Abstract
Zinc as an essential element plays an important role in the balanced integrated nutrition of plants. It is an important microelement for improving the yield and quality of agricultural products, and hence improves animals and human health. Zinc has special physiological functions in all living organisms, such as maintaining the structural and functional integrity of biological membranes, facilitating protein synthesis, gene expression, enzyme synthesis, energy production and the Krebs cycle. Zn deficiency is a universal problem of great importance for agriculture and human health, as a lack of zinc element in the soils reduces crop productivity and qualities, because of the imbalance caused in many physiological functions dependent on zinc and are unable to function normally. The soil factors viz., pH, organic matter, clay percentage, calcium carbonate content are consider as the most important factors that affecting the availability of zinc to plants. Zinc availability in the soils is greatly affected by their total zinc content, organic matter contents, soil moisture status, microbial activity in the rhizosphere, redox conditions, and concentrations of other macro and microelements, especially copper, phosphorus and nitrogen. In arid and semi-arid regions, calcareous soils (rich in calcium carbonate) are widespread, which is distinguished by low zinc availability and consequently low zinc availability and uptake by plants. As zinc is an active element in the biochemical processes, and there are chemical and biological interactions between Zn and some other elements such as phosphorus, iron, copper and nitrogen. Zinc deficiency considered as the most widespread micro nutrient deficiencies in crops and pastures worldwide, which affecting plant growth and causes large losses in crop production and quality. Zn visible deficiency symptoms could be one or more of the following symptoms: interveinal chlorosis, necrotic, bronzing, rosetting of leaves, stunting of plants, dwarf leaves and malformed leaves. Around half of the world's cereal crops are cultivated on zinc-deficient soils; as a result, zinc deficiency in animals and humans is a widespread problem. In many parts of the world zinc deficiency in the early stages of a human's life impaired physical growth, neuro development, brain function, memory, and learning ability. Severe zinc deficiency in human's is characterized by stunting, lack of normal sexual development, impaired immune response, skin disorders, hair loss, loss of appetite, and weak body muscles. Recently, elemental zinc is considered as potential supportive treatment in the therapy of COVID-19 infection. The recommended dietary allowances (RDAs) for zinc as recommended by the Dietary Office of the National Institutes of Health are: 2-3 mg per day for infants, 5 mg per day for children, 8-11 mg per day for adolescents and adults, and 11-13 mg per day for pregnant and lactating women.

Keywords: Zinc; Soils; Bioavailability; Balance. Deficiency; Plant Nutrition; Human health.

Introduction
Zinc (Zn) deficiency is a vital problem in some areas for both plants and human, particularly in developing countries, which mainly dependent on cereal crops to fulfill their need for food and nearly
50 percent of global population is suffering from Zn-deficiency (Alloway, 2008; Cakmak, 2004 &2008). The concern about the problem of zinc deficiency is increasing day by day, as zinc plays many vital roles in the biological functions of both humans and plants, as it is one of the essential micro-elements required for optimal growth and productivity. (Hortz and Brown, 2004; Fraga, 2005; Alloway, 2008; Noulas et al., 2018).

Zinc belongs to the group of eight essential trace elements (manganese, copper, boron, iron, zinc, chlorine, molybdenum, and nickel), which required for proper plant growth and productivity, however, zinc deficiency in agricultural soils has been recognized as a global problem, especially in calcareous soil in arid and semi-arid regions of the world (Bityutski et al., 2017; Noulas et al., 2018; Chen et al., 2019). In such soils, the total zinc content may be relatively high; but the main problem is the low availability of zinc due to the low content of organic matter and the high content of calcium carbonate (Rengel, 2015; Bityutski et al., 2017; Kumari et al., 2018).

Zinc (Zn) plays a fundamental role in many biological processes in plant; as required in various enzymatic reactions, metabolic processes, and oxidation-reduction reactions, and is an essential trace element for proper normal and healthy plant growth and yielding. It is also required for normal health of animals and humans (Noulas et al., 2018). Thus, zinc deficiency stress in plants, normally due to low-zinc bioavailability in soil, causes significant decreases in the productivity and nutritional quality of food and has negative effects on human beings health. Zinc is required as a structural component of a large number of proteins, as it is a cofactor in metaloenzymes (de Figueiredo et al., 2007) involved in protein synthesis and energy production, as well as in the maintenance of biomembrane structural integrity and production of IAA (Indole Acetic Acid), that is responsible for plant growth (leaf elongation) (Hanch & Mendel, 2009; Marschner, 2011).

Zn-deficiency can also help in increasing the level of reactive oxygen species (ROS) that interfere with the mechanisms of cellular detoxification. This can by reducing the activity of anti-oxidative enzymes such as Cu/Zn superoxide dismutase and carbonic anhydrase (Cakmak, 2000; Hacisalihoglu and Kochian, 2003), resulting in reduction in growth and crop production. It is also involved in several biological reactions of cellular metabolism, including biological processes, such as antioxidant defense, protein synthesis, carbohydrate metabolism, auxin metabolism, and stability of genetic materials (Clemens et al., 1999; Broadley et al., 2007).

Zinc dynamics in soil-plant systems have important economic and environmental impacts, as zinc is an essential element for the growth and reproduction of all living organisms (Frassinetti et al., 2006). In the case of low zinc availability in the soil, the growing plants will suffer from some physiological disturbances due to the failure of the metabolic processes in which zinc plays a key role. Zinc is known to be one of the essential elements for feeding plants however, it is only required in low concentrations, which makes it act as an essential micronutrient. Zn-concentration between 30 and 100 µg g-1 DW is sufficient to provide plants with their needs from this vital element, whereas zinc toxicity symptoms are observed in concentrations above 300 µg g-1 DW; for plant species that are not adapted to high-zinc exposure (Van de Mortel et al., 2006; Marschner, 2011). However, high accumulation of zinc in plant can be harmful (Szatanik-Kloc et al., 2009). Therefore, for optimal plant growth, plants need close control over zinc balance and always be within the limits of adequacy (Marschner, 2011).

The growth and yield of grains of both wheat and barley significantly decrease when cultivated in zinc deficient soils (Graham et al., 1999; McDonald et al., 2001). The occurrence of zinc deficiency in humans and animals in certain geographical areas, especially in developing countries, is often closely related to the deficiency of this element in the soil, especially when cereals-based foods are the most important sources of calories local population. Soil zinc deficiency may cause a significant decrease in the yield and quality of many crops. The cultivation of food crops in zinc deficient soils is a major problem, which leads to low yields, low zinc content in food, low income for farmers, and discourages them from investing (Erenoglu et al., 2010). Maintaining an adequate concentration of zinc in rice and wheat grains is important for more than two-thirds of the world's population, especially in developing countries, where rice and wheat are the mainstay of their diet, and zinc can be supplemented in food from sources rich in zinc such as seafood, meat and, leafy vegetables and legumes. (Chen et al., 2000; Anderson et al., 2001; Simon and Taylor, 2001).

Zinc deficiency in the soil reduces the zinc content in the edible parts of the staple food crops and reduces their nutritional value (Welsh & Graham, 2004). For example, growing wheat (Triticum aestivum, L.) on zinc deficient soil in Turkey resulted in reduction in the grains Zn-content by...
approximately 50% lower compared to wheat grown with adequate zinc supply (Cakmak, and Hoffland, 2012). Therefore, a diet consisting of a high proportion of cereal-based and legumes foods, which contain low Zn, is considered as one of the major reasons for the widespread occurrence of Zn deficiency in humans, especially in developing countries (Saxena et al., 1993; Singh, 1993; Ganeshmurthy et al., 2006; Biesalski, 2016). Soil nutrients content and management affect crop productivity and nutrients concentration in plant edible parts. Thus, soil nutrients status has great implications on human and animals health. Globally, nearly one third of arable land is deficient in micronutrients, particularly zinc (Zn) (Cakmak et al., 2017), which leads to underproduction and low nutritional value of cultivated crops, and this ultimately negatively effects on animals and human nutrition (Cakmak 2008; Goudia & Hash 2015). The extent of Zn deficiency in humans has been estimated by considering the absorbable Zn content of the national food supply (Wessells and Brown, 2012). Most of the regions in the world with high incidence of Zn deficiency in humans, found in South and Middle East Asia, Africa and various Latin American countries, where soils have low Zn-availability (Figure 1).

The problem of Zn-deficiency is most common in of arid and semi-arid soils, due to (i) high levels of soil-pH and CaCO₃, (ii) low organic matter content (percentage) (Cakmak, 2008; Gonçalves Junior et al., 2010), (iii) in sandy texture soils, (iv) when high analysis NPK fertilizers are used, (v) enhanced Zn-removal by high yielding varieties and (vi) redox changes in flooded soils (Tandon, 1995; Cakmak et al., 1998). However, low solubility of Zn in soils, rather than low total amount, is the major reason for the widespread occurrence of Zn-deficiency problem in crop plants (Cakmak, 2008). It is very difficult to maintain the optimal amount of bioavailable zinc in the soils because it is mainly from non dissolved compounds with either phosphates, carbonates, sulfides or iron and manganese hydroxides (Kabata-Pendias, 2010). In contrast, free zinc ions and consequently bioavailable Zn, are most common in acidic soils, and highly mobile, and can easily leached from soil (Yun and Yu, 2015). This will limits availability and zinc uptake by plants, resulting in significant decreases in both productivity and nutritional value of food leading to Zn-deficiency in human, which affects more than two billion people (De-Regil et al., 2013; Bailey et al., 2015; FAO, 2015). Approximately one-third of the world's population (two billion people), suffers Zn-deficiency, with prevalence rates ranging from 4 to 73% in various regions (WHO, 2002).

