CHAPTER ~ 2

REVIEW OF LITERATURE

Zinc deficiency is a worldwide nutritional problem in crop production. It is estimated that about 50% of world soils for cereal production have lower available Zn, which reduces grain yield and nutritional quality of grain (Graham and Welch 1996). Though Zn deficiency is considered as one of the most important micronutrient problem in the world. So crop responses to Zn application have been obtained in alluvial, red and lateritic soils and swell-shrink soils of the country (Singh and Behera, 2011). Appropriate amounts of zinc and nitrogen have to be used to cover both the absorptive and antagonistic effects (Shafea and Saffari, 2011**).**

Importance of Zn in crop production

Maize (*Zea mays* L.) is the third most important cereal crop in the world and its total production is more than that of any other cereal grain (FAO 2011). It is often known as the king of crops (Broudly et al. 2007). It is grown in different climatic conditions because of its consistency, drought resistance and various uses. Corn is a plant that grows rapidly and has different nutritional requirements according to soil or climatic conditions (Lucas 1996). Maize is also an important cereal crop in the context of nutrition for humans, poultry and livestock (Nuss and Tanumihardjo *2010*). Thus increasing Zn levels in maize grain could deliver more Zn to people whose diet relies directly or indirectly on maize-derived food. Maize needs great amounts of organic matter, therefore maize grows much better and produces more yield when cultivated in soil that contains enough organic matter (Arora and Singh 2004). In order to grow sufficiently, different elements such as nitrogen, phosphorous, potassium, calcium and magnesium are required in different quantities (Lucas 1996). Nitrogen is a macro element that has an important role within molecules, enzymes, co-enzymes, nucleic acid and cyto chromes. (Uhart and Andrade 1995) reported that a decreased grain yield can be attributed to a lack of nitrogen (Verma and Bhagat 1990). Maize also needs other microelements including zinc. Zinc plays an important role in adjustment of the stomata. It also facilitates the movement of potassium in the guard cells of the stomata. Under conditions where there is a lack of zinc, a decrease of carbonic anhydrous enzyme can lead to a diminished rate of net photosynthesis. The use of zinc serves to increase the density of zinc and protein in seeds, pneumatic organs and the overall quality of seed of production (Ranjan 2003). Zinc is also required in a small quantity, but if too little is available plants will suffer from the malfunction of some enzyme-systems and some other metabolic functions in which zinc has a role. Some observable changes that could occur due to lack of zinc are: chlorosis; a condition that causes the natural green color of leaves to turn bright yellow or even white as a result of a lack of chlorophyll.

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Alkaline soils with high pH have too little zinc available because the solvency of zinc decreases when soil pH increases. In alkaline soil, more zinc can be found than in other kinds of soil. ZnSO4 is used more than any other kind of zinc fertilizer, because of its high solvency (Ranjan 2003). According to Karimian, (1995) the application of nitrogen increased both the density and absorption of zinc by corn (Karimian 1995). Olsen expressed that the interactive effect of nitrogen and zinc is complex, it was also reported that the effect of nitrogen on decreasing zinc absorption was because of the dilution or gathering of zinc on the complex of protein in the root and increasing the absorption of zinc by plants as a result of nitrogen use and decreasing soil pH (Olsen et al. 1995). Zinc also has an antagonistic effect on iron. Brown (1993) showed that in some kinds of bean, the reduction of $Fe^{3}+$ to $Fe^{2}+$ increased with a lack of zinc especially in resistant varieties. The increased Zn/Fe ratio in plant tops in response to increased Zn level suggests that the presence of excess Zn and/or a deficiency of Fe within a plant occurs where Zn may have interfered with Fe in some metabolic function (Brown et al.1993). In plant roots with a shortage of zinc, iron absorption was found to be more effective (Ranjan 2003). Iron absorption and entry to the plant metabolism increased due to the interaction between nitrogen and zinc. But zinc had an antagonistic effect on iron content. Appropriate amounts of zinc and nitrogen have to be used to cover both the absorptive and antagonistic effects (Shafea and Saffari 2011).

