1 ROLE OF ZINC IN PLANT NUTRITION- A 2 REVIEW

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12 ABSTRACT

Zinc is plant micronutrient which is involved in many physiological functions its inadequate supply will reduce crop yields. Zinc deficiency is the most wide spread micronutrient deficiency problem, almost all crops and calcareous, sandy soils, peat soils, and soils with high phosphorus and silicon are expected to be deficient. Zinc deficiencies can affect plant by stunting its growth, decreasing number of tillers, chlorosis and smaller leaves, increasing crop maturity period, spikelet sterility and inferior quality of harvested products. Beside its role in crop production Zn plays a part in the basic roles of cellular functions in all living organisms and is involved in improving the human immune system, due to its insufficient intake, human body will suffer from hair and memory loss, skin problems and weakness in body muscles.

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Key words; Zinc, Plant nutrition, Rice, Bioavailability, Human health

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16 INTRODUCTION

17 Zinc is essential for the growth in animals, human beings, and plants it is vital to the crop nutrition as required in various enzymatic reactions, metabolic processes, and oxidation-18 19 reduction reactions. In addition, Zn is also essential for many enzymes which are needed for 20 nitrogen metabolism, energy transfer and protein synthesis. Zinc deficiency not only retards 21 growth and yield of plants, but it also has effects on human beings. More than 3 billion 22 people worldwide are suffering from Fe and Zn deficiencies, and this condition is particularly widespread in areas where population is heavily dependent on an unvaried diet of cereal-23 24 based foods, in which Fe and Zn are stored almost exclusively in the husk, and are therefore 25 lost during milling and polishing (Cakmak, 2002; Graham et al., 2001).

26 1. Importance of Zn in Humans

Zinc deficiency is common in humans, animals and plants. More than 30% world's population suffers from Zn deficiency (Welch *et al.*, 2002). Zinc plays a part in the basic roles of cellular functions in all living organisms and is also involved in improving the human immune system. The optimum dietary intake for human adults is 15 mg Zn per day. Zinc acts as a catalytic or structural component in various body enzymes.

Unsatisfactory intake and improper absorption of Zn in the body may cause deficiency of Zn. Due to Zn deficiency; the human body will suffer from hair and memory loss, skin problems and weakness in body muscles. Further insufficient intake of Zn during pregnancy also causes stunted brain development of the fetus. Infertility has also been observed in Zn deficient men. Zinc deficiency may cause congenital diseases like Acrodermatitis enteropathica (Lukaski, 2004; Morley, 2004 and Zimmermann, 2001).

As per recommendations of the FAO/WHO (2002) and Hotz and Brown (2004) an average male need 11 mg of Zn daily while an average female needs 9 mg of Zn. During pregnancy

and lactation, the female needs 13 mg to 14 mg of Zn daily. Infants from 7 months to 3 years
need 3 mg, 4 to 8 years need 5 mg and children from 9 to 13 years need 8 mg of Zn daily.
Cakmak, 2002 reported that Zn is stored in the rice husks and grains and with the
consumption of this cereal human zinc deficiency can be decreased. The foods rich in Zn
are beef, pork, chicken, and breakfast cereals, nuts like roasted peanuts, almonds, walnuts,
oats and dairy products like yogurt, cheese and milk.

46 **2. Role of Zinc in Plants**

47 The Zn plays very important role in plant metabolism by influencing the activities of 48 hydrogenase and carbonic anhydrase, stabilization of ribosomal fractions and synthesis of 49 cytochrome (Tisdale et al., 1984). Plant enzymes activated by Zn are involved in carbohydrate metabolism, maintenance of the integrity of cellular membranes, protein 50 synthesis,, regulation of auxin synthesis and pollen formation (Marschner 1995). The 51 52 regulation and maintenance of the gene expression required for the tolerance of 53 environmental stresses in plants are Zn dependent (Cakmak 2000). Its deficiency results in 54 the development of abnormalities in plants which become visible as deficiency symptoms such as stunted growth, chlorosis and smaller leaves, spikelet sterility. Micronutrient Zn 55 56 deficiency can also adversely affect the quality of harvested products; plants susceptibility to injury by high light or temperature intensity and to infection by fungal diseases can also 57 58 increase (Marschner 1995; Cakmak 2000).

Zinc seems to affect the capacity for water uptake and transport in plants and also reduce 59 60 the adverse effects of short periods of heat and salt stress (Kasim, 2007; Disante et al., 61 2010, Peck and McDonald, 2010, Tavallali et al., 2010). As Zn is required for the synthesis 62 of tryptophan which is a precursor of IAA, it also has an active role in the production of an essential growth hormone auxin, (Alloway, 2004, Brennan, 2005). The Zn is required for 63 64 integrity of cellular membranes to preserve the structural orientation of macromolecules and 65 ion transport systems. Its interaction with phospholipids and sulphydryl groups of membrane 66 proteins contributes for the maintenance of membranes (Cakmak, 2000; Kabata-Pendias 67 and Pendias, 2001; Alloway, 2004; Dang et al., 2010; Disante et al., 2010).

