known to reduce availability of Zn. The availability of Zn depends on the content of chelating agents in the soil exuded by plant roots or from the decomposition of organic matter (Lindsay, 1974; Murphy and Walsh, 1972). High correlation between available Zn and soil organic matter has been reported by many workers. Calcium carbonate adsorbs significant amount of Zn resulting in its fixation. The oxides of Fe, Al (Kalbasi et al., 1978) and Manganese (Shuman, 1988) present in soils are capable of adsorbing significant amounts of Zn.

Higher level of available P or applied fertilizer P induces Zn deficiency in plants. Depressive action of P on Zn may be a physiological one largely taking place in roots, restricting translocation to above ground parts (Stucken Holtz, et al., 1966). Soils under forest are rich in Zn while shifting to crop cultivation in some cases, leads to decline in the available Zn (Katyal, 1985).

2.5. Fractionation and extraction of zinc

Micronutrients are generally held within the mineral matter (Miller et al., 1986, Randhawa and Singh 1997) and finer fractions of soils (Follet and Lindsay, 1970, Katyal and Sharma, 1991; Sharma et al., 1999).

Zinc in soils may be divided into five chemical pools viz; water soluble (fraction present in soil solution), easily exchangeable (ions bound to soil particles by electrical charges) adsorbed, chelated or complexed, associated with secondary minerals and held in primary minerals. The fractions of Zn usually separated are exchangeable, organically bound, hydrous oxides of Fe, Al, and Mn bound and residual form.
Himes and Barber (1957) showed that organic matter chelates Zn in soil. Jenne (1968) in a comprehensive review showed how hydrous Fe and Al oxides controlled Zn, Mn, and Cu concentrations in soils through adsorption. Both clays and Fe and Al oxides adsorb Zn and are relatively similar in retention (Shuman, 1976 and 1977). Adsorption of Zn is correlated with CEC (Shuman, 1976, 1977), as higher CEC has higher exchangeable Zn. In the fine textured soils, Zn occurs mainly in the crystalline Fe oxides, silt and clay fraction. In sandy soils, Zn was relatively higher in the exchangeable and organic forms, compared to the fine textured soils and is highly associated with Fe and Mn oxides (Harrison et al., 1981; Iyengar et al., 1981; Kuo and Baker, 1980; Miller and Mc Fee, 1983). Bentonite and illite fixed significant quantities of Zn and Mn and kaolinite fixed little (Reddy and Perkins, 1974). According to White (1957) exchangeable Zn fraction in soil ranged from 1 – 7 per cent, Fe oxide fraction from 30 – 60 per cent and clay fraction from 20 – 40 per cent.

Zinc is bound less tightly by organic matter and as such experience greater leaching losses and are more likely to exist in the exchangeable form in soils (Tyler, 1981 and Miller et al., 1986). Major portion gets accumulated in forms strongly bound to the mineral fraction of the soil (Iyengar and Deb, 1977 and Murthy, 1982). Considerable amount of Zn accumulates in exchangeable and complexed (weakly bound by organic matter) forms, which meet bulk of the plant requirement. The distribution of chemical forms of Zn depends on the physical and chemical properties of soils including soil environment (Prasad and Sakal, 1988 and Hajra et al., 1987).

Singhal and Rattan (1995) in their studies on fractionation of ten alluvial soils from Haryana found that Zn in water soluble and exchangeable pools was virtually non-existent. Major portion of the total Zn in the soils existed in the forms viz., Zn specifically adsorbed on clays, organically bound, occluded by free oxides and residual
Residual Zn constitutes higher percentage of total Zn. Correlation data indicated that these fractions are in a state of dynamic equilibrium and show significant dependence on clay content, organic carbon, CEC and CaCO$_3$. The availability of soil Zn to plants is governed by a dynamic equilibrium among the different fractions of soil Zn whereas relative abundance of these chemical pools depends upon the physical and chemical properties of the soil (Mandal et al., 1986).

Chemical fractionation of soil Zn has been viewed as a means of assessing sources of plant available Zn and as a way of identifying potential extractants for measuring available Zn (Nielson et al., 1986). It has been reported that Zn present in water soluble, exchangeable and complexed forms significantly contribute to the Zn nutrition of plants, whereas, that associated with oxides and other primary and secondary minerals is relatively unavailable (Vittal et al., 1988).