Role of Zn in soil and plant

Zinc is a micronutrient essential for the growth and development of plants, as well as for animals and humans. As far back as 1926 the findings of Sommer and Lipman (Arnon, 1976) for the first time shown that zinc is an essential element for normal plant development, while the extensive use of zinc as a plant nutrient began in the early thirties of last century. It was found that symptoms of zinc deficiency frequently occur in some areas of the world, for example in Australia (Leece, 1976), India (Randhawa et al., 1974) and Turkey (Yilmaz et al., 1995; Cakmak et al., 1999). Today, Zn deficiency is widely recognized and it is considered as one of the most important micronutrient problem in the world, what is well documented in the recent literature (Alloway 2008). According to Alloway (2009), millions of hectares of arable land suffer from an insufficient intake of this element. A number of authors pointed out that, regarding the deficiency of available quantities of micronutrient in soils, the most abundant is zinc deficiency. Sillanpaa (1990) have found that 49% of 190 soil samples originating from 25 countries have an inadequate zinc supply, while Graham and Welch (1996) reported that approximately 50% of global arable land used for cereal production are of low levels of accessibility of these micronutrient. In addition, Zn deficiency is not related to specific areas, but appears equally in cold and warm climatic zones, in arid and humid areas, and on the alkaline and acidic soil as well as on soils with different texture (Rahman et al., 1993). However, the main reason for the appearance of Zn deficiency symptoms is low solubility of Zn in soils, rather than low total Zn content in soil's availability to plants is mostly reduced in calcareous soil or soils with high pH, or soils with high organic matter contents and high levels of available phosphorus, acid leached and sandy soils with low total Zn content. Also, Zn deficiency is manifested more during cold weather and low soil temperature conditions. There are two possible ways for overcoming Zn nutritional problems. Plant breeding represents sustainable and cost-effective strategy, but development of new genotypes is a long-term process. On the other hand, application of Zn containing fertilizers is faster solution to the problem. The Zn deficiency symptoms have been sporadically diagnosed on maize plants which were grown on some neutral to slightly alkaline soils in the Eastern Croatia (Kovacevic et al., 1988). Maize is the first-ranged crop in Croatia and it covers on an average more than 30% of arable land. East Croatia has mainly favourable condition for seed-maize growing. It is well known that maize is highly susceptible to Zn deficiency. This is particularly true for seed maize as parents of hybrids are generally more susceptible to nutritional and any other aspect of stress

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 (Mc Laren and Crawford, 1973; Iyengar *et al.*, 1981; Neilsen *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_2SiO_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).

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.

Necessity of zinc in crop plants

Generally each essential nutrients play certain specific roles in the plant and the presence of each of them in their respective above critical concentration is a necessary to complete its life cycle.

Although Maize (1919) first furnished convincing evidence of zinc as an essential element for higher plants, its essential nature was not generally accepted until Sommer and Lipman (1926) showed that zinc is indispensable for normal growth of plant. Many enzymes require zinc ions (Zn $^{2+)}$ for their activity, and zinc may be required for chlorophyll biosynthesis in some plants. Zinc deficiency is characterized by a reduction in intermodal growth and as a result plants display a rosette habit of growth in which the leaves form a circular cluster radiating at or close to the ground. The leaves may also be small and distorted, with leaf margins having a puckered appearance. These symptoms may result from loss of the capacity to produce sufficient amount of the auxin, indole acetic acid. In some species (corn, sorghum, beans), the older leaves may become interveinously chlorotic and then develop white necrotic spots. This chlorosis may be an expression of a zinc requirement for chlorophyll biosynthesis.

NUTRITIONAL PROBLEM DUE TO ZINC

Human are now facing two global challenges from agriculture: one is to ensure food security, conserve natural resources and protect environments, simultaneously (Tilman et al. *2002*); furthermore, another hidden and ignored one is to increase grain micronutrient (for example zinc, Zn) concentration in main cereal crops to overcome widespread malnutrition especially in developing countries (Bouis and Welch *2010*). And it is also an important cereal crop in the context of nutrition for humans, poultry and livestock (Nuss and Tanumihardjo *2010*). Thus increasing Zn levels in maize grain could deliver more Zn to people whose diet relies directly or indirectly on maize-derived food.

Maize is also an important cereal crop in the context of nutrition for humans, poultry and livestock (Nuss and Tanumihardjo *2010*). Thus increasing Zn levels in maize grain could deliver more Zn to people whose diet relies directly or indirectly on maize-derived food. It also one of the most susceptible cereal crops to Zn deficiency. Because high yielding maize varieties are selected grown, chemical fertilizers are of increased purity and cropping has become increasingly intensive, Zn deficiency in soil-crop system has become more prevalent in last decades (Fageria et al. *2002*). Zinc applications are reported to increase maize grain yield around world (Harris et al. *2007*; Hossain et al. *2008*; Potarzycki and Grzebisz *2009*; Singh and Banerjee *1986*). In China, nearly half of Chinese farmlands were classified as critical Zn deficient soil (Liu *1996*), especially in North China where most of maize crops were planted. As summarized by Zou et al. (*2008*), cases of increase in maize yield by Zn application were frequently reported, and amount of Zn fertilizer used for maize production ranks first among all crops in China.