68 **3.** Zinc Deficiency in Soil

Zinc deficiency can be found in every part of the world and almost all crops respond 69 70 positively to application of Zn (Alloway, 2008). Normal soils inherit their trace elements which 71 include Zn primarily from the rocks through geochemical and pedochemical weathering 72 processes. Besides mineralogical composition of the parent material, the total amount of Zn 73 present in the soil is also dependent on the type, intensity of weathering, climate and 74 numerous other predominating factors during the process of soil formation (Saeed and Fox, 75 1977). Meanwhile, high pH and high contents of CaCO₃, organic matter, clay and phosphate 76 can fix Zn in the soil and give rise to the reduction of available Zn (Imtiaz, 1999). Soils 77 derived from granite and gneiss can be low in total Zn (Krauskopf, 1972). Similarly, total Zn is low in highly leached, acid, sandy soils such as the ones found in many coastal areas. 78 79 Quartz in the soil dilutes Zn from it because the reported concentrations of Zn in quartz are 80 very low, which ranged from 1.0 μ g g⁻¹ to < 5 to 8 μ g g⁻¹ (Helmke *et al.*, 1977 and Brehler and Wedepohl, 1978), According to the Food and Agriculture Organization (FAO), about 81 82 30% of the cultivable soils of the world contain low levels of plant available Zn (Sillanpaa, 1990). The lowest Zn concentrations were always found in Spodosols (28 μ g g⁻¹) and 83 luvisols (35 µg g⁻¹), while higher levels were found in fluvisols (60 µg g⁻¹) and Histosols (58µg 84 85 g⁻¹) (Kiekens, 1995).

86 Generally, Zn deficiency is expected in calcareous soils, sandy soils, peat soils, and soils 87 with high phosphorus and silicon (Alloway, 2008, 2004). The submerged soils are well 88 recognized for the lack of Zn availability to the plants; particularly due to the reaction of Zn 89 with free sulphide (Mikkelsen and Shiou, 1977). Flooding and submergence bring about a 90 decline in available Zn because of the changes in pH value and the formation of insoluble Zn 91 compounds. Meanwhile, the insoluble Zn compounds formed are likely to be with Mn and Fe 92 hydroxides from the breakdown of oxides and adsorption on carbonates, specifically

93 magnesium carbonate. Under the submerged conditions for rice cultivation, Zn is 94 transformed into amorphous sesquioxide precipitates or franklinite; ZnFe₂O₄ (Sajwan and 95 Lindsay, 1988). Zinc deficiency causes multiple symptoms which usually appear 2 to 3 96 weeks after transplanting of rice seedlings, with leaves developing brown blotches and 97 streaks that may fuse to entirely cover older leaves, and plants remain stunted, whereas in 98 severe cases, the plants may die, while those which recover will show substantial delay in 99 maturity and reduction in yield (Yoshida and Tanka, 1969; Van Breemen and Castro, 1980 100 and Neue and Lantin, 1994).

101 4. Zinc under Submerged Soil Conditions

102 Zn deficiency is very common under flooded soil conditions. In acidic soils, Zn is precipitated 103 as Zn (OH)₂ and as ZnS in sulfur-rich and alkaline soils. The availability and solubility of Zn 104 decreases while pH increases. The oxides of Mn and Zn along with CaCO₃ or MgCO₃ are strongly absorbed by Zn under submerged condition. Whereas in calcareous soils. HCO₃ is 105 106 the predominant anion, which mainly reduces Zn transport from root to shoot, but not so 107 much the Zn uptake by roots. Under anaerobic condition Zn forms an insoluble Zn-108 phosphate. Under this condition plant roots will not take up the soluble Zn from the Zn 109 solution as required by the plant. Under submerged conditions, when organic acid 110 concentration increased, the Zn uptake is reduced and this effects the plant growth. The Zn 111 uptake is also reduced under acidic rhizosphere condition due to the release of H⁺ from the 112 roots and the surplus intake of cat ions over anions. Under acidic rhizosphere conditions, Zn 113 is released from acid-soluble fractions (e.g., absorbed Zn, organic matter or Fe (OH) 3) and 114 is available for plant uptake. Generally, rice plants absorb most Zn from solubilization in the 115 rhizosphere because the available Zn in soil is very low in flooding condition (Dobermann 116 and Fairhurst 2000).