Dhane and Sukla (1995) reported the micronutrient status of some soil series of Maharashtra. The positive relationship among various soil fractions suggested the existence of dynamic equilibrium of Zn fractions in soils and the positive significant relationship of solution and exchangeable fractions of Zn with organic carbon suggested the dependence of Zn availability on organic matter content of the soil. Water soluble, exchangeable, and organic complexed Zn, which constituted hardly 5 per cent of the total Zn in soil, accounted for variability in plant available Zn to a great extent (Iyengar and Deb, 1977). According to Murthy (1982) Zn in soluble organic complex and that held by amorphous sesquioxides are the major fractions which influence the availability of Zn.

Different chemical forms of Zn and their relative distribution in soil varies depending on their physical and chemical properties. Water soluble Zn is present in very small quantities, and it is largely controlled by soil pH. Low soil pH favors solubility of
Zn (Saeed and Fox, 1977) and simultaneously prevents its adsorption by soil exchange complex (Bar-Yosef, 1979). In alkaline pH Zn form negatively charged ions. The acid zincate ($\text{ZnO}_2^{2-}$) is the prevalent form in lower concentration of alkali. Probably in alkaline solutions, the hydroxides of Zn are formed (Kanwar, 1976). A change in pH may alter the stability of soluble and insoluble organic complexes of Zn or the solubility of antagonistic ions (Singh and Singh, 1981). Almost 90 per cent of total Zn in soil is present in the residual form (Mandal and Mandal, 1986; Liang et al., 1990) indicating that most of the applied Zn as fertilizer is reverted to the residual fraction (Iyengar and Deb, 1977). Dynamic equilibria among different fractions of soil Zn indicates the depletion in concentration of readily available forms which is replenished by the other pools. Similar observations were made by Sarkar and Deb (1982), Mandal et al. (1986) and Tagwira et al. (1992).

Changes in chemical properties brought about by phosphate addition can alter the equilibrium of Zn in soil, leading to redistribution of Zn in different fractions (Shuman, 1988). Neilsen et al. (1986) reported that a change in pH resulted in redistribution of Zn from residual form to exchangeable/organic forms.

At low pH under reducing conditions, Sims and Patrick (1978) showed that Zn moves into the exchangeable and organic fractions from the inorganic fractions, while at high pH under oxidizing conditions, the reverse was found to be true. If organic matter is added and reducing conditions are present, Zn will become complexed and move into the organic fractions (Shuman, 1988).

2.6. Adsorption reactions of Zn in soil

The adsorption of nutrients is one of the most important solid and liquid phase interaction determining the release and fixation/retention of applied plant nutrients. Adsorption reactions of Zn in soils are important to understand the solid and liquid phase
interactions determining the release and fixation of applied Zn and thereby the efficiency of fertilization. The rate of Zn sorption from solution onto solid surfaces is a dynamic factor that directly or indirectly regulates the amount of Zn in solution at any given time.

Zinc sorption has been described by Langmuir equation (Shuman, 1975; Udo et al., 1970). Several workers also observed that soil having pH in the neutral or alkaline range could adsorb Zn beyond their cation exchange capacities (Misra and Tiwari, 1966; Reddy and Perkins, 1974). pH, CEC, organic matter and clay content, metal oxides etc. are the main soil properties contributing to the Zn sorption process in soil (Shukla and Mittal, 1979; Shuman, 1977; Tapan and Rattan, 2002). Zinc sorption is characterized by an initial fast process followed by a slower and finally steady state condition. The Langmuir adsorption isotherm has been widely applied to study the adsorption of Zn in soil (Jahiruddin et al., 1985; Dhane and Shukla, 1995 and Rupa and Shukla, 1998).

Soil pH contributes greatly to the variation of maximum specific Zn sorption. Also the ratio of clay content to CEC was significantly correlated with specific Zn sorption parameters and was attributed to the interaction of soil clay content with CEC (Karan et al., 1983). Clay content and pH play significant roles in variation of adsorption characteristics of the calcareous soils. Amer (1995) reported that pH was an interacting factor in the DTPA extractable Zn of coarse textured calcareous soils. Davis et al. (1995) observed that lower pH solutions extracted more of the applied Zn. Pardo and Guadalix (1996) demonstrated that sorption of Zn by two Andepts was higher at pH greater than 6. They concluded that strong adsorption or even precipitation of Zn occurred at high pH. Taylor et al. (1995) fitted Freundlich, Langmuir and BET adsorption isotherms to their Zn adsorption data and concluded that Langmuir ‘b’ was correlated with some selected soil properties and that CEC, organic matter pH and clay content were the main contributors to the variations in Zn sorption.
Zinc sorption is strongly dependent on soil pH. The precise role of pH is yet uncertain but metal ion or surface hydrolysis is often implicated (James et al., 1975). Many authors have reported a decrease in solubility and increase in Zn sorption with increasing pH (Bar-yosef, 1979; Barrow 1986; Msaky and Calvet 1990; Stahl and James 1991a and b). Lack of equivalence during exchange and the change in pH during adsorption of heavy metals are the main characteristic of adsorption of heavy metals in soils (Jarvis, 1981; Kurdi and Doner, 1983; Harter, 1983). These changes are caused by the hydrolysis of heavy metal cations (Hodgson et al., 1966). The effect of pH on sorption of Zn by soils generally resembles more closely to its adsorption by oxides than that by silicate clays or organic matter (Mc Bride and Blasiak 1979). Cavallaro and Mc Bride (1984) also showed the oxide constituent of clays to be more important than the organic constituents. The concentration of Zn in soil solution increased rapidly when the pH decreased below the threshold value (Brummer et al., 1983; Sanders and Adams, 1987).