It has been estimated that zinc deficiency is the most widespread micronutrient deficiency reducing crops production and quality worldwide. Nowadays, Zn deficiency is widely recognized and it is considered as one of the most important micronutrient problems in the world. It is estimated that about 50% of world soils for cereal production have lower available Zn, which reduces grain yield and nutritional quality of grain (Graham and Welch 1996). In China, about one-third of the agricultural soils are Zn deficient. Zinc deficiency has been reported on plants grown in calcareous, desert and paddy soils where the main crops affected are rice and maize (Zou et al. 2007).

The major soil factors affecting the Zn availability are neutral to alkaline soil reaction, calcareous soils and acid leached and sandy soils. The Zn deficiency symptoms have been diagnosed on maize plants which were grown on some neutral to slightly alkaline soils in the Eastern Croatia. Maize is a crop species with greater requirements for zinc and more susceptible to Zn deficiency, especially the inbred lines as parental components of hybrids. The objective of this paper was to summarize some previous findings regarding Zn nutritional problems and ways of its alleviations in the area of east Croatia. Response of maize genotypes to different Zn-fertilization treatments, as well as the grain yields and ear-leaf zinc concentration were shown. Results indicated on important role of genotype on Zn content in plant. Also, some results pointed out at complex relations between the Zn content in soil, plant tissue and grain (Rastija et al.)

Micronutrient deficiencies particularly of zinc (Zn) are widespread in field crops all over India because of increased Zn demands of intensive cropping systems and adoption of high yielding cultivars with relatively greater Zn demand (Fageria et al., 2002). Crop responses to Zn application have been obtained in alluvial, red and lateritic soils and swell-shrink soils of the country (Singh and Behera, 2011). Besides some customized products, zinc sulphate ($ZnSO_4$) is the common Zn fertilizer available to the farmers in the market. There is a need to study the efficacy of other Zn containing fertilizers for enhancing crop yield. Micromac-Zn is a Zn, nitrogen (N) and phosphorus (P) fertilizer (21% Zn, 18% P, 9% N) that hds been applied to Zn deficient soils.

Forms, status and distribution of zinc in soils and their responses to crops

The amount and distribution of micronutrients in soils are influenced by parent materials, levels and form of soil organic matter (SOM), pH, Eh (oxidizing conditions), mineralogy, particle size distribution, soil horizon, soil age, soil forming processes, drainage, vegetation, and microbial, anthropogenic and natural processes (Baligar et al, 1998; Stevenson, 1986; Tate, 1987). Zinc deficiency is a worldwide nutritional constraint for crop production. About 50% of soils used for cereal production in the world contain low level of plant available Zn, which reduces not only grain yield but also nutritional grain quality (Graham and Welch, 1996). The principal Zn ore is sphalerite (ZnS) but Zn also occurs as silicates and carbonates in the Earth's crust. Total Zn concentration in soils range from10 to 300 mg kg $^{-1}$, with a mean concentration of 50mg kg $^{-1}$. Zinc occurs as the divalent cat ion (Zn^{+2}) in soils and does not undergo reduction in nature, due to its electropositive nature (Krauskopf, 1972). In comparison with Cu, Zn migrates further in soil and is known as the mobile of heavy metals. Divalent Zn is sorbed less strongly than Cu, probably because the covalent bonds holding Cu^{2+} are stronger than those of Zn^{2+}. Zinc also substituted for Mg in montmorillonite type clay minerals. Organic matter forms coordination complexes with Zn; they may be present in both the soil organic matter and soluble organic complexes in soil solution (Hodgson et al, 1966). Zinc that may become available for plant uptake is present as Zn^{2+} in the soil solution, exchangeable Zn in the cat ion exchange sites, organically complexed Zn in solution and organically complexed Zn in the solid phase (Iyenger and Deb, 1977). Besides, being absorbed by the carbonates of magnesium and calcium and hydrous oxides and silicate clay content in soils, zinc forms relatively insoluble hydrous oxides [$Zn(OH)_2$] and also of $ZnCO_3$.

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 in to 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 were 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 and 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.