This paper aims to review and discuss aspects related to the role and dynamics of zinc in the agricultural biological system of soil, water, plants and humans: from the origins of zinc in soil and water to the distribution of zinc deficiency in the soil and the factors that affect its availability. For plants, improving understanding of the different relationships between factors affecting the content, behavior and availability of zinc in the soil and its important role in the growth and productivity of different crops improving their nutritional value and their relationship to human health.
1. Zinc in the soils

Normally, the total Zn in the soils is ranged between 10 to 300 mg kg\(^{-1}\), with an average of 50 mg kg\(^{-1}\) (Lindsay, 1972). However, the average of available Zn; as extracted by dithizone does not exceed 1 to 3 mg kg\(^{-1}\). The problem is this very small amount of available-Zn is due to one or more of adverse factors. The remainder is fixed in the soil in an insoluble or non-exchangeable form and difficult to be available to plant (Stahl and James, 1991). The content of Zn in unfertilized and uncontaminated soil is related to the chemical composition of its parent materials and the extent of weathering processes (Chesworth, 1991). In the magmatic rocks, it ranges between 40 to 120 mg kg\(^{-1}\), whereas in the sedimentary rocks Zn contents vary from 80 to 120 mg kg\(^{-1}\) in argillaceous sediments and shales soils, while it ranges only between 15–30 mg kg\(^{-1}\) in sandstones soil and 10–25 mg kg\(^{-1}\) in lime stones and dolomites soils (Kabta-Pendias and Pendias, 2001). Generally, in agricultural soils Zn is mostly unevenly distributed and its content ranges between 30 and 100 mg kg\(^{-1}\) (Barber, 1995; Mall, 1992), with an overall mean of around 64 mg kg\(^{-1}\) (Kieknes, 1995). In addition, some other; Martens and Smolders, 2013, indicate that total content of contents in unfertilized and Zn-non contaminated soils can vary widely and ranged between 10 to 100 mg kg\(^{-1}\). The mean Zn-contents in worldwide soils was 64 mg kg\(^{-1}\) as shown in Table (1) (Kabta-Pendias and Pendias, 2001). However, soils containing available-Zn less than 0.5 mg kg\(^{-1}\) (DTPA-extractable Zn) are considered Zn deficient for most crops.

| Soil type          | Abundance (mg kg\(^{-1}\)) |
|--------------------|----------------------------|
| Mean               | 64                         |
| Light sandy        | 31–61                      |
| Medium loamy       | 47–61                      |
| Heavy loamy        | 35–75                      |
| Calcareous         | 50–100                     |
| Organic            | 57–100                     |

Source: Kabta-Pendias and Pendias, (2001)

1.1- Behavior of zinc in the soils

In the nature, Zn is found in the earth’s crust as one of the components of rocks or in Zn-rich ores, which are locally formed by natural geological process and are located in soils all over the world. Mertens and Smolders, 2013 stated that, Sphalerite or Wurzite are most economically important ores that contain typically 5-15% Zn as zinc sulfates followed by Smithsonite (zinc carbonates) and Hemimorphite (Zn silicates), which contain lesser Zn minerals. Zn availability in soil is assessed with chemical extraction procedure (Chen et al., 2019).

The behavior of zinc in the soils is a complex process, as it depends on the dynamics of many heterogeneous soil compounds (Alexakis, 2011), that enables the presence of zinc in several forms, whether soluble or bound to soil particles (Abreu et al., 2007). The availability of Zn in the soils is strongly dependent on zinc distribution in different soil fractions, as it is exists in three main fractions: (i) water soluble-Zn (including Zn\(^{2+}\) and soluble organic fractions); (ii) the insoluble Zn colloidal adsorbed and exchangeable fraction (associated with clay particles, humate compounds and Al and Fe hydroxides); and (iii) minerals and complexes zinc (Lindsay, 1979; Barrow, 1993; Alloway, 1995; Barber, 1995). Differences in physical and chemical reactions in the soil can significantly affect the balance between the three organic and inorganic fractions (Tessier et al., 1979; Gismera et al., 2004; Leite et al., 2020). Therefore, the study of different Zn-fractions in the soils is required for better understanding of Zn availability and the crop need for fertilization (Zahedifar, 2017). Determination of Zn fractionation in the soils can provide enough information about zinc behavior in soil and crops need for fertilization. Tessier et al., 1979; Rauret et al., 1999; Leite et al., 2020 specified the pools of Zn fractions present in soils as follows: (i) Zn bound to ion-exchanging sites, and Zn associated with (ii) carbonates; (iii) organic matter; (iv) Fe and Mn oxides; and (v) a residual fraction. Different Zn fractions in the soils are greatly differ in in the mode of binding to the soil particles and therefore, in their solubility and availability to plant. The exchangeable-Zn fraction is the most accessible and available form for plants. Availability of Zinc in other fractions (bound to carbonates, organic matter, and Fe and Mn oxides forms), depending upon the soils physicochemical characteristics, and could be considered relatively labile or tightly bound (Sposito et al., 1982; Peppicelli et al., 2018). While, the Zn pools of...
the residual fraction is not mobile and relatively inactive and cannot be soluble or available to plants (Khoshgoftarmanesh et al., 2018). However, different soil zinc fractions are in a dynamic equilibrium with each other, and Zn distribution between all fractions must be distinguished. Zinc fractions are strongly affected by soil chemicals characteristics, such as soil-pH, and DOC (dissolved organic carbon) (Impa et al., 2012), and CEC (cation exchange capacity) (Khoshgoftarmanesh et al., 2018). Usually, soil-Zn is more available in the soils contain more organic matter (Alloway 2009; Iratkar et al., 2014); due to its large surface negative charge; measured as CEC) (De Santiago-Martín et al., 2014), and due to the important role of dissolved organic matter in increasing Zn availability and distribution in the soils (Dehghanian et al., 2018). Generally, zinc availability and distribution in each soil fraction depends on soil organic matter content, pH, and temperature (Tiller et al., 1984), texture, structure, amount and clay minerals type (Spark et al., 1995; Leite et al., 2020), cation exchange, metal oxide fractions (Guadalix and Pardo, 1995; Stahl and James, 1991) and transformations in the source material (Fontes and Alleoni, 2006). The distribution of Zn between different soil fractions can be determined by soil-specific precipitation, complexation and adsorption reactions. The dominant factor determining soil Zn distribution is soil pH because that Zn is more readily adsorbed on cation exchange sites at higher pH and CaCl2 displaces adsorbed Zn at lower pH. Thus, soluble Zn and the ratio of Zn2+ to organic Zn-ligand complexes increase at low pH, especially in soils contain low soluble organic matter.

In addition, soil type, moisture, clay types and mineral contents, weathering rates, diffusion and mass flow rates, soil organic matter, and soil biota and plant potential to uptake zinc will also affect Zn availability and distribution in the soil. It was found that insoluble zinc represent > 90 percentage of total Zn in soil and is unavailable for plant uptake. Exchangeable Zn in the soil typically ranges between 0.1 and 2 mg Zn kg−1 soil. Concentrations of soluble Zn in the soil solution are low, typically between 4 × 10−10 and 4 × 10−8 m (Barber, 1995), even in Zn-contaminated soils (Knight et al., 1997). There are several Zn-ligand complexes found in the soil solution that may be not easy to directly measure, and speciation models, based on total dissolved zinc concentrations of and ligands, their stability constants and mineral equilibrium reactions, are often used to inference (Barak & Helmke, 1993; Zhang et al., 2006). Numerous Zn-ligand complexes can exist in soil solution, which might be difficult to directly measure; Zn2+ typically accounts up to 50 % of the soluble Zn fraction and is the dominant plant available-Zn fraction. However, in calcareous soils, Zn2+ may be as low as 10−11:10−9 m and can negatively affect crop growth and productivity (Hacisalihoglu & Kochian, 2003). The total Zn in the soils does not considered a realistic indication of the Zn availability for plants, as it is easily interacts with some other soil elements, that is varies according to the soil physical or chemical properties and water parameters resulting in a temporary increasing followed by a decreasing in available Zn for plants (Impa et al., 2012). Many factors affect the availability of zinc in the soil and the ability of plants to absorb it. Under certain circumstances, Zn solubility and hence its availability for plants decreases due to existence high levels of calcium carbonate, phosphate, metal oxides, high pH and low content of organic matter and soil moisture (Robson, 1994; Cakmak and Hoffland, 2012). In addition, Zn bioavailability and mobilization in the soils are greatly influenced by some environmental conditions. It is noticed to be associated with the distribution of zinc in soil fractions that can be measured to understand how much this metal influenced by the environment. It is important to distinguish between the total quantities of Zn in the soils and the amounts that can be transferred into more soluble forms, and becoming bio-available for plants uptake (Begum et al., 2016). In general, the order of presence of zinc forms in the soils remains as follows: exchangeable zinc <organic zinc<zinc carbonates<iron-zinc crystals bound to manganese oxide> residual zinc (Jangir et al., 2019).

1.2. Zinc deficiency in the Soils

Zinc deficiency in the soils can be found in most cultivated or cultivable soils in all parts of the world and most crops respond positively to Zn-application (Welch and Graham, 2004). At global level, about one-third of arable soils are deficient in micronutrients, particularly zinc (Zn) (Cakmak et al., 2017), and this eventually affects crop productivity and human nutrition. Approximately 2–3 billion people all over the world are suffering from micronutrient deficiencies, especially in developing countries (Figure 1), where these affect the health of at least half of the population in such countries (Goudia and Hash 2015). In alkaline soils, which cover at least 30 % of the arable land globally, Zn availability to plant roots is very low (Chen & Barak, 1982; Cakmak, 2002; Alloway, 2009). Zinc dominates the list of micronutrients deficient in Sub-Saharan Arable soils (SSA), whose zinc as
micronutrients is inherited mainly from parent rocks through geochemical and biochemical weathering processes (Kihara et al., 2017). Besides the mineral composition of the parent material, the total amount of zinc present in the soil also depends on the type and severity of climate and many other dominant factors during the soil formation process (Saeed and Fox, 1977). Soils derived from granite and gneiss can be low in total zinc (Krauskopf, 1972). Similarly, total Zn is low in highly leached acid sandy soils such as the ones found in many coastal areas (Alloway, 2008). In addition, quartz in the sandy soils dilutes Zn concentrations because of it contain very low amounts of zinc, which ranged from 1.0 mg kg\(^{-1}\) to < 5-8 mg kg\(^{-1}\) (Brehler and Wedepohi, 1978). Meanwhile, high soil pH, high calcium carbonate content, high organic matter, low moisture, high clay and phosphates can fix zinc in the soil reduce the zinc available to plants, and plants can suffer from zinc deficiency (Imtiaz, 1993 & Alloway, 2008).

![Figure 2: Schematic diagram of soil factors causing lack of zinc available for plant roots. Adapted from Alloway, (2008)](image)

Generally, Zn deficiency in the soils is expected in calcareous soils, sandy or peat soils, and soils with high silicon and phosphorus content (Alloway, 2004 & 2008). Also, the submerged soils are well recognized to have low Zn availability and plants can suffer from Zn-deficiency (Mikkelesen & Shiou, 1977). Flooding and submersion conditions bring about a decline in available Zn because of the changes in pH value, particularly due to the reaction of Zn with free sulphide and the formation of insoluble Zn compounds (Mikkelesen & Shiou, 1977). According to the Food and Agriculture Organization (FAO), about 30% of the cultivable soils of the world contain low levels of available Zn (Sillanpää, 1990). The lowest Zn concentrations were always more pronounced in Spodosols (28 mg kg\(^{-1}\)) and luvisols (35 mg kg\(^{-1}\)), while higher levels were found in Histosols (58 mg kg\(^{-1}\)) and fluvisols (60 mg kg\(^{-1}\)) (Kiekens, 1995). Meanwhile, insoluble zinc compounds are likely to be formed as a result of reaction with manganese and iron hydroxides, decomposition of oxides and absorption of carbonates, specifically magnesium carbonate, and under submerged conditions as in the case of rice cultivation, the zinc turns into amorphous deposits or franklinite; ZnFe\(_2\)O\(_4\) (Sajwan & Lindsay, 1988). The conversion and distribution of different forms of zinc and iron under submersion conditions for forty soils were studied by Wani and Khan (2013). They found that > 83% of total Zn occurred in the relatively inactive clay lattice-bound form, while a smaller fractions, viz. 1.09, 1.82, 2.27 and 11.70% of the total zinc occurred as water-soluble plus exchangeable, organic complexed, and crystalline sesquioxide bound, and amorphous sesquioxide-bound forms, respectively.