Barrow (1987) and Xie and Mackenzie (1990) reported that phosphate sorption will increase the negative charge of particles thereby increase the Zn sorption. When a phosphate fertilizer is added, the soil pH may change due to dissolution of P or due to P sorption. This affects the equilibrium of Zn in soils (Tagwira et al., 1992). The increase in the amount of Zn sorbed by a soil previously treated with phosphate may be a consequence of either an increase of the negative surface charge of soil particle, creation of specific sorption sites on oxide surfaces or precipitation of hopeite (Xie and Mackenzie, 1989).

Adsorption - desorption processes control the concentration of Zn in the ambient soil solution bathing plant roots and govern the availability of Zn to crops (Sinha et al., 1975). Many soil properties, like soil carbonate, organic matter, and clay
contents and pH decide the extent of Zn adsorption and desorption, which in turn influence the availability of both natural and applied Zn fertilizer to the growing crops. The clay, silt and carbonates could provide sites for Zn adsorption (Udo et al., 1970; Shuman, 1975). High soil pH encourages more hydrolysis of Zn$^{2+}$ resulting more adsorption of Zn by soil exchange complex (Yosef, 1979).

Bingham et al. (1964) found that Z$^{2+}$ can be held exchangeable and the amount in excess of CEC of soils are retained as Zinc hydroxide. Zn adsorption is known to be pH dependent (Peralta et al., 1981; Pardo and Guadalix, 1996) and is related to CEC of soils (Shuman et al., 1975). In several studies Zn adsorption has been described primarily by the Langmuir equation (Dhane and Shukla., 1995) or Freundlich equation (Krishnaswamy et al., 1991; Sarkar et al., 1989; Buchter et al., 1989). Kuo and Mikkelson (1979) reported that at a high Zn concentration, Zn adsorption can be described only by the Freundlich equation. Zinc sorption follows Langmuir adsorption isotherm and adsorption capacity is correlated with clay, organic matter and pH (Shukla and Mittal, 1979; Shuman, 1977 and Trehan and Sekhon, 1977).

2.7. Estimation of zinc availability

Only a small fraction (1 – 4 per cent) of Zn applied has been found to be utilized by crops, with a large portion of it getting fixed in soils in forms less available to plants (Iyengar and Deb, 1977). Complex, water soluble and organically bound fractions were the most important fractions contributing to plant uptake. Less than 5 per cent of soil Zn is present in these fractions. Bulk of the applied Zn is accumulated in the residual and acid soluble fractions. Only 10 to 35 per cent of applied Zn is found in the water soluble, exchangeable and complexed fractions and thus remained unavailable to
plants. About 20 – 60 per cent of applied Zn was recoverable by complexing agents like DTPA.

Commonly used extractants for Zn include water, neutral salts, weak and strong acids and chelating agents. Some of the extractants are 2N MgCl₂, 0.5M NH₄OAc (pH 4.8) and 0.2M MgSO₄ CO₂ saturated water, 0.5N KCl + HOAc at pH 3.2, 0.1N MgSO₄ + H₂SO₄ to soil pH, 0.1N HCl, NH₄OAc-dithizone etc. (Viets and Lindsay, 1973). Some of the chelating agents used as extractants are EDTA at concentrations 0.007 to 0.05N buffered at near neutral pH (Viets and Lindsay, 1973). White (1957) used 5 N HCl at pH 8 for Zn, and Shuman (1979) used 0.1N HCl, a common Zn extractant for predicting plant availability. 0.05 M CaCl₂ (Mc Laren and Crawford, 1973), 1M NH₄OAc (Gupta and Chen, 1975), and 1N MgCl₂ (Gibbs, 1973) have been used for exchangeable Zn, Cu and Mn. Manganese chloride solution has been found suitable as a predictor of Zn uptake (Martens, 1968; Stewart and Berger, 1965). DTPA (0.005M DTPA + 0.01M CaCl₂ + 0.1M Triethanolamine buffered at pH 7.3) is found to be a promising extractant for establishing availability of Cu, Fe, Zn and Mn in soil (Lindsay and Norwell, 1978).