Crops responses to Zn have been documented in many countries and on numerous crops. Some Zn sensitive crops are corn, citrus, field beans, rice and some fruits and vegetables. Broadcast applications of Zn sources should be incorporated into the soil because Zn movement in soil is restricted. Schulte and Walsh (1982) showed that $ZnSO^4$, ZnO and Zn fertilizer were equally effective for corn, edible bean and vegetables with band and broadcast applications. However, about twice as much Zn was required for broadcast as banded applications. Zinc oxide must be finely ground to be effective for correcting Zn deficiencies (Mengel, 1980).

Many factors such as pH, soil organic matter (SOM), temperature, moisture (stress), soil texture, nature and amount of clay minerals present, nature and amount of organic matter present in the soil, soil salinity and alkalinity, quality of irrigation water affect the availability of micronutrients to crop plants. The effects of these factors vary considerably from one micronutrient to another as well as in their relative degree of effectiveness. Available concentrations of Co, Cu, Ni and Zn increased with increased amounts of clay (Lee et al, 1997). Katyal and Deb (1982), in their review on "Nutrient Transformations in soils-micronutrients" strongly viewed that lack of adequate information on the behavior of micronutrients in relation to soil properties does not apparently permit extrapolation of many results on micronutrients which are already available. The distribution of available Zn in soils conducted earlier with special emphasis to Indian soils, are presented here under on the following sub-heading.

a) Status of available zinc content in surface soils.

b) Nature and vertical distribution of available form of zinc in the soil profiles.

c) Some important factors affecting availability of zinc and degree of association among them.

d) Status and distribution of available zinc in soils with respect to deficiency, adequacy and excess levels.

Status of available zinc content in surface soils

Indispensability of Zn as an essential nutrient for plant growth was established by Sommer and Lipman (1926). Zinc that may become available for plant uptake is present as Zn^{2+} in the soil solution, exchangeable Zn on the cat ion exchange sites, and organically complexes Zn in solution and organically complexed zinc in the solid phase (Iyenger and Deb, 1977). Considerable information on range of available Zn (ppm) along with other cationic micronutrient content in surface soils have been generated from different states of India

Besides the range of available Zn reported above, examination of literature also brings out some relevant information on the same from number of states. Sahu et al. (1990) reported available status of Zn in 8 different soil groups of Orissa. The range and mean values of Zn observed were 0.3 ppm in black soil to 4.6 ppm in red soil with a mean of 1.25 ppm. Karan et al. (1992) in their analysis of 3624 composite samples (0-15 cm) from red and lateritic soils of Bankura, Midnapore and Purulia districts of West Bengal observed available zinc to range from 0.1 to 19.73 ppm with a mean of 1.28 ppm. Ghosh et al. (1992) reported results of soils analyses from Jalpaiguri (2092 samples) and Cooch-Bihar (640 samples) districts of West Bengal and it was found that available Zn ranged from 0.1 to 10.0 ppm with a mean of 0.88 ppm in Jalpaiguri and 0.1 to 40.1 ppm with a mean of 1.53 ppm in Coochbehar district. Mandal and Mete (1991) studied the content of Zinc along with Fe, Mn and B in soil samples of the rice growing areas of West Bengal. They found a variation of the Zn content in the soils and Zn concentration ranged from 2.7 to 7.5 ppm. Based on the critical levels most of the soils were well supplied with available zinc. In the Testa and Terai alluvial soils of West Bengal, Ghosh et al. (1993) observed widespread Zn deficiency.They detected that 16 to 68% of the 2700 soil samples analysed were deficient in Zn. Sharma ert al (2001) studied the micronutrient status in soils of Rajgarh District of Madhya Pradesh, India. The DTPA-Zn (ppm) content ranged from 0.02 to 2.18 ppm (mean 0.38 ppm) in their observation. Bandyopadhyay et al. (1997) reported that the amount of DTPA extractable Zn ranged from 2.24 to 9.19 ppm in the soils collected from a few flower-growing areas of West Bengal. Though the realative amount of DTPA- extractable Zn recorded in Kola hat (2.24 ppm) and Memari (2.24 ppm) were lower with respect to other places but distributed above the deficiency level. While studying the distribution of different forms of zinc Vasudeva and Ananthanarayana (2002) observed a range of 0.04 to 2.3 $\mu g\ g^{-1}$ exchangeable Zn in the Karnataka soils. Although the exchangeable pool was very low in the entire soils when compared to other fractions but it is important from the plant availability point of view. In coastal soils of West Bengal, Bhtatacharya et al. (2002) reported that the DTPA-extractable Zn in the soils under study ranged from 0.24 to 0.78 mg kg^{-1} with a mean value of 0.42 mg kg^{-1}. Majhi and Bandyopadhyay (1991) recorded a range of 0.3 to 1.9 mg kg^{-1} of available Zn for the coastal soils. In a study on the status of available micronutrients in the rice growing soils of Odisha, Pal et al. (2002) observed that DTPA- extractable zinc content in the soils of Orissa varied from 0.98 to 3.78 mg kg^{-1} indicating that the soils are well supplied with available zinc.