### 1.2.1. Factors causes zinc deficiency in the soils

Most of the zinc present in soil occurs on surfaces of clays, hydrous oxides, and organic matter, and little of it is found in the soil solution (Armour et al., 1990). In arid and semi-arid soils, calcite soils and the slightly acidic, leached soils of warm and tropical climates are most inclined to Zn deficiency, however, crops cultivated in such soil are not equally susceptible to Zn deficiency, where at the same soil, only some crops may suffer from Zn deficiency, while others are not affected. Generally, major Zn deficiency is common in soils with the subsequent characteristics:(i) Soils poor in zinc (parent...
material), (ii) soils of high pH (e.g. Calcareous & heavy limed soils, (iii) soils rich in phosphorus (heavy P-fertilization), (iv) high soil moisture, (vi) soils of low or high organic matter content. Under these conditions, the available-Zn will be low and they will suffer from a lack of zinc (Zn-deficiency), which reduce their growth and productivity (Figure 3), and impaired quality of the cultivated crop (Lindsay, 1972; Takkar and Randhawa, 1978; Pendias and Pendias,1992; Alloway, 2004).

Figure 3: Schematic diagram of Zn-deficiency causes and their implication on crops. Adopted after: Alloway, 2004; Lindsay, 1972; Pendias and Pendias, 1992; Takkar and Randhawa, 1978).

1.2.1.1 Parent material of soils (Soils of low Zn content)

Distributions of zinc and other micronutrient vary with parent materials and profile depths (Verma et al., 2005). Zn-concentration in the soils parent material is one of the major factors affecting the soils zinc content, which is mainly depend on the chemical decomposition of the soil parent materials and the extent of weathering processes (Chesworth, 1991). It has been reported that shale soils are rich in carbonate and bound trace metal fractions (Hiller, 2006), while soils derived from false bedded sandstones are usually rich in Fe & Mn oxides that bound trace metal fractions (Gideon et al., 2014). Total zinc in the soils were in decreasing order of Imo clay shale >false bedded sandstones > coastal plain sands > alluvium, respectively. On the other hand, available zinc concentrations were found to be low and varied among the soils of different parent materials in a decreasing order as follows: alluvium > Imo clay shale > false bedded sandstones > coastal plain sands (Okoli et al., 2016). The amounts of Zn in natural (unfertilized and unpolluted) soils are typically lower than 125 ppm (Hussain et al., 2013). The soils derived from gneisses and granites and also those originating from sandstone (Sandy soils) and limestone (Calcareous soils) contain low total Zn content (Pendias and Pendias, 1992; Barak and Helmke, 1993; Lantican et al., 2003). Quartz particles contain rare zinc and are not able to adsorb cations and so the adsorptive capacity of a sandy soil is dependent on its low content of clay or silt-sized material and organic matter content, and due to their high infiltration rates. (De Datta, 1989; Alloway, 2009). More Quartz in sandy soils dilutes soil Zn, which is very low in nature; ranges between 1 - 8 µg g⁻¹(Brehler and Wedepohi, 1978). Also highly leached acid sandy soil contain low total Zn (<30 µg g⁻¹), and generally have low available Zn (Stahf &James, 1991).In the magmatic rocks, zinc is ranges between 40 to 120 mg kg⁻¹, whereas in the sedimentary rocks Zn contents vary from 80 to 120 mg kg⁻¹, in argillaceous sediments and shales soils, Zn content only ranges between 15–30 mg kg⁻¹ in sandstones and 10–25 mg kg⁻¹ in limestones and dolomites as shown in Table 2. (Kieknes, 1995; Kabata-Pendias & Pendias, 1999 &2001).
soil solution (Kabata-Occur in alkaline soils more than acidic one. Research has established that with increasing soil pH, the availability of Zn decreases. When pH increased from pH 5 to pH 8, the availability of Zn under alkaline conditions is attributed to the precipitation of Zn as Zn (OH)₂ hydroxides (Förstner, 1995). It was found that negative significant correlation (r= - 0.94) was found between exchangeable-Zn and soil pH, while a positive significant correlation (r=0.92) between inorganic Zn concentrations and soil pH was noticed (Torri and Lavodo, 2008). Soil acidity increases is increased by leaching basic cations such as Ca²⁺, Mg²⁺, K⁺, and Na⁺ far beyond where they are released from the parent material, leaving H⁺ and Al³⁺ ions at the places of cation exchange; Also, dissolving carbon dioxide in soil water produces carbonic acid, which hydrolyses and releases H⁺ ions; Humic residues resulting from decomposition of soil organic matter, which produces high-density carboxyl and phenolic groups that dissociate to release H⁺ ions; Nitrification to produce H⁺ ions; Nitrogen removal in plant and animal products; And inputs from acid rain and nitrogen uptake by plants (White & Broadley, 2005). Zinc availability is highly dependent on soil pH, which considers the most important limiting factor, causing lower zinc availability and affecting the physiological and morphological processes in the plants (Singh et al., 2005; White& Broadley, 2005). At low soil pH, zinc is usually soluble due to high desorption and low adsorption capacity. At intermediate soil pH, the trend of trace element adsorption increases up to complete adsorption within a narrow pH range called the pH-adsorption edge (Bradl,2004). For instance it was found that at pH 5.3, the adsorption of Zn onto a sediment composite consisting of Al, Fe, and Si-oxides was 53% (Bradl, 2004), while, about 50% of Zn sorbed onto humic acids between pH 4.8 - 4.9 (Bradl, 2004). The fate of readily available of zinc depends on both the properties of their ionic species formed in soil solution and that of the chemical system of soil apart from soil pH itself (Kabata-Pendias, 2010). Higher carbonate contents in alkaline soils also absorb more Zn and hold it in a non-exchangeable form (Udo et al., 1970). Such factors contribute to lower availability of Zn at higher soil pH values, especially in calcareous soils. The low availability of Zn under alkaline conditions is attributed to the precipitation of Zn as Zn (OH)₂ or ZnCO₃(Saeed and Fox, 1977; Shukla & Mittal, 1979; McMahon et al., 2019). The solubility constant values for ZnCO₃ and the hydroxides indicate that soils with a high pH typically contain a small amount of available zinc. Saeed and Fox, (1977) and Shukla & Mittal (1979) reported that in soils with high hydroxyl (OH⁻)- contents, it is difficult to obtain any response to zinc fertilization, due to the high soil pH, since when the soil pH is above 6, it is usually availability of zinc is very low (Fig.4). It was found that Zn- concentration in the soil solution decreases from 10⁻⁴ (6.5 µg g⁻¹) to 10⁻¹⁰ M (0.007 µg L⁻¹) when pH increased from pH 5 to pH 8 (Kieknes, 1995). Therefore, it is expected that Zn deficiency will occur in alkaline soils more than acidic one. Research has established that with increasing soil pH, the solubility of most micronutrients and particular Zn will decrease, leading to low availability of Zn in soil solution (Kabata-Pendias, 2010). Any decrease or increase in soil pH produces distinct effects on

| Soil type                        | Abundance (mg kg⁻¹) |
|----------------------------------|---------------------|
| Mean                             | 50-55               |
| Magmatic rocks                   | 40-120              |
| Argillaceous sediments           | 80-120              |
| Sandstones soil                  | 15-30               |
| Limestones and dolomites soils   | 10-25               |

Source: Kieknes, (1995); Kabata-Pendias & Pendias, (1999 & 2001)

1.2.1.2 Soil pH

Soil pH controls the solubility, mobility, and bioavailability and translocation in (Förstner, 1995). This is largely dependent on the partition of the zinc between solid and liquid soil phases through precipitation-dissolution reactions (Förstner, 1995). A negative significant correlation (r= - 0.94) was found between exchangeable-Zn and soil pH, while a positive significant correlation (r=0.92) between inorganic Zn concentrations and soil pH was noticed (Torri and Lavodo, 2008). Soil acidity increases is increased by leaching basic cations such as Ca²⁺, Mg²⁺, K⁺, and Na⁺ far beyond where they are released from the parent material, leaving H⁺ and Al³⁺ ions at the places of cation exchange; Also, dissolving carbon dioxide in soil water produces carbonic acid, which hydrolyses and releases H⁺ ions; Humic residues resulting from decomposition of soil organic matter, which produces high-density carboxyl and phenolic groups that dissociate to release H⁺ ions; Nitrification to produce H⁺ ions; Nitrogen removal in plant and animal products; And inputs from acid rain and nitrogen uptake by plants (White & Broadley, 2005). Zinc availability is highly dependent on soil pH, which considers the most important limiting factor, causing lower zinc availability and affecting the physiological and morphological processes in the plants (Singh et al., 2005; White& Broadley, 2005). At low soil pH, zinc is usually soluble due to high desorption and low adsorption capacity. At intermediate soil pH, the trend of trace element adsorption increases up to complete adsorption within a narrow pH range called the pH-adsorption edge (Bradl,2004). For instance it was found that at pH 5.3, the adsorption of Zn onto a sediment composite consisting of Al, Fe, and Si-oxides was 53% (Bradl, 2004), while, about 50% of Zn sorbed onto humic acids between pH 4.8 - 4.9 (Bradl, 2004). The fate of readily available of zinc depends on both the properties of their ionic species formed in soil solution and that of the chemical system of soil apart from soil pH itself (Kabata-Pendias, 2010). Higher carbonate contents in alkaline soils also absorb more Zn and hold it in a non-exchangeable form (Udo et al., 1970). Such factors contribute to lower availability of Zn at higher soil pH values, especially in calcareous soils. The low availability of Zn under alkaline conditions is attributed to the precipitation of Zn as Zn (OH)₂ or ZnCO₃(Saeed and Fox, 1977; Shukla & Mittal, 1979; McMahon et al., 2019). The solubility constant values for ZnCO₃ and the hydroxides indicate that soils with a high pH typically contain a small amount of available zinc. Saeed and Fox, (1977) and Shukla & Mittal (1979) reported that in soils with high hydroxyl (OH⁻)- contents, it is difficult to obtain any response to zinc fertilization, due to the high soil pH, since when the soil pH is above 6, it is usually availability of zinc is very low (Fig.4). It was found that Zn- concentration in the soil solution decreases from 10⁻⁴ (6.5 µg g⁻¹) to 10⁻¹⁰ M (0.007 µg L⁻¹) when pH increased from pH 5 to pH 8 (Kieknes, 1995). Therefore, it is expected that Zn deficiency will occur in alkaline soils more than acidic one. Research has established that with increasing soil pH, the solubility of most micronutrients and particular Zn will decrease, leading to low availability of Zn in soil solution (Kabata-Pendias, 2010). Any decrease or increase in soil pH produces distinct effects on
metal solubility (Figure 4). This may probably depend on the ionic species of the elemental metals and the direction of pH change.