117 5. Soil Factors Associated with Zn Deficiency

118 All types of soil may be affected by Zn including: loams, sands, clays (with all classification), 119 loess, alluvium, and soils formed from basalt, sandstone, granite, volcanic ash and many 120 other rocks. In general, soils of arid and semi arid regions and the slightly acidic, leached 121 soils of warm and tropical climates are most inclined to Zn deficiency, however, crops are 122 not equally susceptible to Zn deficiency and at the same soil some crops may suffer from Zn 123 deficiency while others are not affected (Takkar and Randhawa, 1978). Lindsay (1972); 124 Pendias and Pendias (1992) and Alloway (2008) reported that major Zn deficiency causes 125 include: (i) Soils of low Zn content (Parent material), (ii) soils with Restricted Zones, (iii) pH, 126 (iv) soils low in organic matter, (v) Microbially inactivated Zn, (vi) Cool soil temperature, (vii) 127 Plant species and genotypes (viii) High level of available phosphorus and (ix) Effects of 128 nitrogen. Zn deficiency problems may occurs in soils with the subsequent characters; (a) 129 strongly alkaline in reaction (b) high phosphorus status by application of phosphatic fertilizers may reduce use of zinc (c) leached sandy soils (d) acid soils of low total Zn status 130 131 developed on highly weathered parent material (e) calcareous soil (f) peat and muck soils (g) 132 permanently wet (water logged) and (h) high bicarbonate and magnesium in soils or irrigated 133 water (Alloway, 2004, Benton 2003).

134 5.1 Parent Material of Soils and Zn Content

The amounts of Zn in unpolluted soils typically are lower than 125 ppm (Di Baccio et al., 135 136 2003; Hussain et al., 2010). The major factors affecting the concentration of Zn in soils is the 137 concentration of Zn in soil parent material. The soils derived from gneisses and granites can 138 be low in total Zn and also those originating from sandstone and limestone had lower Zn 139 contents (Barak and Helmke, 1993 and Pendias and Pendias, 1992). Quartz (sand) in the 140 soils also dilutes soil Zn as concentrations of Zn in quartz are very low which range between 1 - 8 μ g g⁻¹ (Brehler and Wedepohl, 1978). Also total Zn is low (< 30 μ g g⁻¹) in highly leached 141 142 acid sands. Zinc deficiency may occur in such soils which are inherently low in Zn. The total Zn concentrations in soils vary between 10 to 300 μ g g⁻¹ with an average of 50 μ g g⁻¹ 143 (Lindsav, 1972). But the average available Zn varied from 1 to 3 μ g g⁻¹ (extracted by 144 145 dithizone). The problem is that only a small amount of soil Zn is available to the crop because of one or more adverse factors. The remainder of the total Zn is fixed in the soil in an insoluble or unexchangeable form and difficult to make available to crop (Stahl and

148 James, 1991).

149 **5.2 Soil pH**

150 Zinc availability is highly dependent on pH. When the pH is above 6, the availability of Zn is 151 usually very low. The availability of Zn in alkaline soils is reduced due to lower solubility of the soil Zn. The concentration of Zn in the soil solution decreases from 10^{-4} (6.5 µg g⁻¹) to 10^{-1} 152 ¹⁰ M (0.007 µg L⁻¹) with an increase from pH 5 to pH 8 (Kiekens, 1995). Thus it is more 153 probable that Zn deficiency will occur in alkaline rather than acidic soils. The solubility 154 155 constant values of ZnCO₃ and hydroxides suggest that a soil having high pH would usually 156 contain a small amount of available Zn. In the case of soils characterized by high contents of 157 hydroxyl (OH) ions, it is difficult to get a crop response even to applied Zn. The lower 158 availability of Zn under alkaline conditions is attributed to the precipitation of Zn as Zn (OH)₂ 159 (Shukla and Mittal, 1979) or ZnCO₃ (Saeed and Fox, 1977). The higher carbonate contents 160 in alkaline soils also absorb Zn and hold it in an unexchangeable form (Udo et al., 1970). All these factors contribute to the low availability of Zn at higher pH values. Liming of acidic soils 161 162 increases pH and also the Zn fixing capacity, particularly in soils with high P levels (Alloway, 163 2004). The movement of Zn in limed soils is considerably lower than in acidic soils (Mortvedt 164 and Giordano, 1967) so that absorption of Zn by the crop may be low. Liming can thus reduce the Zn uptake (Shukla and Moris, 1967) and induce Zn deficiency (Viets, 1966). 165

166 **5.3 Soil Organic Matter**

167 Low organic matter contents in soils give rise to Zn deficiency as it is observed that available 168 Zn increases with increase in organic matter in soil. Soil organic matter is an important soil 169 constituent which originates from decomposition of animal and plant products. The most 170 stable organic compounds in soil are humic substances such as humic and fulvic acids. Both 171 of these substances contain a relatively large number of functional groups (OH, COOH, SH) which have a great affinity for metal ions such as Zn²⁺. Fulvic acids mainly form chelates with 172 Zn over a wide pH range and increases the solubility and mobility of Zn (Kiekens, 1995). 173 174 Simple organic compounds such as amino acids, hydroxy acids and also phosphoric acids 175 are effective in complexing Zn, thus increasing its mobility and solubility in soils (Pendias 176 and Pendias, 1992). An increase in the organic matter contents of a soil will increase its Zn 177 availability; however, if the organic matter content in soil is too high, like in peat and muck 178 soils, this can also contribute to Zn deficiency due to the binding of Zn on solid state humic 179 substances (Katyal and Randhawa, 1983).