Nature of vertical distribution of zinc in the soil profiles

When parent materials weather to form soil, the micronutrients undergo varied chemical and physical modification that affects both their content and distribution in different parts of the soil profile and their availability to plants. Information regarding the depth-wise distribution of zinc is important in understanding the nature of movement of zinc in subsoil. In case of soil profiles from Punjab, the distribution of zinc in soil profiles was uniform. However, Singh and Randhawa (1969) did not find any relationship of Zn distribution with depth of citrus orchard soils of Bhatinda district in Punjab. Bansal et el. (1969) reported that Zinc content of some soils from Madhya Pradesh decreased with depth. Generally in many Indian Soils, accumulation of zinc in some horizon has been reported to follow the accumulation of clay.

Singh and Sekhon (1975) also observed erratic pattern of distribution of Zn in different soil associations. Though the analysis of twenty representative soil profiles collected from different agro-climatic soil zones of the Punjab and Haryana States and Kulu and Kangra districtyes of Himanchal Pradesh, Grewal et al. (1969) observed a decrease in available Zn content in the lower horizons from the surface layer. Tripathy et al. (1969) also analyzed soil samples from 26 tropical soil profiles collected from cultivated fields of 18 districts of all the agro-climatic regions of Uttar Pradesh. They observed that available zinc almost invariably decreases towards lower depth except in few cases where the fourth layer of the profile found to contain more available zinc than the corresponding surface layers. The tendency to accumulate zinc than the corresponding surface layers. The tendency to accumulate zinc in the top layer of soil has been attributed to the the regular turn over through crop residues. In their studies with 40 representative surface and subsurface samples of rice fields covering eight major soil groups in the state of Odisha, Sahu et al. (1990) also reported that the available Zn content of the subsurface layer (15-30 cm) were less than in the surface soils (0-15cm). While studying the vertical distribution of DTPA-extractable micronutrient of ten soil series, representing Entisols and Inceptisols in Haryana (India), Sangwan et al. (1999) observed a mean value of 0.31 mg kg^{-1} Zn and depth wise distribution of available Zn followed a regular trend which decreased with depth. Swain et al. (2002) studied distribution of Zn along with other cationic micronutrients in seven soil profiles representing distinctly identical soil series of southern West Bengal. Despite the wide variation of Zn content in the surface layer, the DTPA-Zn concentration exceeds those in the subsurface layers and the mean values decreased with increased in the depth. Singh et al. (2011) studied distributions of surface and subsurface Zn, Cu, Fe and Mn as influenced by different cropping systems in Typic Ustocrepts soils of Punjab, India.

Raina et al. (2003) found that on an average the zinc content of surface soils of Shimla and Kullu district was 2.93 and 3.14 mg kg^{-1} where as in the subsurface soils, it was 1.08 and 1.83 mg kg^{-1}, respectively. It has been attributed to the fact that fertilizer application, especially the micronutrients in these areas are negligible. Thus, continuous removal of Zn by plants in absence of adequate replenishment might have lead to the deficient levels of Zn in these soils. The higher level of Zn content in surface soils may be ascribed to more weathered soil conditions, favorable soil pH and high organic matter content. In a study conducted on distribution of DTPA-extractable micronutrients in eight representative soil profiles of older alluvial plain of central Haryana (India), it was observed that available Zn decreases with increase in depth. The mean value for available Zn was 0.38 mg kg^{-1} (Singh et al. 1997).

Sharma et al. (2002) studied the surface and profile distribution of total and diethylene triamine penta acetic acid (DTPA) extractable zinc, copper, manganese and iron in entisols of Punjab. They observed higher DTPA extractable micronutrients in surface horizons that decreased in subsurface horizons. The DTPA extractable Zn varied from 0.08-1.88 mg kg^{-1} in the soils studied.