![Figure 4: Zinc and other nutrients availability as affected by soil-pH.](image)

In contrast, Förstner, (1995) found that a decrease in soil pH by one unit resulted in a ten-fold increase in metal solubility Rengel (2001), observed that the solubility of divalent elemental metals decreases a hundred-fold while trivalent ones experience a decrease of up to a thousand-fold due increasing soil-pH by one unit. Low available concentrations of trace element at high soil pH may also be caused by precipitation with carbonates, chlorides, hydroxides, phosphates, and sulphates (Cui, et al., 2016).

Apatite and lime application to soils produced the highest effect on pH and simultaneously decreased the concentrations of available, leachable, and bio accessible of some micronutrients (Cui, et al., 2016). Liming of acidic soils enhances soil pH and the Zn fixing capacity; particularly when soils contain high P levels (Alloway, 2004). The mobility and availability of zinc in calcareous soils is much less, than in acidic soils, so the uptake of zinc by crops may be low, and it is a zinc deficient crop (Viets, 1966; Shukla and Moris, 1967).

1.2.1.3. Soil Organic Matter & Dissolved Organic Carbon

Soil Organic Matter (SOM) and Dissolved Organic Carbon (DOC) is the most important soil constituent that originates from decomposition of animal and plant residues. Adding organic materials such as crop residues, compost, livestock manure, green manure, and municipal bio-solids to the soil has many benefits to the soil including zinc nutrition as well as additional supply of some other benefits as improving soil structure and enhancing ion exchange capacity and water storage capacity, drainage and aeration and reducing soil salinity (Dhaliwal et al., 2019).

Soil organic carbon (SOC) content is the most important component in maintaining soil quality due to its essential role in improving physical, chemical and biological properties of soil (Dahliwal et al., 2019). Dissolution and availability of micronutrients in the soil as well as their absorption capacity by plants is greatly affected by soil organic matter as noted in many research findings, either in a direct and indirect way (Rengel et al., 1999, Dahliwal et al., 2019). Humic acid and fulvic are the two most stable organic ingredients in the soil. Both of these substances contain a relatively large number of functional groups (OH, COOH, SH) that have a high affinity to metal ions such as Zn$^{2+}$. Low organic matter in soil give rise to Zn deficiency, however, if the organic matter content in soil is too high, like in peat and muck soils, this can also causes Zn deficiency due to the binding of Zn on solid humic substances (Katyal & Randhawa, 1983). He et al., (2019) noticed a remarkable decreasing in concentration of free Zn$^{2+}$ ions in the presence of dissolved organic carbon, which could prove Zn binding. A decrease in the concentration of free elements in the soil solution may occur due to the binding of some minerals to the organic matter, but the dissolution of these organometallic compounds enhances the availability of these minerals in the rhizosphere root zone by increasing the concentration of total dissolved ions, which in turn depend on the movement of zinc and the degree of dissolution of
the complexes. Dissolved organic carbon (DOC).

The reactions of humic acids with zinc as well as the stability of the complexes formed are greatly influenced by the pH, mineral concentration, and chemical properties of soil organic molecules (Boguta and Sokolowska, 2016; Bogutat et al., 2016). The interaction of fulvic acids (FAs) with zinc could also have a beneficial role for the agricultural sector in developing effective formulations of highly stable compounds containing both organic carbon and zinc (Ray et al., 2018). The main difficulty is that both FAs molecules and Zn$^{2+}$ ions exhibit high sensitivity to changes in the pH, concentration of free metal ions, and the presence of competing ions (Wang et al., 2016&2018). Thus, Zn is chelated by FAs and increases its solubility and mobility over a wide range of soil-pH (Kiekens, 1995).

Chelating zinc with organic matter is largely responsible for increasing the accessible root forms of these nutrients and prevents the formation of insoluble forms such as carbonates and oxides in the soil (Schulin et al., 2015). Addition of organic matter to the soil stimulates microbial exudation of organic bonds (enhancing microbial biomass carbon), nutrient supply through mycorrhizal fungi, protection against root pathogens and other activities of microbes that collectively aid in the development of the root system, so zinc is one of the acquisition an essential micronutrient ability that ultimately enhances plant growth and enhances crop productivity (Schulin et al., 2015). In addition, some simple organic compounds such as amino acids and hydroxyl acids are effective in complexing zinc, thus increasing its mobility and solubility in the soil (Bendias and Bendias, 1992).

1.2.1.4. Soil texture

Soil texture plays an important role in managing soil nutrients because it affects the soil’s ability to retain nutrients. For example, soils with a fine texture tend to have a greater capacity to hold soil nutrients. In soil fertility, coarse soils such as sandy soils generally have lower nutrient retention and nutrient retention capacity compared to fine soils. Therefore, sandy textured soils contain low Zn levels, while heavier textured ones like clay soil absorb more Zn and contain more Zn, and this adsorption is mainly affected by soil CEC and pH (Ellis & Knzek, 1972). In this respect, Shuman (1975) and Lorenz et al., (2000) observed that soils rich in clay or organic matter had more adsorptive capacities and higher bonding energies for zinc than sandy soils, which low in organic matter. Clay soils have higher CEC values and therefore have highly reactive sites and can retain more Zn than lighter sandy textured soils (Shukla & Mittal, 1979). Cation Exchange Capacity (CEC) was found to be higher in heavier soils than sandy soils; as clay particles having a much higher cation exchange sites. (Stahl & James, 1991). Consequently, Zn deficiency is more occurred in sandy soils than in clayey soils. In this context, Reddy and Perkin, (1974) proved that a certain amount of the Zn adsorbed on the clay was not exchangeable and not available to the plants and un-extractable by 0.005 M DTPA. This depends not only on clay amount but on clay type, since it was found that biddellite clay show up the highest capacity to fix Zn (70%), followed by vermiculite (59%) and the lower by montmorillonite (55%). Clay systems containing hydrated mica with significant proportions of minerals such as kaolinite and vermiculite stabilized about 40% of added zinc, while clays consisting of mixed minerals, stabilized over 50% of applied zinc (Rahmatullah & Sandhu 1985). Moreover, colloidal components such as kaolin are the components responsible for the chemical behavior of zinc in the soil (Wang et al., 2011). Specifically, the surface of kaolin is the basis of many phenomena, in particular adsorption, which occurs at the interface of the solid solution, and is affected by properties of the soil solution such as ionic strength; PH values (Zhu, et al., 2012). Reddy and Perkin, 1974) found that kaolinite stabilizes zinc to a lesser degree than bentonite or illite due to higher CEC that contribute to the fixing of Zn more strongly, thus making it unavailable to plants.

1.2.1.5. High soil phosphorous content

Deficiency of both phosphorous (P) and zinc has been reported as one of the major constraints for plant growth, development and harvesting of optimal crop yield, with high nutritional value (Marschner, 2011). The interaction of P and Zn in the soil is often called “P-induced-Zn deficiency.” As is well known, both P and Zn are considered the two nutrient components known to have antagonism in the soil plant system (Singh et al., 2005). There is a debate about the cause of this phenomenon. Some authors assert that an excess in phosphorus can lead to a decrease for zinc (Rose et al., 2015), while others concluded that this deficiency occurs due to the ability of some phosphate fertilizers to raise the soil pH, thus increasing the availability of negatively charged compounds. They hold zinc and reduce
the amount available to plants (Carneiro et al., 2008). Another group of authors believes that excess phosphorus in soil leads to rapid growth that is not accompanied by adequate zinc absorption, resulting in lower levels of zinc resulting from the dilution effect (Ova et al., 2015). Soils rich in phosphates, both from native phosphorus and due to heavy use or prolonged use of phosphate fertilizers, can reduce the absorption of zinc by plants (Dadlich and Somani, 2007; Alloway, 2008). In this context, many researchers mentioned that higher application of P-fertilizers caused Zn deficiency symptoms in plants (Sharma et al., 1968; Clark, 1978; Loneragan et al., 1979; Singh et al., 1986). It has been found that the addition of phosphate fertilizers reduces plant zinc availability in the soil (Pongrac et al., 2019) or zinc accumulation in the roots (Nichols et al., 2012), or affects zinc absorption. By plant nutritional status P, which affects root system size, root exudate release, and dissolved transport in both xylem and phloem (White et al., 2012 &2013; Bouain et al., 2014; Zhang et al., 2016). Generally, the major Zn deficiency in crop production has been attributed to heavier phosphate fertilizer application that inhibits Zn solubility in soil as well as its translocation within plant (Robson and Pitman, 1983). However, Carrol & Loneragan (1969) reported that precipitation of Zn\(3_{\text{P}}{{O}_{4}}\) does not affect the factor responsible about with zinc deficiency induced by high phosphorus in the soil. In plant tissues, interaction between Zn and P was reported to affect Zn\(^{2+}\) uptake and detoxification in some hyper accumulator plants by the precipitation of Zn-phosphate (Zn\(_{3}\)(PO\(_4\))\(_2\)) (Küpper et al., 1999; Vollenweider et al., 2011; Adriano et al., 1971) suggested that the reason for this Zn-deficiency caused by P-Zn interaction is due to the interference of P with the absorption, transport or use of Zn. Studies of the interaction between P and Zn began in 1936 (Barnette et al., 1936), and studies of this phenomenon are still continuing to arrive at an explanation for this phenomenon (Nichols et al., 2012; White et al., 2013; Bouain et al., 2014, Zhang et al., 2016). In general, there are four possible causes responsible for zinc deficiency caused by the P and Zn reaction, which include (1) the P-Zn reaction in the soil; (2) A slower rate of zinc transfer from the roots to the shoots; (3) A slight dilution effect on zinc concentration in the plant as a result of the growth responses to phosphorous; (4) Disruption of metabolism within plant cells associated with imbalance between P and Zn (Olsen, 1972). It was reported that formation of an insoluble Zn\(_{3}\)(PO\(_4\))\(_2\) in the soil reduced the available Zn to a deficient concentration. However, these suspicions were disproved, with Aulakh & Malhi, (2005). In this context, Cakmak and Marschner (1987) indicating that Zn\(_{3}\)(PO\(_4\))\(_2\) was a good source of zinc in sorghum. Cakmak and Marschner (1987) found that high concentrations of P in plant tissues reduce the water-soluble Zn and physiological availability of Zn\(^{2+}\) and P level can be considered an indicator of zinc deficiency. Thus, it has been reported that excessive zinc accumulation does not result in phosphorous deficiency (Zhao et al., 1998).

1.2.1.6. Soil moisture (flooded/aerobic soils)

Zinc is present in soil from different sources, including plant residues, which are bound to sulfur or organic matter and are oxidizable, reducible and exchangeable. Under submerged or flooding condition, redox potential is low; and zinc in soil is more easily precipitated as zinc sulphide (ZnS), zinc carbonate or zinc hydroxides (Mikkelesen & Shiou, 1977; Kirk, 2004; Impa & Johnson-Beebout, 2012; Rehman et al., 2012). Therefore, zinc deficiency is much more common on submerged soil than on dry soil. The bioavailability of zinc in soil is mainly regulated by adsorption and absorption reactions and solubility relationships between solution and solid phases (Figure 5).