180 5.4 Soil Texture

181 Lighter textured soils (sands) contain low levels of Zn. Finer texture soils like clay have higher CEC values and therefore have highly reactive sites and can retain more Zn than 182 lighter textured soils (Shukla and Mittal, 1979). Therefore heavier textured soils with larger 183 184 CEC have higher capacities for Zn adsorption than light textured soils (Stahl and James, 1991). Consequently, Zn deficiency is more likely to occur in sandy than clayey soils. Clay 185 186 soils adsorb Zn and this adsorption is controlled by CEC and pH (Ellis and Knezek, 1972). 187 Nelson et al., (1953) showed that a certain portion of the Zn adsorbed on the clay was not 188 exchangeable but was acid soluble. This portion of Zn was not available to the plants. Reddy 189 and Perkin (1974) found that kaolonite fixes less Zn than bentonite or illite. Thus clays such 190 as bentonite and illite with higher CECs contribute to the fixing of Zn more strongly, thus 191 making it unavailable to plants.

192 **5.5 Phosphate Fertilizers**

Soils with higher phosphate levels, either from native P or due to application of phosphate fertilizers, can cause Zn deficiency stress in crops (Alloway, 2008). Heavy application or prolonged use of phosphatic fertilizers reduces Zn uptake by plants. This effect may be due to the physiological imbalances within the plant (Olsen, 1972). Zinc deficiency due to phosphorus application is termed "P-induced Zn deficiency" (Singh *et al.*, 1986).

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199 **5.6 Soil Flooding**

200 Zinc deficiency is more often associated with flooded soil than dry soils. For example, rice 201 plants under submerged conditions suffer from Zn deficiency in calcareous soils. But wheat 202 grown in the same soil following rice grows normally (Kausar et al., 1976). Zinc deficiency 203 due to flooding was a result of Zn reaction with free sulphide (Mikkelsen and Shiou, 1977). 204 Under the submerged conditions of rice cultivation, Zn is changed into amorphous 205 sesquioxide precipitates or franklinite; ZnFe₂O₄ (Sajwan and Lindsay, 1988 and Singh and 206 Abrol, 1986). Thus a delay in Zn application until after flooding for rice minimizes Zn fixation 207 by sesquioxides (Mandal and Mandal, 1986).

208 5.7 Soil Temperature

209 In warm and moist soils, Zn uptake was higher in rice than in maize (Zea mays L.) (Bauer 210 and Lindsay, 1965). Temperatures below 16°C during growth caused decreased Zn uptake 211 in maize tops (Ellis et al., 1965). It appears that Zn deficiency was associated with cool and 212 wet seasons. Soil temperature effects appear to be due to the rate of Zn mineralization 213 (Takkar and Walker, 1993). Other factors which can cause Zn deficiency in plants are high 214 light intensity and long day-lengths (Marschner and Cakmak, 1989). Besides the natural soil 215 and environmental factors, soil management practices carried out by man often causes Zn 216 deficiency beside this plants can also suffer from Zn deficiency under adverse climatic 217 conditions such as drought or compaction (Alloway, 2008).

218 6 Zinc Interaction with Other Nutrients

219 Interactions occur between the micronutrients and some macronutrients. 'Interaction' may be 220 defined as "an influence, a mutual or reciprocal action of one element upon another in 221 relation to plant growth" (Olsen, 1972). Another factor is the differential response of plants to 222 one element in combination with varying levels of a second element applied simultaneously 223 i.e. the two elements combine to produce an added effect not due to each of them acting 224 alone (Olsen, 1972). Such interactions may take place in the soil and within the plant. These 225 interactions should be taken into account when providing adequate micronutrient supply to 226 plants. Other nutrients may interact with Zn by affecting its availability from soils and its 227 status in the plant throughout the growth process, especially Zn absorption, distribution or 228 utilization. These interactions may enhance or reduce plant growth as a response to Zn. 229 Where an interaction does occur, it is necessary for the diagnosis and treatment of Zn 230 deficiency to identify the factors and its sites and modes of action (Loneragan and Webb, 231 1993). Some important interactions of Zn with other nutrients will be discussed below.

232 6.1 Phosphorus-Zn Interactions

233 The study of the interaction between P and Zn started in1936 (Barnette et al., 1936) and till 234 now, this important plant growth disorder is still under investigation. The interaction is usually 235 termed 'P-induced-Zn deficiency'. This disorder in plant growth is associated with high levels 236 of available P or with application of P to soil. The Zn deficiency symptoms can be prevented 237 by the application of Zn fertilizers. The actual causal relationship and mechanisms are still 238 not fully understood. In general, four possible causes have been considered responsible for 239 P-induced-Zn deficiency. These include (i) a P-Zn interaction in soil: (ii) a slower rate of 240 translocation of Zn from the roots to shoot; (iii) a simple dilution effect on Zn concentration in 241 plant tops due to growth responses to P; (iv) a metabolic disorder within plant cells related to 242 an imbalance between P and Zn (Olsen, 1972).