Soil extraction techniques to measure the status of available micronutrients for plants are important in the diagnosis, deficiency or toxicity. The proportion of applied Zn that may be extracted by a particular reagent is presumably determined by the physical and chemical properties of soil as well as the extraction conditions. Chowdhury et al., (1992) studied the effect of extraction period and soil to solution ratio on extraction of Zn and concluded that the amount of DTPA and EDTA extractable Zn was almost unaffected by those factors. Mehlich 3 (Mehlich, 1984), EDTA (Sposito et al., 1982., Miller et al., 1986), DTPA (Lindsay and Norwell,1978) were confirmed for their ability to extract simultaneously Cu, Zn, Fe and Mn. Lee et al. (1978) and Mandal and Haldar(1980) confirmed DTPA - TEA as a universal micronutrient extractant by
repeated results obtained from acid, reduced and metal polluted soil. Al Jaloud et al., (1995) also reported it a good extractant to estimate micronutrient availability in soil.

Numerous authors have recommended the use of Mehlich 3 (Mehlich, 1984) because it not only extracts simultaneously various nutrients but also shows good correlation between the amount extracted from the soil, the amount absorbed by the plant, and the crop response (Walworth et al., 1992; Junus and Cox, 1987; Rohman and Cox, 1988). According to Sims (1989), Mehlich 3 has been adopted to suit a wide range of soils and might be considered a universal extracting solution. Walworth et al. (1992) have found Mehlich to be as effective as DTPA - TEA and a good alternative since it is a multi element extracting solution.

Another test used to extract simultaneously macro and micronutrients is the SS solution (Soltanpour and Schwab, 1977). Rohman and Cox (1988), comparing Zn, Mn, Cu concentrations extracted by SS solution and Mehlich 3 found strong correlation between methods as well as between SS solution and plant uptake. As per Lindsay and Cox (1985), improvements upon soil test may not lead to an ideal universal extracting solution, but help to standardise successfully a process and improve interpretation by adding important factors that affect the extent to which nutrients are available and can be extracted.

According to Davis et al. (1995) lower pH solutions extracted more of the applied Zn, but more neutral solutions extracted Zn were better correlated with Zn uptake. On the other hand Mehlich 1 which had a lower pH, had better correlation with both applied Zn and leaf Zn than did Mehlich 3. Shortening the DTPA extraction time to 30 minutes resulted in better correlation than the standard two hour extraction time. The optimum soil Zn extractant should be useful not only for prediction of plant Zn concentration but also for detection of applied Zn levels. According to Haddad and
Evans (1993), 0.05 M HCl are suitable for acidic soils and extractants like EDTA are suitable for calcareous soils. Reducing DTPA solution pH from 7.3 to 6.0 improved the correlation with applied Zn but reduced correlation coefficient relating DTPA extractable Zn to leaf Zn. In general lower pH solutions extracted more of applied Zn, but more neutral solutions extracted Zn amounts which were correlated with leaf Zn concentration. On the other hand, Mehlich 1 had lower pH and better correlations with both applied Zn and leaf Zn than did Mehlich 3.

According to Gupta and Shukla (1999), among four extractants viz., DTPA, 0.1N HCl, Ammonium acetate – EDTA and HCl + H$_2$SO$_4$, 0.1N HCl has the greatest extraction capacity for Zn followed by ammonium acetate + EDTA, DTPA and double acid. 0.1N HCl extracted about 50 per cent more than double acid. The former being fairly a strong acidic reagent, might have reacted with sparingly soluble and occluded forms of Zn and thereby extracted greater amount of Zn compared to latter (Iyengar and Deb, 1977).

Availability of DTPA extractable micronutrients was affected by soil properties such as pH, organic carbon, sand, silt, clay content etc. However, the variation in DTPA extractable micronutrients in relation to these soil characteristics may not be uniform for all soils in general, especially in acid soils (Sakal et al., 1988; Singh and Choudhary, 1990).