Soil properties including pH, oxidation and reduction potentials, organic matter, oxide generation and sulfur content in soil are most important factors affect the reactions of adsorption, absorption, solubility, and precipitation of zinc in the soil (Alloway, 2009). It is expected that some of these factors will change after switching to aerobic cultivation or changing the cultivated crop. For instance, rice plants grown under submerged conditions suffer from zinc deficiency in calcareous soils, while wheat grown in the same soil after rice grows naturally (Kauser et al., 1976).

The pH of the soil under submerged conditions turns to a neutral, while under aerobic conditions, it is returns to the original (Ponnamp eruma, 1972). Redox potential will increase under aerobic condition (Gao et al., 2002). This leads to the formation of iron and manganese oxides, in which zinc can be absorbed and be less available to plants. Under aerobic conditions, zinc precipitation is reduced as zinc sulfide (ZnS) (Carbonell-Barrachina et al., 2000). Switching to aerobic culture may increase the number and types of iron oxidizing / reducing bacteria (Chen et al., 2008), the soil organic matter content may decrease under aerobic conditions due to the oxidation that occurs to it and this may in turn significantly affect the concentration and profile of zinc in the soil solution. Precipitation of Zn as
zinc sulphide (ZnS) decreases under aerobic conditions (Carbonell-Barrachina et al., 2000). Gao et al., (2006, 2010) observed in field studies in calcareous soil, that shifting from flooded to aerobic, rice suffered from Zn deficiency. The cultivation shift to aerobic may also lead to an increase in the number and diversity of Fe-oxidizing/reducing bacteria (Chen et al., 2008), which may consequently affect concentration and forms of Zn in the soil solution.

Figure 5: Soil processes affecting Zn bioavailability in soil solution after; Gao et al., (2011).

Under flooding field study by Gao et al., (2010), the precipitation of ZnS was not expected because the soil redox potential never got as negative as the level suitable for the formation of ZnS. In contrast, the decreased Zn availability upon flooding in the pot study by Johnson-Beebout et al., (2009) coincided with a very low redox. They found in a pot experiment with calcareous soil that both soil-available Zn and plant Zn uptake increased with the oxidized soil compared with flooding one. This discrepancy in results could be due to the difference in soil sulfur content and achievable redox conditions in the two studies. In addition, under the submerged conditions of rice cultivation, zinc is converted into amorphous deposits or franklinite deposits; ZnFe₂O₄ (Singh & Abrol, 1986; Sajwan & Lindsay, 1988), or formed with phosphates insoluble zinc phosphate, and plant roots will not be able to absorb their zinc requirements from the soil solution and this affects plant growth and productivity.

Due to the very low availability of zinc in soil under flooding conditions, rice plants absorb most of their Zn-requirements from solubilizing Zn in the rhizosphere (Dobermann & Fairhurst, 2000). On the other hand, in a non-flooding irrigated paddy soil, the exchangeable-Zn was increased and Zn bounded to sulfurs or organic matter was decreased. Thus, non-flooding irrigation management led to more extractability, solubility and bioavailability of Zn in top surface paddy soil (Mikkelesen & Shiou, 1977). These combined observations have important implications for water management of rice on different soil types.

1.2.1.7. Soil temperature

Soil temperature effects appear to be due to the rate of Zn mineralization (Takkar & Walker, 1993). Zinc deficiency appears to have been associated with cold and wet seasons. In warm and moist soils, Zn uptake was higher in rice (Oryza sativa) than in maize (Zea mays L.) (Bauer & Lindsay, 1965). Temperatures below 16°C during growth decreased Zn availability and uptake in maize tops (Ellis et al., 1965). In addition, high light intensity and long day-lengths can cause Zn deficiency in plants (Marschner & Cakmak, 1989). Therefore, adverse climatic conditions such as drought or compaction cause Zn deficiency besides the environmental factors and soil management practices (Alloway, 2008). Zinc availability was noticed to be low under adverse climatic conditions such as drought or in compacted soils. This Zn-deficiency is common in tropical and temperate climates, but is most widespread in the Mediterranean type of climate regions (Sillanpää & Vlek, 1985).
2. Zinc in the Plants

The requirement of zinc for plant life was questioned until 1926 when Sommer and Lipman (1926; https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3648702/-bib4) showed that zinc was required for the growth and development of sunflowers and barley. This finding resulted in zinc being generally recognized as essential for higher green plants. Maze’ (Broadley et al., 2007) mentioned the essentiality of Zn in plant nutrition for the first time in year 1951. Zinc is the only metal encountered in each enzyme class: Oxoacid-reductase, transferases, hydrolases, lyases, isomerases, and ligases (Webb, 1992). In addition, it plays an important physiological role in plant metabolism by affecting the activities of hydrogenase and carbonic anhydrase, stabilization of ribosomal fractions and synthesis of cytochrome (Tisdale et al., 1984).

At the organism level, the important role of "zinc finger" as a structural component as it regulates transcription is worth mentioning (Klug, 1999; Englbrecht et al., 2004; Broadley et al., 2007). The regulation and maintenance of gene expression required to withstand environmental stresses in plants also depends on the adequacy of zinc in the plant (Cakmak, 2002). The plant enzymes activated by zinc are involved in maintenance of cellular membrane integrity, carbohydrate metabolism, protein synthesis, and regulation of auxin and pollen formation (Marschner, 2011 and Andresen, et al., 2018).

2.1. Zinc absorption, transport and accumulation

The absorption, transport, distribution and accumulation of zinc depends on the level of zinc supply of the plant, which depends on the root volume as well as mycorrhiza, which increases the surface of absorption and reduces the distance over which the zinc and other nutrients transported in the soil, and feeder canister ore (Marschner, 2011).

Seed germination and early seedling nutrition depend upon the amount of nutrient elements within seed, as seed embryo contains Zn among other nutrients to supply the early seedling growth with its need from this essential element (Lott & Spitzer, 1980). Thereafter, plant develops different mechanisms to acquire nutrients from growing media for further growth, and these mechanisms varies for different plant species (Graham et al., 1992). It was found that wheat genotypes vary in their potential to absorb and translocate zinc within the plant, and they show an altered response to Zn-deficiency, and while maize is the most cereal crops affected by zinc deficiency in soil (Moussavi-Nik et al., 1997). The conventional cereal crops synthesize more phytate compounds, resulting in higher phytate-to-Zn ratio, leading to lower Zn bioavailability for plant nutrition (Akhtar et al., 2019). Transfer of zinc to the root surface occurs mostly by diffusion, and this process is influenced by soil pH and moisture content (Rattan & Deb, 1981; Marschner, 1995). Soil alkalinity reduces zinc availability due to its absorption and / or formation of less soluble compounds. The elevation of soil pH resulted in formation of zinc hydroxide, fixation to iron oxide (FeO), chemical absorption over calcite and absorption on soil colloids (Alloway, 1995). For instance, an increase in soil pH from 5.5 to 7.0 caused 45 times decrease in concentration of Zn in the soil solution (Sarkar & Wynjones, 1982; Marschner 2011). In general, alkaline calcareous soils are deficient in Zn (> 0.5 mg kg-1 DTPA-extractable) (Alloway, 1995). As that, the accumulation of iron oxides around carbonate minerals in alkaline calcareous soils, which characterized with a pH more than 8, exacerbates the problem of Zn-deficiency in alkaline calcareous (Uygur & Rimmer, 2000).

Zinc available forms include free ions, labile Zn and soluble organic zinc complexes (Alloway, 1995). The Zn availability in the soil is greatly affected by low-to very high (>3%) OM, high carbonate/bicarbonate, persistent water logging, and high concentrations of calcium (Ca), magnesium (Mg), sodium (Na) (Lindsay, 1972). Soil and plant factors affecting Zn-availability, uptake, transportation and accumulation in grains of cereals and possible involved molecular mechanisms are illustrated in Figure (6), (Cakmak, 2004; Bashir et al., 2006).

Zinc deficiency in plants associated with total soil Zn content is defined as primary deficiency, while the deficiency due to other soil factors is classified as secondary deficiency (Sillanpää, 1982). The Zn deficiency is reported to become severe under rain fed conditions, especially in sandy soils of tropical regions due to strong leaching (Ekiz et al., 1998; Bagci et al., 2007). Soil phosphorus is another key factor that affecting the zinc availability.

Since year 1970, the interaction between phosphorus and zinc has been reported in mineral nutrition of many crops (Warnock, 1970; Marschner & Schropp, 1977; Loneragan et al., 1979); however, precise role of P is not clear yet as how it affects Zn availability and translocation from root.
to shoot (Chaudhry & Loneragan, 1970). In confirmation of this, Zhang et al., (2012) found that the heavier use of phosphorous fertilizers reduced the zinc concentration in wheat grains from 17 to 56%, while other micronutrients (iron, copper, manganese) were not affected or possibly increased. In soils with low zinc, the excessive use of phosphate fertilizers exacerbates the problem of zinc deficiency in the soil and its implications on crop growth and productivity (Drissi et al., 2015; Ova et al., 2015). Under both field and controlled conditions, P application decreased tissue Zn concentration in wheat (Zou et al., 2001; Zhang et al., 2012) and other crops (Singh et al., 1988, Broadley et al., 2010) primarily due to chemical interactions of P in the growing media (Verma and Minhas, 1987). Indeed, upon increased phosphate fertilization, an increase in plant growth occurs, which is not matched by an increase in zinc absorbed and translocated into foliage, which leads to a dilution of zinc concentration at the cellular level (Loneragan et al., 1979). This is reported in beans, wheat, cotton, flax, soybean, tomato, grapes and citrus (Cakmak and Marschner 1986; Barrow, 1987; Singh et al., 1988; Webb and Loneragan 1988 & 1990).

Figure 6: Illustrates soil and plant factors affecting zinc availability, uptake, transport and accumulation in grains of cereals and possible molecular mechanisms involved. Adopted from Cakmak et al., (2004), Bashir and Nishizawa (2006), Bashir et al., (2006)

The Zn disorder was investigated in wheat; it is binding within the root cells due to the formation of Zn phytate, the most common organic compound responsible to limit Zn translocation within plant, especially in cereals (Cakmak and Marschner 1987; Singh et al., 1988). In addition, the results exhibited that the increases in P rates caused substantial decrease in shoot and grain Zn concentrations. However, the negative effect of P was mitigated by the mycorrhizae association, which facilitated zinc uptake through an extended rooting system (Ova et al., 2015). Plant absorption of zinc is affected by the presence of arbuscular mycorrhizae (AM). The mycorrhizal association works to expand the surface area of plant roots, and to increase the root surface area of which the plant can absorb water and nutrients (Subramanian et al., 2013; Thompson et al., 2013). All plants with arbuscular mycorrhizae symbiosis showed a higher concentration of zinc (Lehmann et al., 2014). In particular, plants growing in marginal soils follow the symbiotic pathway between the plant and the mycorrhizae to acquire nutrients that slow its diffusion into the soil such as phosphate, Cu$^{2+}$ and Zn$^{2+}$(Evans & Miller 1988; Sylvia et al., 1993; Watts Williams et al., 2013).