243 It was suspected that formation of an insoluble Zn_3 (PO₄)₂ in the soil reduced the Zn 244 concentration in soil to deficient levels. But these suspicions were disproved by Brown et al 245 (1970) who observed that Zn_3 (PO₄)₂ was a good source of fertilizer for sorghum. The 246 investigation of this precipitation as a mechanism that causes Zn deficiency continued till 247 1970. Carrol and Loneragan (1968) reported that maximal or near maximal yields were 248 found with legumes at 0.05 µM Zn in flowing culture and with cereals at 0.01 µM. This 249 evidence indicates that precipitation of Zn_3 (PO₄)₂ is not involved in P-induced -Zn deficiency. 250 Many researchers have reported that applied P accentuated Zn deficiency symptoms in 251 plants (Loneragan et al., 1979; Sharma et al., 1968). The higher P levels in soil reduced the

252 Zn concentrations in the plant tops and also reduced total Zn contents (Singh *et al.*, 1986; 253 Clark, 1978). These scientists suggested that P-Zn antagonism existed in the roots of the 254 plants. Other studies suggested that although P decreased the Zn concentrations in the 255 tops, the total Zn contents either increased or remained the same (Boawn and Brown, 1968; 256 Boawn and Leggett, 1968). The cause of this P-induced-Zn deficiency has been suggested 257 to be due to interference by P with the uptake, translocation, or utilization of Zn (Adriano *et al.*, 1971).

259 6.2 Nitrogen-Zn Interactions

260 Zinc deficiency can be increased or ameliorated in plants with the application of nitrogen 261 fertilizers. The interactions resulting from the effects of N application helps to promote plant 262 growth and, to a lesser extent, in changing the pH of the root environment since application 263 of N promotes the growth of plants, it is possible to find positive interactions between 264 increasing levels of Zn and N fertilizers (Alloway, 2004). Chaudhry and Loneragan (1970) 265 reported that wheat grown on N deficient soil with adequate levels of all nutrients except N 266 and Zn, did not respond to Zn application in the absence of NH_4NO_3 fertilizer, however, a 267 strong response to Zn application was observed in the presence of N fertilizer.

268 On the other hand, in soils low in Zn and high in fertility, N fertilizers have ameliorated (or 269 intensified) Zn deficiency by affecting Zn absorption through changing pH (Viets et al., 1957). 270 As ammonium ions have an acidifying effect, ZnSO₄ application with concurrent dressings of N were very effective in controlling Zn deficiency where ZnSO₄ alone had no effect (Viets et 271 al., 1957). It was also observed that NH_4^+ salts inhibited Zn absorption from low Zn²⁺ 272 273 concentration, in a short term study with wheat (Chaudhry and Loneragan, 1972b). Ammonium ions inhibited Zn²⁺ absorption more strongly than alkali and alkaline earth 274 anions, but were competitive with alkali and alkaline earth cat ions. So NH4⁺ effect would be 275 diminished by relatively high concentrations of competing ions in soil. Thus any direct effect 276 277 of NH_4^+ on Zn absorption would disappear.

278 6.3 Macronutrient Cations-Zn Interaction

Macronutrient cations such as Ca, Mg and K inhibit the absorption of Zn by plants from 279 280 solution. They need to be considered when interpreting the results of solution culture 281 experiments involving Zn nutrition, however, in soil they seem to be less effective in the 282 inhibition of Zn absorption compared to the effects of their salts on soil pH. Zinc 283 concentrations were highest in legumes grown in solution culture at constant pH with the 284 lowest Ca level at which the plants were not Ca deficient. Zinc concentrations progressively 285 decreased with increasing Ca concentrations in solutions (Bell et al., 1990). This finding that 286 Ca inhibits Zn absorption was in accord with a short term study conducted by Chaudhry and 287 Loneragan (1972). They found that increasing concentrations of Ca (NO₃)₂ from 0 mM to 40 288 mM inhibited the rate of Zn absorption by wheat seedlings in a non-competitive manner, 289 however, higher Ca concentrations (100mM) had no additional effect on Zn absorption. This 290 inhibition was attributed to Ca as varying the anions and had little effect on Zn absorption, 291 whereas substituting other cat ions for Ca had similarly negative effect.

292 In soils, the effects of Ca compounds on Zn nutrition are variable, due to the effects of its 293 salts on soil pH. Zinc concentrations in plants growing in soil treated with CaSO₄ (which 294 decreased the soil pH from 5.6 to 4.8) increased slightly but decreased strongly when an 295 equivalent amount of CaCO₃ was applied (which increases the soil pH from 5.7 to 6.6) (Wear 296 and Evan, 1968). The macronutrient cat ions K, NH₄ and Mg all inhibited the rate of Zn 297 absorption strongly from solutions of low Ca concentrations; with increasing Ca 298 concentrations, the inhibitory effects weakened and in the case of two ions (K, Mg) tested at 299 sufficiently high Ca concentration (2.5-10 mM) eventually disappeared, suggesting that they 300 operate through the same mechanism as Ca (Chaudhry and Loneragan, 1972).