Vadivelu and Bandyopadhyay (1995) studied depth wise distribution of Zn along with other micronutrients and their relationship with $CaCO_3$,pH and organic carbon in the soils of Arabian Sea Island (Lakshadweep). The content of DTPA-extractable Zn do not appear to follow a definite trend of distribution through depth of the Pedons and have no correlation with $CaCO_3$, pH and organic carbon. Gupta et al. (2003) also reported that the available (DTPA-extractable) Zn ranged from 0.05-1.09 mg kg^{-1} in all the horizons within the profiles studied in six established soil series of Madhya Pradesh with a mean value of 0.37 mg kg^{-1}.They observed that the surface horizon contained higher amount of available Zn, which progressively declined with depth in all the profiles of different Series.

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). P^H, 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 P^H play significant roles in variation of adsorption characteristics of the calcareous soils. Amer (1995) reported that P^H was an interacting factor in the DTPA extractable Zn of coarse textured calcareous soils. Davis *et al*.(1995) observed that lower P^H 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 P^H. 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 P^H 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 P^H 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 1991 a 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 Zn^{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). In a rice-based cropping system soils are often subjected to different moisture regimes, which may influence desorption of adsorbed Zn and thus limit Zn availability to crops. Laboratory and greenhouse experiments were conducted to study the effect of moisture regimes with or without organic matter addition on changes in desorption of adsorbed Zn in soils and its utilization by rice and maize plants. Three different moisture regimes, flooded–dried, alternate wetting and drying and preflooding, with (50 g kg^{-1}) and without (0 g kg^{-1}) added organic matter were imposed in two Alfisols and two Inceptisols of West Bengal, India. Percent desorption of adsorbed Zn was significantly higher in Alfisols (64.5%) than in Inceptisols (45.5%). Desorption was also significantly higher under flooded–dried (61.4%), alternate wetting and drying (67.1%), and preflooding (47.3%) moisture treatments than in the control (43.4%). Organic matter application enhanced desorption under flooded–dried and alternate wetting and drying but decreased it under preflooding. The variation in Zn desorption among soils and moisture treatments is the result of changes in soil P^H, Fe-oxides, bonding energy constants, and free energies for Zn adsorption. Greenhouse experiments showed that dry matter yield and uptake and utilization of Zn for maize were higher under flooded–dried. For rice, yield and Zn accumulation were higher under preflooding treatments compared to the control in which the soils were not subjected to these pre-plant moisture treatments. Soil-zinc data and plant response were in close agreement, except in Inceptisols for rice under preflooding with added organic matter treatment. Results indicated a more efficient use of Zn fertilizer where maize followed rice and where rice was grown after preflooding thesoils (Mandal et al. 2000)

Zn adsorption and desorption behavior of soils Adsorption of Zn in soils

The adsorption process, which refers to surface Zn accumulation on soil components, may, in some cases, by accompanied by penetration of the adsorbed Zn by diffusion into the adsorbent body, leading to further adsorption of the adsorbed species. The general term sorption sometimes used to denote both of these processes taking place simultaneously. Both adsorption and desorption studies have indicated the fertility status of soil, particularly under long-term fertilizer trials dealing with both organic and inorganic materials. The main motivations for describing adsorption curves are (1) to identify the soil constituents involved in adsorption (Adams *et al.* 1987, Langanathan *et al.* 1987), (2) to predict the amount of fertilizer needs of soil to meet the demand of plant uptake for an optimum yield (Fox and Kamprath 1970, Greenland and De Datta 1985), and (3) to study the nature of the adsorption process to learn more about the mechanism of the process (Brown 1985). A variety of isotherm shapes are possible, depending upon the affinity of the adsorbent of the adsorbate. In general, for Zn Langmuir and Freundlich adsorption equations have been used extensively by different workers (Williams 1971, Sanyal *et al*. 1993. Reddy *et al.* 2001).

Equation developed by Langmuir (1918) has been adopted to interpret the reaction between the soil constituents and Zn.

The equation is given as:

$$C / x/m = (1/ kb) + (C/b) \quad \text{......................(1)}$$

$$\text{Or, } x/m = kbc / 1+kc \quad \text{............................(2)}$$

Where, x/m = µg Zn adsorbed per g soil

C = equilibrium Zn concentration in µg / ml

b = adsorption maximum

k = constant related binding energy of the soil for Zn

The Freundlich equation is given as:

$$x/m = KC\ 1/n$$

Where ‘k’ and ‘n’ are constants.

Langmuir equation has been used extensively to describe the adsorption of $ZnSO_4$by soils, clays and sediment (Reddy *et al.* 2001, William 1971, Sanyal *et al.* 1993).