The symbiosis of the plant and the mycorrhizae improves root morphology, facilitates absorption of nutrients and enables the host plant to withstand seasonal stress (Subramanian et al., 2008). Synthesis of zinc phosphate in root apoplastic cells may be another reason for zinc fixation and for the unequal distribution of zinc within the root and shoots (Youngdahl et al., 1977; Cakmak & Marschner, 1987). The Zn$^{65}$ labeling technique was used to highlight the role of P levels in the unequal distribution of zinc at root and shoots. Results revealed that, elevated P tissues have been reported to reduce water-soluble
zinc, causing a decrease in zinc availability at the physiological level (Rahimi & Schropp, 1984; Cakmak & Marschner 1987). That is why the high phosphorous content of plants is considered an additional stress factor that may exacerbate the feeding disorder in plants, especially zinc (Loneragan et al., 1982; Cakmak & Marschner, 1986; Webb & Loneragan, 1988). A higher root-to-stem ratio represents a greater decrease in shoot growth compared to the root, which is typical evidence of P deficiency (Cakmak et al., 1994; Watts-Williams et al., 2013 and 2014). Under such conditions, P application may boost shoot growth and resulted in Zn dilution. However, this phenomenon is not deemed as the only mechanism responsible for negative effects of higher P application on tissue Zn concentration (Lambert et al., 1979; Loneragan et al., 1979; Singh et al., 1988; Zhang et al., 2012).

The decrease in the mycorrhizae proliferation when phosphorous was used is also the cause of the decreased absorption and accumulation of zinc by crops (Teng et al., 2013). In another study, zinc accumulation in wheat decreased with the addition of phosphorus up to 100 kg ha⁻¹ in alkaline limestone soils. However, improvement of zinc absorption was observed with mycorrhizae inoculation (Zhang et al., 2016). In addition, root-induced changes in soil pH and release low and high molecular weight exudates, which play an important role in increasing the availability of zinc in the soil and making it available for absorption by the crops grown on soils of low Zn. Also, roots induced acidification through Fe oxidation and cation-anion intake imbalance causes a release of zinc from these soluble fractions so that the zinc is ready to taken up by rice plants which, might be often depend on this solubilization process for the bulk of their Zn need (Kirk and Bajita, 1995). In lowland rice, rhizosphere acidification can enhance the utilization of not only P but also zinc (Kirk and Saleque, 2005).

Excretion of organic acids or phytosiderophores that are able to increase the bioavailability of zinc in the root zone is another mechanism for reducing zinc deficiency in lowland rice. The changes in the pH in the rhizosphere are the result of the roots secretion of protons (H⁺) and hydroxyl (OH⁻) or bicarbonate ions (HCO₃⁻) due to the cationic imbalance in the plant, the development of carbon dioxide through respiration, and the secretion of low molecular weight organic acids (LMWOAs).

The form of nitrogen supply has the most prominent effect on the cation/anion uptake ratio and, consequently, on the pH of the soil surrounding the roots (Marschner, 2011). As rice is grown in anaerobic soils, this can lead to the release of O²⁻ ions from the roots and this leads to increased H⁺ protons release, which reduces the soil pH and increases the bioavailability of zinc to plants (Kirk and Bajita, 1995). Also, rice roots taken up nitrogen primarily as NH₄⁺, resulting in a release of H⁺ by roots and a consequent decrease in rhizosphere pH and then increased Zn-availability. On the other hand, in the case of aerobic rice cultivation, the shift of the dominant N-uptake form from NH₄ to NO₃⁻ is expected to lead to exudation of OH⁻ into the rhizosphere resulting in an increase in rhizosphere pH with a subsequent reduction in Zn availability.

Generally, rice plants absorb most of their zinc needs from the soluble in the rhizosphere because the amount of available Zn in soil is very low under flooding condition (Dobermann & Fairhurst, 2000). The shift in rhizosphere pH because of changing N dynamics may be the cause of the observed reduction in Zn uptake in rice grown in aerobic fields compared to anaerobic flooded calcareous soils (Gao et al., 2006). Under Zn deficiency, lowland rice increased citric acid and citrate exudation and the citrate exudation capacity of different rice genotypes found to be related to their tolerance to Zn deficiency (Hoffland et al., 2006).

2.2. Zinc functions in the plants:

The optimum growth and productivity of crops in general is maintained through adequate intake of zinc in its bivalent form (Zn²⁺), which performs many important functions in plants,

- As an essential nutrient for all organisms for the activation of many enzymes in plant cells, such as alcohol dehydrogenase, carbonic anhydrase, and RNA polymerase (McCall, 2000; Castillo-González et al., 2018).
- Zn is involved in the metabolism of RNA and ribosomal content in plant cells that stimulate carbohydrate, protein and DNA synthesis (Memon et al., 2017; Mohamed et al., 2019).
- In addition, zinc is an essential component of the many enzymes such as oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases (Webb, 1992). Zinc is also required for the manufacture of carbonic anhydrase, a zinc-containing metallo enzyme, which plays a vital role in photosynthesis processes, due to its property to convert CO₂ to HCO₃⁻ reversibly (Bhat et al., 2017).
Zinc is also required for the manufacture of amino acid tryptophan, which is a precursor of a hormone auxin (IAA), the essential hormone for growth, which acts as a catalyst for growth (Amberger, 1982; Brown et al., 1993; Alloway, 2004; Brennan, 2005; Lin et al., 2005; Hänsch & Mendel, 2009).

Zn is required to form nucleic acids, proteins, pollen formation, fertilization and germination (Marschner 2011; Hegazy et al., 2016). Zinc is also involved in the formation of Rubisco, along with several biochemical reactions being activated in photosynthesis, metabolism of carbohydrates, and lipid and nucleic acid synthesis (Brown et al., 1993; Alloway, 2004; Tsonko and Lidon, 2012; Kisko et al., 2015; Samreen et al., 2017).

Zinc regulates the pH of chloroplasts and protects stromal enzymes from denaturation during rapid and drastic changes in lighting conditions (Bhat et al., 2017).

Under Zn-deficient conditions, plant growth is inhibited due to formation of reactive oxygen species (ROS), which are considered the primary factor responsible for that (Cakmak, 2000).

It plays an important role in managing reactive oxygen species (ROS) and protecting plant cell from oxidative stress, as well as regulating stomatal function by means of regulation of potassium content in plant cells (Alscher et al., 1997; Cakmak, 2000; Amiri et al., 2016; Samreen et al., 2017; Venkatachalam et al., 2017).

In the thylakoid lamellae, Zn reduces the production of toxic hydroxyl radicals in Haber–Weiss reactions because the high affinity of Zn with cysteine and histidine (Cakmak 2000; Alloway, 2004; Brennan 2005; Disante et al., 2010; Tsonko and Lidon, 2012).

In general, plants with zinc deficiency are more susceptible to disease and oxidation, and the presence of zinc in SOD and CAT acts as an aid protecting the plant from oxidative stress, and acts as a defense mechanism against harmful pathogens. (Grewal et al., 1996; Streeter et al., 2001; Marschner, 2011; Helfenstein et al., 2015). Zinc plays an important role in the production of oxygen radicals and eliminating their toxicity. Zinc contributes to the synthesis of Cu-Zn-SOD enzyme, which is a major enzyme involved in removing toxic O$_2^\cdot$ radicals, which can be harmful to membrane lipids and proteins (Robson, et al., 2012; Castillo-González et al., 2018). Zinc is essential for the integrity of cellular membranes and contributes to the maintenance of membranes and ion transport systems. This is through its interaction with phospholipids and sulphydryl groups of membrane proteins (Cakmak, 2002; Alloway, 2004; Dang et al., 2010; Disante et al., 2010; Kabata-Pendias and Pendias, 2001, Robson, et al., 2012). Zn-finger transcription factors are involved in the development and function of flower tissues such as anthers, tapetum, pollen and pistil secretory tissues, and it is likely that VvZIP3 plays a major role in natural flowering and fruit growth (Sharma, et al., 1987; Kobayashi et al., 1998). Zinc seems to affect the plant capacity to uptake and transport water and reduces the adverse effects of heat and salt stresses (Barceló and Poschenrieder 1990; Kasim, 2007; Disante et al., 2010; Peck and McDonald, 2010; Tavallali et al., 2010; Tsonko and Lidon, 2012).  

2.3. Zinc deficiency in the plants

Marschner (2011) reported that adequate zinc concentrations required for normal growth and optimum yields for most crops ranged between 15-20 mg kg$^{-1}$ dry weights. Zinc deficiency occurs below this level as has been reported in many research works (Skoog, 1940; Alloway, 2004; Disante et al., 2010). Zinc deficiency occurs when the plant is unable to take in sufficient amounts of this essential element from its growth medium. Zinc deficiency leads to abnormalities in plants, which become visible as symptoms of deficiency such as stunted growth, chlorosis and young leaves, and sterility of spikelets. Skoog (1940) observed disturbances in stem elongation in tomatoes due to zinc deficiency. Zn 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 (Marschner, 1995 and 2011). Zinc deficiency can negatively affect the quality of the harvested products; as it increases susceptibility to infection with fungal diseases and resulting damage due to higher light intensity or temperature and (Marschner, 1995 and 2011).

The symptoms exhibited by plant suffering deficiencies of certain other essential nutrient elements are, in some cases, similar to those of zinc deficiency and may be confused with those of zinc or be seen together with the zinc deficiency symptoms where multiple micronutrient deficiencies occur (Cakmak and Hoffland, 2012). Zinc deficiency in plants can be increased or decreased with nitrogen
fertilization due to the role nitrogen in promoting plant growth and, to its role, in changing the pH in the root environment (Alloway, 2004). Since ammonium-N ions in soil have an acidic effect, the use of \( \text{ZnSO}_4 \) with simultaneous dressings of ammonium-N fertilizers was found to be effective in treating zinc deficiency compared to using \( \text{ZnSO}_4 \) alone (Viets et al., 1957).

The heavier application of phosphorous fertilizers can reduce the availability of zinc in the soil (Pongrac et al., 2019) or the accumulation of zinc in the roots (Nichols et al., 2012), or affect the absorption of zinc through the nutritional status of the plant P, which affects the growth of Roots, root growth, and dissolved transport in both xylem and phloem (White et al., 2012; White et al., 2013; Bouain et al., 2014, Zhang et al., 2016). It was found that plants growing in soil rich in phosphorous or fertilized with large quantities of phosphate fertilizers suffer from zinc deficiency. The reason for this deficiency is due to the P-Zn antagonism relationship that leads to P reduces zinc absorption, transport or use (Adriano et al., 1971; Clark, 1978; Singh et al., 1986). Calcium was found in a short-term study conducted by (Chaudhry and Loneragan, 1972) to reduce Zn absorption. In legumes, it was noticed that zinc concentrations progressively decreased with increasing Ca concentrations in growing medium (Bell et al., 1990). Zinc deficiency in rice causes multiple symptoms that usually appear two to three weeks after planting rice seedlings, with brown spots and streaks that may merge to completely cover old leaves, and plants remain stunted, while in severe cases, plants may die, while those who recover they will show a significant delay in ripening and a decrease in yield (Yoshida and Tanaka, 1969; Van Breemen and Castro, 1980; Neue and Lantin, 1994).