301 6.4 Copper-Zn Interactions

Loneragan and Webb (1993) reported that Cu and Zn may interact in several ways: Zn
 strongly depresses Cu absorption, Cu competitively inhibits Zn absorption and Cu nutrition
 affects the redistribution of Zn within plants.

305 A very strong Cu-Zn antagonism has been observed in wheat growing on soils deficient in 306 Cu and Zn (Kausar et al., 1976). In N-Cu-Zn experiment, Chaudhry and Loneragan, (1970) 307 found that N fertilizer increased grain yield in the absence of Zn and diluted Cu 308 concentrations to deficiency levels in plant. Addition to that, Zn along with N fertilizer 309 intensified the Cu deficiency so severely that grain yield was lower than in the control plants 310 (without NH₄NO₃). In this case, Zn intensified Cu deficiency in plants by depressing Cu 311 uptake. This may be a result from competitive inhibition of Zn on Cu absorption (Bowen, 1987). The competitive inhibition of Cu²⁺ ion on Zn²⁺ absorption has been established in 312 313 short term studies (Giordano et al., 1974). While Zn severely depressed Cu uptake by 314 wheat, Cu did not depress Zn absorption in the same experiment. The reason for the 315 difference in soil and solution culture results may be the form of these ions present in the soil 316 and solution. In solution studies, the Cu and Zn were present as divalent ions whereas in 317 most of the soils they are predominantly present as complex forms and a much higher proportion of Cu is complexed compared to Zn (Geering and Hodson, 1969). So Zn 2+ 318 activity would be much higher than Cu²⁺ activity at the absorbing sites making it an effective 319 320 competitor in Cu absorption and making its absorption less sensitive to competition from Cu 321 (Loneragan and Webb, 1993).

322 6.5 Iron-Zn Interaction

323 The interaction between Zn and Fe is also complex like P-Zn interaction. The increased 324 application of Zn had little effect (Norvell and Welch, 1993) or decreased (Safaya, 1976) Fe 325 concentrations in the shoot. In the same way, higher levels of Fe generally have only a 326 depressive effect on Zn concentration in plant tissues (Zhang et al., 1991b), although it has 327 been shown to increase have no effect on or to decrease the rate of Zn absorption by plant 328 roots (Giordano et al., 1974). These conflicting reports are probably due to differences in 329 experimental details, especially in plant species and the concentration, ionic state and 330 complexation of Fe.

331 Iron (Fe²⁺) at low concentrations (10 μ M) had no effect on the rate of Zn absorption by wheat seedlings from solutions containing 1 or 10 μ M Zn and 50 mM Ca(NO₃)₂ (Chaudhry and 332 Loneragan, 1972b). But at higher concentrations (100 µM Fe²⁺), and at concentrations likely 333 334 to occur in flooded rice soils, Fe completely suppressed the Zn absorption by rice seedlings 335 from a solution of 0.05 µM ZnCl₂ with no Ca (Giordano et al., 1974). Iron deficiency 336 increased Zn concentrations in shoots of plants (Agarwala et al., 1979) and also the rate of 337 Zn absorption in both dicotyledonous plants (Romheld et al., 1982) and grasses (Zhang et 338 al., 1991b). In dicotyledonous plants, the mechanism for increasing Zn absorption is 339 probably the acidification of the rhizosphere resulting from Fe deficiency (Marschner and 340 Cakmak, 1989). For grasses, the release of phytosiderophores under Zn deficiency is 341 responsible for the higher Zn absorption rate as phytosiderophores have enhanced the 342 mobilization of Zn from calcareous soils (Zhang et al., 1991b and Treeby et al., 1989). In a 343 similar way, under Zn deficient conditions, Fe accumulated in the shoots of Zn deficient navy 344 beans and corn plants are possibly due to the acidification of the rhizosphere and the 345 release of reductants and phytosiderophores ((Ambler and Brown, 1969 and Jackson et al., 346 1962).