Similarly Freundlich equation has also been used extensively to describe the adsorption of sulphate and phosphate by soils (Reddy *et al.*

2001, Fitter and Sutton 1975, Sanyal *et al.* 1993). Freundlich equation is empirical in nature, justification for its application to adsorption from dilute solutions was presented by Kipling (1965). Moreover it implies that the affinity (bonding energy) decreases exponentially with increasing surface coverage, a condition that is perhaps nearer to the reality than assumption of constant binding energy as in the simple Langmuir equation. Reddy *et al.* (2001) examine the k and n values obtained from Freundlich isotherm of sulphate foundnd in the soil with high retention capacity at lower in values.

Desorption of Zinc in soil

The process of desorption refers to the reversible release of adsorbed Zn into the soil solution phase. Desorption of once adsorbed Zn from soil and clays often has been shown to be irreversible leading to a large hysteresis effect (Reddy *et al.* 2001). The adsorption isotherm was thus displaced to the left of the sorption isotherm. Such hysteresis effect leads to an over estimation of the replacing ability of soil to supply Zn to the solution, when Zn solution isotherms are used for the purpose (Barrow 1985). Moreover, it has also been suggested that because adsorption equilibrium was slow, and apparent adsorption during the desorption step is possible (Barrow 1983). The diffusive migration of initially adsorbed S beneath the adsorbing sulphate may also be cited as a probable reason for apparent reversibility of S desorption as has been mentioned by Barrow (1985) in case of phosphate desorption.

Yield responses of crops to zinc fertilization

Abhichandani (1955) reported through his study at Central Rice Research Institute, Cuttack that the spraying of paddy crops with zinc sulphate and treatment of seed with zinc sulphate increased the yield markedly. But treatment of seed with zinc sulphate before sowing had not yielded any beneficial effect. Singh and Jain (1964) observed a significant increase in paddy yield with zinc application was found to be superior to soil application. Singh et al (1979) compiled the results of about 1400 field experiment conducted from 1967 to 1977 and reported striking increase in the yield of wheat, maize, rice, bajra and raya with Zn application in 75 out of 82 districts. Significant yield increase of grain was observed in more than 50% of the trial Takkar and Radhawa (1980) reported results of about 3000 field experiment in the various state and shows average responses of cereals, millets, pulses and oilseed crops ranging from 1.0 to 6.7 quintals/hectare to varying levels and Zn application

Critical level of zinc in a soil and plants.

Based on the multi-location fertilizer experiment, critical level of Zn below which, crops will response to their application have been worked out for different crops. Above this level, crop response either diminishes at a faster rate or is negligible. Therefore, it helps to identifying a soil test value beyond which application of fertilizer is not require. Critical level depend on soil, crop, cultivars, soil test method and season. Although and non-responsive, it does not tell anything about how much fertilizer to be applied in quantitative terms relative to the level of soil test value. Lot of works has been done in micronutrients and also level of Zn on soils for different crops.

Crop productivity response to Zn fertilization

Yields, yield components and N, P and K uptake increased with increasing N and Zn rates. In plants, micronutrient deficiencies have gained much importance worldwide because of the increasing concerns over the effects of low levels of micronutrients especially Zinc (Zn) in human food (Cakmak, 2002; Welch and Graham, 1999). Zinc deficiency in soils is common in areas receiving less rainfall. Limited or no use of Zn fertilizers in conjunction with unbalanced fertilization further aggravated Zn deficiency in soils and consequently lower Zn contents in grains (Rashid and Rayan, 2004). Behavior of Zn in soils highly depends upon pH, CaCO3 contents, and amount of other nutrients11especially of P in soil (Rahmatullah *et al*., 1994). Zinc has specific vital role in growth, development, and quality of crops (Loneragen *et al*., 1982). It plays a pivotal role in biosynthesis of proteins and amino acids. The application of Zn therefore, has shown significant effects on yield, uptake of nutrients and quality parameters of crop. Rizvi *et al*. (1987) carried an experiment on maize to understand the effect of Zinc on maize yield and Zn concentration in leaves and grains as well. Zn was applied ranging from 0 to 20 kg per hectare. Effect of Zn on dry matter, stalk, and cob yield was not significant but yield of grain was significantly increased. Critical Zn concentration in leaves was 14 mg $ZnKg^{-1}$ while optimum dose was 5 Kg Zn ha^{-1}. Teama (2001) studied the effect of seed soaking with trace elements (200 ppm $ZnSO_4$. $7H_2O$ or $MnSO_4$. H_2O) on maize yield and uptake of N under different levels of N fertilizer (90, 105, 120, and 135 kg N/ha). All the studied traits were highly significant due to different N fertilizer levels, trace element treatments and their interaction except for the interaction effect on ear diameter. Increasing the N levels led to taller plants and high seed protein content. In all the traits, the use of single trace element for soaking was better than the control. They concluded that Zn was the best single trace element. Dwivedi *et al*. (2002) observed that use of Zn up to 5 kg ha^{-1} enhanced the maize grain yield up to 19 % over control. The optimal dose for zinc was found to be 7.1 kg ha^{-1} generating highest yield of 29.8 q ha^{-1}. The uptake of Zn also increased with the application of Zn. Increasing zinc levels also increased nitrogen, phosphorus, and potassium uptake. Protein content also increased significantly with increase of Zn over control.