Several authors (Kauser et al., 1976; Safaya, 1976; Zhang et al., 1991; Loneragan and Webb, 1993; Noevell and Welch, 1993) have reported the interaction between zinc and other micronutrients. A strong Cu-Zn antagonism relation has been observed in wheat growing on soils deficient in Cu and Zn (Kauser et al., 1976). Cu and Zn might interact in several ways, Cu competitively inhibits Zn absorption and affects the redistribution of Zn within plants, and Zn strongly depresses Cu absorption (Loneragan and Webb, 1993). The interaction between Zn and Fe is also a complex process. The increased application of Zn had a little effect or decreased Fe concentrations in the shoot of plants (Safaya, 1976; Noevell and Welch, 1993). In the same way, higher levels of iron generally have an inhibitory effect on zinc concentration in plant tissues (Zhang et al., 1991).

Crops that respond to zinc differ in their requirement from this essential element to complete their life cycle (Marschner, 2011). The expected response of different crops when grown in a deficient soil to zinc is illustrated in Table 3.

Table 3: Potential for a crop response to zinc when applied to zinc deficient soils.

| Large response to Zn | Moderate response to Zn | Small response to Zn |
|---------------------|-------------------------|---------------------|
| Apple, dry edible beans, corn, onion, snap bean, sweet corn | Grape, lettuce, potato, soybean, tomato | Alfalfa, asparagus, barley, canola, carrot, clovers, grass pasture, oat, peas, rye, sugar beet, sunflower, wheat |

2.3.1 Types of Zn-deficiency Symptoms

The different types of Zn-deficiency symptom in plants are summarized by Skoog 1940); Weir and Cresswell, 1993; Weir et al., 1995; Alloway, 2008 and Rudani et al., 2018) as follows:

**Chlorosis:** This is a change in the color of the leaf from a regular chlorophyll green color to a pale green and yellow, or even white in some cases. Chlorosis appears between the ribs of grains and herbs (monocotyledons) and between the veins of plants with broad leaves (dicotyledons) and this is referred to as inter-venous. Young leaves are the most affected by Zn-deficiency, but in some cases, both old and new leaves are chlorotic.

**Necrotic spots on leaves:** These occur in areas of chlorosis due to the death of leaf tissue on areas of chlorosis.

**Bronzing of leaves:** Color of chlorotic areas may turn to bronze.

**Rosetting of leaves:** Zinc-deficient in dicotyledons often have shortened internodes, so the leaves cluster on the stem to take a flower shape.

**Stunting of plants:** Stunted plants may occur because of reduced internode elongation or reduction in plant growth.

**Dwarf leaves ('little leaf'):** Small leaves that often show chlorosis, necrotic spots or bronzing,
Malformed leaves: leaves are often narrower or have wavy margins.

Some visual symptoms on leaves of some crops towards Zn deficiency could be summarized as in Figure (6; A-F):

A: Wheat plant showing Chlorosis and necrotic patches on the leaves
B: Sugar cane showing distinctive interveinal chlorosis on the leaves.
C: Oil seed rape plant showing small thickened leaves with bleached patches
D: Cotton leaves showing large areas of interveinal chlorosis.
E: Soya bean showing interveinal chlorosis and bronzing of the lower leaves.
F: Apple plant showing shortened internodes giving a rosette appearance

Photos courtesy: IPNI, IANR and Yara-Phosyn.

Fig. 6: Zn-deficiency symptoms in some crops
- In Wheat: plants showing Chlorosis and necrotic spots on the leaves, (Fig. 6A),
- In Sugar cane: plants showing distinctive interveinal chlorosis on the leaves (Fig. 6B),
- In Oil seed rape: plants showing small thickened leaves with bleached patches (Fig. 6C), In Cotton: leaves showing large areas of interveinal chlorosis (Fig. 6D),
- In Soybean: leaves showing interveinal chlorosis and bronzing of the lower leaves. The symptoms of Zn deficiency in soybean appear first on older and/or fully expanded leaves as pale green plants (Fig. 6E),
- In Apple: plants showing shortened internodes giving a rosette appearance (Fig. 6F).

2.4. Zinc toxicity in the plants:

It is rare for zinc toxicity to occur in plants, unless it has been reported in some crops. Jain et al., (2013), have reported sensitivity of soya bean, sweet potato and rice towards toxic Zn concentration. Spinach as edible leafy vegetable crops tends to accumulate high Zn-concentrations in their leaves (Boawn and Rasmussen, 1971; McKenna et al., 1993). Normally, toxicity of Zn has been reported on acid soils, which have high Zn-content or in soils over fertilized with zinc (O'Sullivan et al., 1997). Zinc is also present in some fungicides, and may accumulate if there is excessive use of such fungicides. When soil contains high concentrations of zinc, it becomes toxic and its toxic effects depend on the bioavailability of Zn, exposure time, plant genotype, and plant development stage. Zinc toxicity may cause severe growth reduction or prevent the establishment of transplanted cuttings of sweet potato. In solution culture experiments, Zn concentration above 10 µM in the root medium decreased sweet potato growth. At 50 µM Zn, dark red-brown pigmentation were develops, especially near veins on older leaves (Figure 7 A & B), growth was completely stopped (Figure 7 A), and death of roots was evident (O’Sullivan, et al., 1997).

Young leaf chlorosis induced by zinc toxicity may be due to reduced absorption of Fe2 + and Fe3 +, and, in some cases, could lead to cell death (Sturikova et al., 2018). The growth retardant is the result of inhibition of mitosis, as reported in (Jain et al., 2010 and Reis et al., 2018). They reported that excess zinc leads to a significant decrease in the mitotic index of Saccharum spp. and Triticum aestivum L, respectively. This decrease in mitotic activity could be due to inhibition of DNA synthesis, given
that zinc plays an important biological role in DNA synthesis (Memon et al., 2017; Mohamed et al., 2019). In *A. thaliana*, treatment with zinc concentrations higher than 0.1 zinc became toxic (Jain et al., 2013). Whereas when leaves are exposed to a high level of zinc (i.e. higher than 20 mg Kg\(^{-1}\) Zn), many abnormal functions have been observed in the plant. This level of toxicity degrades the leaf tissue and at the same time lowers the productivity of the plant by making its growth stagnant.

Zinc plays an important role in the production of oxygen roots in addition to removing toxins from them. The enzyme Cu-Zn-SOD is essentially localized in chloroplasts; in some plants, it is found in the thylakoid lumen whereas in others it is bound to the thylakoid (Rao and Chaitanya, 2016). Zn participates in the synthesis of Cu-Zn-SOD enzyme, a key enzyme involved in the removal of toxic O\(^{-2}\) radicals, which can be harmful to membrane lipids and proteins (Castillo-González et al., 2018; Robson, et al., 2012). At high zinc concentrations, it becomes toxic; however, when zinc-tolerant plants are exposed to toxic levels of zinc, they accumulate zinc in the cells of their root cortex and in the leaves, specifically in the cell walls or vacuoles (Robson, 1994). Yellowing and inhibition of young leaf growth are two of the most frequently identified manifestations of zinc toxicity, possibly due to reduced absorption of Fe\(^{2+}\) and Fe\(^{3+}\), and may in some cases lead to cell death (Sturikova et al., 2018). Phosphorous can be used to reduce the toxic effect of zinc excess since the interaction between Zn and P in plant tissues leads to zinc precipitation and reduces its toxic effect (Cakmak and Marschner 1987; Küpper et al., 1999 and Vollenweider et al., 2011). However, it was reported that high Zn concentration in Zn-hyper accumulator plants did not induce P-deficiency (Zhao et al., 1998).

2.4.1. Effect of excess-Zn on seed germination

Seed germination is greatly influenced by seed content and the availability of zinc in the growing medium and this effect mainly depends on the plant species (Balafrej et al., 2020). The results of several studies revealed that excess zinc concentration in the growing medium significantly reduced the germination of several plants (Marichali et al., 2014; Gokak & Taranath 2015; Zhi et al., 2015; Ivanov et al., 2016; Marichali et al., 2016). For example, Basha & Selvaraju, 2015; Gupta et al., 2016; Nanda & Agrawal, 2016; Bae et al., 2017) reported that high Zn-concentrations considerably reduce the germination of *Vigna unguiculata*, *Cassia angustifolia*, and *Glycine max*.

2.4.2. Effect of excess- Zn on roots development:

Plant roots are an important part affecting the bioavailability of the soil’s indigenous and exogenous Zn. It is well known that roots interact with the rhizosphere and causes several modifications in the rhizospheric soil proprieties, as the pH, microbial activity, chemical equilibrium, mobility, and
Zn-bioavailability (Clemente, 2010; Seshadri et al., 2015). Such modifications are induced by root exudates that affect the nutrients and metal availability. Root exudates are released in the soil by root cells, including low molecular weight compounds (phenolic compounds, amino acids, organic acids, and sugars) and compounds of high molecular weight (polysaccharides and proteins) (Chen et al., 2017; Hou et al., 2017). In Arabidopsis halleri, (Tsednee et al., 2014), observed that roots release nicotianamine (NA), a main chelator, which has a beneficial effect on improving Zn’s solubility and thus Zn availability and uptake. In Hordeum vulgar, Lolium perenne L., and different dicots species, roots produce organic compounds, which form complexes with Zn, thus promoting its solubility, and mobility and availability (Wei-Hong et al., 2007; Degryse et al., 2008; Versieren et al., 2014).

In addition, exposure of the roots to excess Zn caused major alterations in the architecture of their roots (Disante et al., 2014). In fact, several studies revealed that plants exposed to high concentrations of heavy metals exhibited changes in their root morphology and developed more root branching with marked curvature and higher branching ratio in the area of contact with the metal (Bochicchio et al., 2015; Emanverdian et al., 2015; Küpper & Andresen, 2016; Mustafa & Komatsu, 2016). The suppression of root elongation due to excess Zn has been explained by the loss of cell root tips viability, inhibition of cell proliferation and subsequent elongation (Marichali, et al., 2016 and Li et al., 2020). In Senna multijuga and Erythrina crista-galli, it was noticed that high concentration of zinc in the soil induced a linear decrease of the root-specific superficial area, and reduces their capacity for water and nutrient absorption (Scheid et al., 2017). In Beta vulgaris L., Zn-excess in growing media induces a reduction in the root growth, displaying a brown color with short lateral roots and arrested metabolism processes in the roots (Sagardoy et al., 2011). In several plant species, roots are commonly generated hydrogen peroxide (H$_2$O$_2$) and superoxide anion (O$_2^-$) as reactive oxygen species (ROS), when exposed to excess Zn in growing media (Miller et al., 2007 and Anwaar et al., 2015), which leads to disassembly of the thylakoids (Li et al., 2013).