347 **7. Dilution Effect**

348 When the rate of plant growth is faster than the rate of uptake of a particular nutrient, the 349 concentration of the nutrient is "diluted" in the plant (Singh et al., 1986; Olsen, 1972). These 350 researchers also showed that in wheat and bean the yield and total Zn content increased 351 with P application while the Zn concentrations in plants decreased. A response in yield was 352 found for applied P, so a dilution effect on Zn is largely accountable for this effect. In general, 353 this interaction occurs when the soil is deficient in P and/or slightly deficient in available Zn. 354 The growth rate increases due to applied P but the rate of Zn uptake does not increase fast enough to maintain Zn concentration in plants. In some cases of P-induced-Zn deficiency the 355 356 dilution effect only partially explains the data (Singh et al., 1986). The applied P reduces the

357 Zn concentration in the tops of the plant while the yield response to P is minimal (Singh *et al.*, 1986).

359 8. Distribution of Zn in Plant Roots and Tops

360 Zn is an essential micronutrient involved in a wide variety of physiological processes 361 (Cakmak, 2000; Reeves and Baker, 2000; Doncheva et al., 2001; Stoyanova and Doncheva, 362 2002; Di Baccio et al., 2005; Broadley et al., 2007). Zn uptake varies among plant species 363 and is determined by the composition and concentration of the growth media. Zn uptake 364 occur as divalent cation or as complexes with organic ligands and display a linear pattern 365 with its concentration in the nutrient solution of soils (Kabata-Pendias and Pendias, 2001), roots load it via xylem to the shoot tissues (Broadley et al., 2007). The Zn translocation to 366 367 roots xylem occurs via symplast and apoplast but its high levels have also been detected in 368 the phloem, denoting that this metal is translocated through both xylem and phloem tissues 369 (Brennan, 2005; Broadley et al., 2007, Haslett et al., 2001).

370 9. Zinc Efficiency

371 Zn efficiency can be defined as "the ability of plants to maintain high yields in soils with low 372 Zn availability". Many mechanisms are perhaps involved in Zn efficiency (Rengel, 2001). 373 Depending on the nature of experiments and plant species, the most significant mechanisms 374 may be Zn utilization in tissues (Hacisalihoglu and Kochian, 2003) and Zn uptake (Genc et 375 al., 2006). Under Zn deficiency, Zn-efficient genotypes have a high activity of Cu/Zn 376 anhydrase (Hacisalihoglu et al., 2003a; Yu et al., 1999; Cakmak et al., 1997) and carbonic 377 anhydrase (Hacisalihoglu et al., 2004; Rengel, 1995). Zn efficiency and Zn uptake are very 378 susceptible for plant growth and its total content in soil is influenced by several soil 379 properties like pH, CaCO₃, organic matter content, crop, as well as cultivars and nutrient 380 interactions in soil environment. There is no precise mechanism used in determining Zn 381 efficiency is available so far; however, several crops have been evaluated for their Zn 382 efficiency like: beans (Ambler and Brown, 1969; Hacisalihoglu et al., 2001; Hacisalihoglu et 383 al., 2003b), wheat (Graham and Raangel 1993; Cakmak et al., 1997a) and rice (Brown et a.l, 384 1993; Clark, 1990; De Datta and Neue, 1993; Nand, 2002; Geo, 2007).

385 9.1 Zinc Deficiency in Plants

386 Zinc is an essential micronutrient for plant growth and plays an important role in the catalytic 387 part of several enzymes (Fageria, 2002). Many researchers observed that Zn is closely 388 related to the nitrogen metabolism pathway of plants, thus causing a reduction in protein 389 synthesis for Zn deficient plants. Zinc deficiency significantly affects the root system 390 including root development (Fageria, 2004). Zinc deficiency affects the absorption of water 391 and nutrients from soil and thus resulting in growth and yield reduction in the plant. Epstein and Bloom (2005) indicated that the flowering and fruiting process were greatly reduced 392 393 under severe Zn deficiency.

394 9.2 Zinc deficiency Symptoms in plants

Visual symptoms of Zn deficiency in plants are fairly characteristic and are relatively easy to 395 396 identify. These distinctive symptoms are useful for recognizing acute Zn deficiency and for 397 indicating Zn responsive soils, but not the hidden or marginal deficiencies. The most 398 common symptoms of Zn deficiency include: stunted growth, shortened internodes and 399 petioles, and small malformed leaves (little leaf) which results in the "rosette" symptom in the 400 early growth stages of dicotyledons and "fan shaped" stems in monocotyledons (Snowball 401 and Robson, 1986). The deficiency symptoms first appear on young leaves as Zn is 402 immobile under conditions of deficiency. These leaves remain small, cup upward and 403 develop interveinal chlorosis and necrotic spots on the upper leaf surfaces which later join to 404 each other to form brown necrotic and brittle patches. The necrosis is often more noticeable 405 on middle aged leaves which eventually wilt, bend and collapse (Brennan et al., 1993). Zinc 406 deficiency is typically patchy, even within a single field and symptoms develop rapidly but 407 depend greatly on the degree of stress (Kubota and Allaway, 1972). Enzyme activity, like 408 ribonuclease activity or carbonic anhydrse activity can be used as an index for precise 409 information. This is particularly important in the initial stages of growth when micronutrient 410 requirements of plants are very low and the total contents of Zn fail to provide precise 411 information about the hidden deficiency. Zinc deficient plants are unthrifty, lack vigor; give

patchy appearance with short and thin stems. In young plants interveinal areas are with dark
 brown necrotic lesions (Benton 2003).