Tariq *et al*. (2002) concluded that different zinc levels combined with 120 kg nitrogen per hectare, 90 kg P_2O_5 per hectare and 60 kg K_2O per hectare increased yield and yield components over control. In zinc deficient soils, Zn content in leaves and soil increased with the application of Zn. They further concluded that zinc application is vital for maize under deficient soil conditions. Latha (2003) studied the influences of Zn enriched organic manures on maize nutrition. Organic amendments (FYM, poultry manure and biogas slurry) enriched with varying levels of $ZnSO_4$ were applied to determine their effect on the uptake of major and micro-nutrients at different growth stages (vegetative, tasseling and harvest of maize) and observed positive effect of Zn and manure addition on uptake of macro and micronutrients at different stages of maize. Abunyewa and Quarshie (2004) observed that Zinc sulphate application significantly influenced maize grain yield in a three-year trial. $ZnSO_4$ was applied at three rates to maize. Grain yield due to Zn application ranged between 0.9 to 3.2 t ha-1 representing 8412to 108 % increase in three-year period. $ZnSO_4$ application also resulted in significant increase in soil Zn level. Gill *et al*. (2004) noted that combined fertilization of P and Zn increased shoot dry matter, shoot concentration of P and Zn and their uptake compared to control. Application of Zn increased shoot P concentration in maize (19%). Combined application of both P and Zn caused 56% increment in shoot P content in maize over control.

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.

Randhawa *et al*. (1969) reported that soil application of 10 ppm $ZnSO_4$ 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 $ZnSO_4$ to be much superior to broad cast and spray application.

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 $Znha^{-1}$ 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.

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). Application of 5 kg $Znha^{-1}$ 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.

Correction of zinc deficiency through chemicals.

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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 Znha^{-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.

Nanotechnologies for increasing the crop use efficiency of fertilizer-micronutrients

Billions of people and many soils across the planet suffer from micronutrient (MN) deficiencies impairing human health. In general, fertilization of deficient soils, according to soil test, with MNs alone and in combination with nitrogen, phosphorous, and potassium (NPK) baseline treatment increases crop yield. The soil applied fertilizer-MN use efficiency (MUE) by crops is <5 % due to a lack of synchronization between the fertilizer-MN release and their crop demand during growth. Nanotechnology and biotechnology have the potential to play a prominent place in transforming agricultural systems and food production worldwide in the coming years. MNs added in microcapsules and nanocapsules, nanomaterials (NMs), and nanoparticles (NPs) are taken up and translocated within plants when grown to maturity, increasing crop yield and MN concentration in plants. Noteworthy, many of the effects of NPs and NMs on crop yield and quality, human health, and associated environmental risks remain to be explored. Increasing MUE requires synchronizing the release of nutrients from fertilizers with crop demand during the growing season (Monreal et al. 2016)

Nanotechnology in Agriculture

India ranks third in the number of research publications in nanotechnology, only after China and the US. This significant share in global nanotech research is a result of sharp focus by the Department of Science and Technology (DST) to research in the field in the country.

The application of nano materials in agriculture aims in particular to reduce applications of plant protection products, minimize nutrient losses in fertilization, and increase yields through optimized nutrient management. The potential of nanotechnology in agriculture is large, but a few issues are still to be addressed, such as increasing the scale of production processes and lowering costs, as well as risk assessment issues. In this respect, particularly attractive are nano particles derived from biopolymers such as proteins and carbohydrates with low impact on human health and the environment. For instance, the potential of starch-based nanoparticles as nontoxic and sustainable delivery systems for agrochemicals and biostimulants is being extensively investigated.