2.4.3. Effect of excess-Zn on plant shoots

Photosynthesis processes and consequently plant growth is one of the mechanisms that affected by zinc toxicity (Khan & Khan, 2014). For example, in Solanum lycopersicium, toxic Zn-concentration (43 ppm) caused leaf chlorosis and negatively reduced plant growth due to its adverse on photosynthetic electron transport, loss of plasma membrane integrity, and a decrease of bio-membrane permeability, which result in photosynthesis impairment (Monnet et al., 2001; Cambrollé et al., 2012; Vijayarengan & Mahalakshmi, 2013). Linked with lack of photosynthetic activity in plant foliage, reactive oxygen species (ROS), such as O$_2^-$ or H$_2$O$_2$ are generated, which leads to disassembly of the thylakoids (Azzarello et al., 2012; Li et al., 2013). Beta vulgaris L. plants grown with excess zinc showed symptoms of stress such as rolling the edges of leaves inward and reduced overall metabolism due to reduced photosynthetic efficiency (PSII) (Sagardoy et al., 2011). Zinc stress reduces the rate of photosynthesis and induces the generation of reactive oxygen species (Li et al., 2013), by catalyzing ROS-producing enzymes, such as nicotinamide Adenine Dinucleotide Phosphate Hydrogen Oxidases (NADPH), to replace the basic cations from specific enzyme binding sites, Or inhibit enzyme activities (Hussain et al., 2013). This can lead to lipid oxidation, protein impairment, enzyme inactivation, and DNA damage (Miller et al., 2007). Proline accumulation in the aerial parts of plants is a widespread process among higher plants in response to excess zinc and other heavy metal stresses. It is hypothesized that proline increases plant tolerance to heavy metal stress through several mechanisms, such as (1) osmoregulation, (2) stabilization of protein synthesis, and (3) enzyme protection against denaturation (Tripathi & Gaur, 2004). In addition, proline accumulation has been shown to alleviate metal-induced oxidative stress by cleaning up toxic ROS (Michael & Krishnaswamy, 2011).

3. Zinc in human health

The importance of zinc in the nutrition of higher animals was reported in 1919 by Birckner when he discovered the presence of zinc in egg yolks as well as in cow and human milk, and from here it was inferred that the element zinc has an important nutritional function, and considered an essential element in human nutrition (White and Broadley, 2005; Graham et al., 2012). At year 1963, only three enzymes were known that required zinc for their activities, but now >300 enzymes and >1000 transcription factors are known to require zinc for their normal activities (Anderson et al., 2001; Barnett et al., 2010; Prasad, 2017). Zinc is also essential for tissue growth, wound healing, taste acuteness, connective tissue
growth and maintenance, immune system function, prostaglandin production, odor, vision, taste and appetite, healthy skin growth, mineralization of bones, hair and nails, proper thyroid function, blood clotting, and cognitive functions, cell division, sperm production, protein and DNA synthesis, and embryo development (Bhowmik et al., 2010). Zinc in the human body interacts with a large number of enzymes and proteins, and around 3,000 protein and 300 enzymes are Zn-dependent (Anderson et al., 2001; Andreini et al., 2006; Barnett et al., 2010; Krezel & Maret, 2016). It plays an important structural, functional and regulatory role, activates cellular metabolism and stimulates the immune system (Lukaski, 2004; Morley, 2004; Bonaventura et al., 2015). Zn is necessary element for proper human growth and development during, especially childhood, adolescence, and pregnancy. It has been estimated that one-third of the world’s population lack sufficient Zn for adequate nutrition, and to be at risk of Zn deficiency, which is especially prevalent in children under 5 years age, due to their relatively large demand for Zn to support growth and development requirement from this element (Wessells & Brown, 2012). Zinc remains a serious health problem in developing countries, mainly due to insufficient dietary zinc intake. The reason for this is the dependence of the population on cereal-based foods with small Zn concentrations, which cannot meet the human need for this vital element. Because, most modern cereal varieties naturally contain very small concentrations of zinc (Cakmak and Kutman, 2017). In addition, approximately 50% of wheat-cultivated soils globally are poor in bio-available-Zn. The major factor contributing to deficiency of zinc in human is high phytate-containing cereal protein intake, especially in the developing countries, and nearly 2 billion of the world’s population may be subjected to zinc deficient (Prasad, 2017). As well, every year, about half a million children under the age of five die from diseases associated with zinc deficiency (Stein et al., 2005; Black et al., 2008; Krebs et al., 2014).

Daily intake of zinc is important for humans because the mammalian body has a limited potential to store zinc, and the daily requirement of humans for zinc varies according to gender and physiological stage (Hambridge and Krebs, 2001). According to the National Institute of Health Office of Dietary Supplements, recommended dietary allowance (RDAs) for Zn are 2-3 mg day\(^{-1}\) in infants, 5 mg day\(^{-1}\) in children, 8-11 mg day\(^{-1}\) in adolescents and adults, and 11-13 mg day\(^{-1}\) for pregnant and lactating women (Table 4). The US adequate-Zn intake or what is called “Recommended Daily Allowance” (RDAs) is 8.0–13.0 mg day\(^{-1}\) and the UK guidance daily “Reference Nutrient Intake” (RNI) is 7.0–13.0 mg day\(^{-1}\) for adults (Department of Health (UK), 1991; Institute of Medicine (USA), 2001; FAO/WHO, 2002; Hotz & Brown, 2004).

Table 4: Recommended Dietary Allowances (RDAS) of Zinc for human (mg day\(^{-1}\))

| Age      | Male | Female | Pregnancy | Lactation |
|----------|------|--------|-----------|-----------|
| 0-6 months | 2 mg* | 2 mg* |           |           |
| 7-12 months | 3 mg  | 3 mg  |           |           |
| 1-3 years  | 3 mg  | 3 mg  |           |           |
| 4-8 years  | 5 mg  | 5 mg  |           |           |
| 9-13 years | 8 mg  | 8 mg  |           |           |
| 14-18 years| 11 mg | 9 mg  | 12 mg     | 13 mg     |
| 19+ years  | 11 mg | 8 mg  | 11 mg     | 12 mg     |

*Adequate Intake (AI)

Source: Institute of Medicine, Food and Nutrition Board, Washington, DC: National Academy Press, (2001).

3.1. Zinc deficiency in human

Unfortunately, the diets of many people around the world lead to a deficiency of zinc in their diet (White and Broadley, 2009; Bouis and Welch, 2010; Stein, 2010; Sayre et al., 2011). This is due to the sourcing of food products from lands that are poor in zinc, which leads to the consumption of products containing low Zn concentrations. It is estimated that nearly a third of the world’s population consumes less zinc compared to the US RDAs and that zinc deficiency contributes to 1.9 percent % of the total burden of disease from major health hazards worldwide (WHO, 2002; Hotz and Brown, 2004). This has considerable socio-economic negative impacts (Solomons, 2000; Stein, 2010). Zinc deficiency is recognized as one of the major nutrient disorders in human nutrition and is more marked in children (Boonchuay et al., 2013), and in developing countries (Darton-Hill et al., 2005; Stein, 2014). Zinc
deficiency is associated with a wide range of illnesses and diseases in humans (Black et al., 2008; Gibson, 2012; Krebs et al., 2014; Gibson, 2015; Terrin et al., 2015), including stunted growth (more severe in children), impaired immune system function (Prasad, 2009; Barnett et al., 2010), cancer (Hotez and Brown, 2004), susceptibility to infectious diseases, iron deficiency anemia, poor birth outcomes in pregnant women (Prasad, 2009; Graham et al., 2012), severe dermatitis in children (Fig. 8ab), hair loss (Fig. 8c), white spots on nails (Fig. 8d), change in hair color from black to reddish brown (Maret and Sandstead, 2006), skin problems, weak body muscles, pneumonia in children (Stein et al., 2005; Das and Green, 2013), and changes in neuro-sensory (abnormal taste sensation) and delayed wound healing (Prasad, 1998). High rates of morbidity and death from diarrhea, pneumonia, and skin infections in children can also occur from food-related illnesses, as seen in developing countries (Darton-Hill et al., 2005; Stein, 2014), and can lead to infertility in men (Hafeez et al., 2013). Another adverse clinical effect of zinc deficiency in human is impairment of cognitive function (memory loss), increased oxidative stress, and regularity of inflammatory cytokines (Prasad, 2017). Poor zinc homeostasis is associated blood sugar disease; in both type 1 and type 2 diabetes (Janson et al., 2009; Chen et al., 2000; Anderson et al., 2001; Simon and Taylor, 2001; Wijesekara et al., 2009 and Foster and Samman, 2010), as zincuria is one of the symptoms of diabetes (McNair, 1981; Cunningham et al., 1994; Wijesekara et al., 2009). Lymphocyte proliferation is also affected by zinc deficiency due to zinc being involved in DNA synthesis and cell division. Tymulin, a hormone involved in the maturation of T lymphocytes and zinc plays an important role in its formation, and thus is adversely affected by Zn- deficiency (Prasad, 1995). Zinc deficiency impairs brain function (Maret and Sandstead, 2006). In view of global COVID-19 Pandemic, potential protective effect of Zn is of particular interest. It is considered as potential supportive treatment in the therapy of COVID-19 infection due to its immune modulatory antiviral property, as well as its ability to regulate the inflammatory response as well as direct antiviral effect (Zhang and Liu, 2020).

![Figure 8: Zinc deficiency symptoms in human](Source: Allnutriments.blogspot.com (2012))

Conclusion and outlook

Zinc is an important micronutrient required for normal growth and development of plant and human, since all living organisms need zinc to survive. Millions of hectares of cropland are affected by Zn deficiency, especially in rice and wheat in arid and semi-arid regions having alkaline calcareous nature of soils, and approximately one-third of the world’s population suffers from an inadequate intake of Zn. All living organisms required zinc to survive and to complete their life cycle. Therefore, Zinc is an important nutritional micronutrient for normal growth and development of plant and human. Ensuring adequate zinc intake by the plants is a key component of efforts to increase crop yield and quality, improve nutritional value and maintain human health, especially in developing countries. Therefore, plants require a necessary and continuous supply of zinc throughout their entire growth phases to achieve optimum productivity. Basic knowledge of the amount and dynamics of zinc (Zn) in soil, water and plants is an important and priority research topic, especially in areas where zinc deficiency is prevalent such as arid and semi-arid regions in developing countries in order to achieve sustainable solutions to the problem of zinc deficiency in crops and people. Low genetic potential of existing cereal crop cultivars to uptake and accumulate Zn in grains is a major limitation factor for crop production and human health. To overcome the Zn deficiency problem in plant and human, future way forward
demands extensive research in fields of nutrient cycling and zinc fluxes in soil–plant systems using modified techniques/application methods, agronomic practices, exploration of new nutrient sources including inorganic as well as develop new cultivars with improved nutrient use efficiency. The potential of zinc bio-fortification as an additional feature of the already existing demands related to yield, quality, insect / pest resistance, etc. is an important process for raising plant zinc levels. In addition, understanding the mechanisms of zinc accumulation in Zn hyper accumulators plants will greatly contribute to breeding and engineering new species of staple crops that have the required zinc concentrations.

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