414 The visible symptoms in rice are: wilting due to loss of turgidity in the leaves, basal chlorosis of the leaves, delayed development of the plants, " bronzing" of the leaves and in some 415 416 cases death of the rice seedling (Neue et al., 1998). Neue et al (1998) stated that the 417 common symptoms of Zn deficiency in rice are: chlorosis in the mid rib at the base of the 418 youngest leaf within 2-4 weeks after sowing or transplanting and the appearance of brown 419 spots on the older leaves. The spots enlarge, coalesce and give the leaves a brown color. 420 Zinc deficient plants show stunted growth and reduced tillering. If the deficiency is not too 421 severe the plant may recover after 4-6 weeks but maturity is delayed and yields of 422 susceptible cultivars are reduced. The most noticeable symptom is the plant's loss of 423 turgidity, where plants fall over and float on the surface of the water. The basal leaves 424 become pale green and after 3-7 days the leaves become chlorotic. It is important to note 425 that visual symptoms of Zn deficiency in rice vary, to a certain extent, with soil type, cultivar 426 and growth stages. Symptoms can be mistaken for those of of N, Mg, Mn or Fe deficiencies 427 which are often combined with Zn deficiency, making it difficult to distinguish between the 428 symptoms of the two. Therefore, plant analysis is required for confirmation (Dobermann and 429 Fairhurst, 2000; Alloway, 2004, 2008).

430 **10. Zinc Critical Levels in Plants**

431 Zinc deficiency is one of the major constraints in world food production. It is therefore 432 essential to identify the Zn-deficient areas, and the different causes of deficiency. It would 433 help in planning the appropriate strategies to correct these Zn deficiencies. Although Zn is 434 being used as a fertilizer, an understanding of efficient and economical methods to correct 435 Zn deficiency on a long term basis and in a specific cropping system is desirable. It was 436 reported by Katyal and Randhawa (1983) that there is a strong relationship between Zn 437 concentration in tissues with the growth and yield of crops. The critical limits of Zn in plants indicates deficiency as suggested by Dobermann and Fairhurst (2000) are :< 10 mg kg⁻¹ 438 definite Zn deficiency, 10-15 mg kg⁻¹ very likely,15-20 mg kg⁻¹ likely and >20 mg kg⁻¹ 439 440 unlikely (sufficient). In most crop species leaf sufficiency range for Zn 15 to 50 ppm in the dry 441 matter of mature plants and in most cases 15 ppm Zn is considered as critical value (Benton 442 2003). Zinc deficiency can be corrected through the application of Zn fertilizers, recycling 443 crop residues, natural organic manures and cultivation of Zn efficient genotypes (Singh, 444 2008).

445 **11. Zinc Toxicity**

446 The threshold of Zn toxicity varies among plant species, time of exposure to Zn stress and 447 composition of the nutrient growth medium. Plant growth inhibition extends in E. maculata 448 and E. urophylla by five weeks after addition of 400-1600 mM ZnSO4, whereas Pisum sativum became inhibited after 1000 µM Zn application (Soares et al., 2001, Doncheva et al., 449 450 2001). Photosynthesis is strongly affected in plants exposed to heavy metals excess 451 (Prasad, 1999). High Zn concentrations in plants can cause phytotoxicity. The yield may be 452 reduced when plant leaf Zn concentrations reaches about 300 - 1000 µg Zn g⁻¹. A typical phytotoxicity critical concentration is about 500 µg Zn g⁻¹ (Chaney, 1993). The best way to 453 454 identify Zn deficiency in crops is the determination of Zn concentrations in tissues, however, 455 the results should be interpreted in full recognition of the interaction of Zn with other nutrients 456 because the deficiency of one nutrient may result in excess accumulation of other nutrients 457 by a plant (Katyal and Rawdhawa, 1983).

458 **12. Effect of Zn on Microbial Activity**

459 Microorganism requires various nutrients for their growth and metabolism. Among the 460 nutrients, Zn is an element present in the enzyme system as co-factor and mental activator 461 of many enzymes (Vankatakrishnan *et al.*, 2003). According to Vankatakrishnan *et al.* 462 (2003); Baath (1992) and Doelman and Haanstra (1984), the solubilization of Zn might limit

463 464	the growth of bacteria at higher levels (>13.60 mg kg ⁻¹). Furthermore, cell growth as well as microbial populations and their activity in soil were badly affected under high levels of Zn.
465	13. Conclusion
466	Our extensive review of literature has shown that Zn is very essential plant nutrient for all
467	types of crops. It is deficient in all parts of the globe with different types of soils. Under these
468	conditions application of Zn fertilizer is necessary for healthy crop growth and higher yields.
469	Soil and foliar applications of Zn fertilizer are recommended for correcting deficiencies. Soil
470	dressings of Zn chelates, sulfates and oxides should be broadcast and mixed in the soil. Soil
471	applied Zn had residual effects for subsequent crops but foliar sprays have no residual effect
472	and fresh applications must be made to each crop.
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