2.8. Crop responses to application of zinc

Zinc deficiency is considered the most widespread micronutrient deficiency in cereals worldwide, causing severe reductions in grain yield and quality (Cakmak et al., 1996; Graham et al., 1992). In our country, widespread micronutrient deficiencies are associated with specific soil properties and cropping system (Takkar, 1996). Among micronutrients, Zn deficiency was found widespread in Indian soils. About 48 per cent
of Indian soils are deficient in available Zn (Katyal and Rattan, 1990; Sakal, 2001). Deficiency of micronutrients has become a major constraint to productivity, stability and sustainability in many soils. Wheat production increased, on application of Zn, in various parts of India (Mahapatra et al., 1970). Kanwar and Randhawa (1964) reported that ZnSO₄ application in acid soils of Kangra increased the wheat yield significantly over N, P and K. Kanwar and Joshi (1964 a) found that the foliar as well as soil application of Zn SO₄ to local wheat produced significant yield increase.

Randhawa et al. (1969) reported that soil application of 10 ppm ZnSO₄ increased the maize yield significantly in six out of nine Haryana soils in pot experiments. Soil application was better than spray application. Khera and Brar (1970) observed band placement of ZnSO₄ to be much superior to broadcast and spray application.

In the case of paddy also, Zn application gave good response in pot culture studies with Tarai soils (Mahapatra et al., 1970). Malligaward et al. (1987) also reported that soil application of Zn showed higher Zn uptake by Lucerne crop.

Zn deficiency in Indian soils and responses to its application on various crops has been reported by Tiwari and Dwivedi (1993). Application of 5 kg Zn ha⁻¹ increased the average maize yield from 63.9 to 74.8 g ha⁻¹. Kochar et al. (1990) and Tiwari and Dwivedi (1993) also reported that 5 kg Zn ha⁻¹ was suitable dose for maize. The successive increase in Zn levels from 0 to 10 kg ha⁻¹ significantly increased the K uptake up to the level of 5 kg Zn ha⁻¹ and then decreased significantly at higher level. Application of green manure increased the Zn content in rice grain and straw significantly (Swarup, 1980). Abdul Salam and Subramanian (1988) reported synergistic interaction between Zn and N.
The optimum dose of Zn for different crops ranged from 5 to 10 kg ha\(^{-1}\). Response of crops to Zn application varied widely because of marked difference in soil characteristics, available Zn status of soils and crop variety characters (Ramsakal, 2001). Among the different Zn fertilizers, chelated source are more effective than inorganic sources (Adriano, 1986).

2.9. Rubber growing soils in South India

In India the cultivation of rubber traditionally is confined to a narrow tract in the western side of Western Ghats mainly in the Kerala state. The soils of this tract were laterite and lateritic types, red soils, forest soils and alluvial soils. (George, 1961, George, 1962; Koshy and Varghese, 1972). There soils are acidic in reaction with pH range being 4.5 - 6.0 and deficient in available P and K (Karthikakuttyamma et al., 1976, Pushpadas and Karthikakuttyamma, 1980; Karthikakuttyamma et al., 2000). Available K status is low in the soils in most of the conventional rubber growing region (Joseph et al., 1990). The available Mg status is high in the northern district of Kerala, Karnataka, Goa and Maharasthra region and Kanyakumari district in Tamil Nadu and low in the southern districts of Kerala (Pushpadas and Karthikakuttyamma, 1980; Karthikakuttyamma et al., 2000). As per the recent reports, majority of the soils in the traditional rubber growing tract are red ferruginous. Rubber growing soils of Kerala and Tamil Nadu have been characterized as per modern soil taxonomy and 62 soil series were identified. Out of the 62 series 51 were under Ultisols, nine under Inceptisols and two under Entisols (NBSS and LUP, 1999). Joseph et al. (1995) assessed the DTPA extractable Fe, Mn ,Zn and Cu status of the soils in the traditional rubber growing tract of India and found that the Zn status ranged from traces to high. Later on in an extensive study covering 9682 surface soil samples covering the entire rubber growing areas of Kerala and Tamil Nadu, NBSS
and LUP (1999) reported that 41.0 per cent of these soils are deficient in DTPA extracted available Zn.

2.10. Zinc in rubber nutrition

Zinc deficiency symptoms are not commonly observed in rubber plantations. At the same time, deficiency symptoms are reported from nurseries and young plantations especially in the second or third year of planting. The characteristic symptom is that the leaf lamina becomes very much reduced in breadth relative to its length. Frequently, the lamina become twisted and the margins appear wavy or undulating. In severe cases entire leaves in the top whorl will be completely affected and will look like ribbons with wavy margins. In the nursery plants, yellowing of leaves and narrowing of leaf blade with wavy, margins are the typical deficiency symptoms (Shorrocks, 1964; Karthikakuttyamma et al., 2000). Joseph et al. (2007) reported that application of Zn through two sources viz., zinc sulphate or zinc oxide significantly improved the availability of Zn in the soil and enhanced the growth of rubber seedlings.