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A review on Distribution and mobility of Zinc in soil under climate change scenario

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ABSTRACT

Zinc (Zn) is one of the most critical plant nutrients in soil, among 17 essential plant nutrients. The activities of Zn in soil depend on different soil characteristics, parent material, climatic conditions, and cropping systems (vegetation). The distribution of Zn decreases with an increase in sandy soils, increasing pH or lime content with depth, mounting soil moisture regime, and being low in organic matter. In general, the solubility of Zn is highest in soil reactions of 4.5 to 6.0 in organic soils and 5 to 7 in mineral soils. Soil reaction and organic matter level regulate the behavior of zinc and the plant pools available. The formation of dissoluble stable organic-metal complexes and organo-metal complexes through the organic substance plays role in the availability of Zn. Adsorption and desorption are the critical processes in soil that regulate the behavior of Zn in soil and act as a division between the solution and solid phases. Zinc is released from soil minerals or added through organic and inorganic fertilizers, and equilibrium reactions become operative between the solution and the exchangeable phase of the soil. The application of the organic amendment will decrease the potential for leaching. The adsorption, desorption, and equilibrium behavior of Zn in soil are affected by soil reactions, organic sources, cation exchange capacity, clay content, and Fe/Al oxides.

Keywords: *Adsorption, Mobility, Desorption, Zinc, Distribution, Soil mineral, organic amendment.*

Introduction

Hidden hunger and malnutrition are both involved in the human body and might be caused by a short supply of micronutrients. The deficiency of micronutrients is a foremost threat to human health [8]. Interest in micronutrients has increased rapidly within the last decade because of recent research demonstrating that they play significant roles in plant disease resistance and root-stress resistance as plant foods are important sources of these micronutrients for animals [57; 94;62]. India ranked 107 among 121 nations on the Global Hunger Index (GHI) basis in 2021, mainly due to micronutrient deficiencies. The issues of malnutrition can be addressed through suitable micronutrient interventions [60]. Fighting micronutrient malnutrition has been notorious as a basic component of three of the eight Millennium Development Goals of the General Assembly of the United Nations, aimed at alleviating the world's gravest health and poverty issues [93]. In this circumstance, it is essential to focus on reducing micronutrient starvation by correcting deficiencies in soils and crops and enhancing nutrient content in edible plant parts.

Among all the micronutrients, zinc is one of the most important elements for maintaining good health and happiness in humans. Its deficiency can cause serious health issues as it is an essential nutrient for life and is required for proper metabolic functions [3]. Approximately 17% of the worlds population faces the problem of malnutrition due to a deficiency of zinc [71]. Supplementation with zinc promotes proper crop nutrition and human health. Malnutrition can be reduced by supplying zinc-enriched foods [39;97].

In India, Zn is now considered the 4th most essential yield-limiting nutrient in cultivated land. The zinc deficit in Indian soils is likely to increase from 49 to 63% by 2025, as most of the marginal soils are showing a zinc shortage [83]. Zinc is essential for soil, plants, and animals as involved in physiological and nutritional functions [18]. Zn plays numerous roles in the function of plants and is measured as an essential micronutrient [41;31;5]. Zn is an essential micronutrient that helps in the formation of tryptophan, a precursor of indole acetic acid responsible for growth stimulus [54]. it is requisite for several enzyme systems and the synthesis of auxin [6;11] and it plays a key role in the synthesis of the carbonic anhydrase (CA) enzyme, which helps in the transport of carbon dioxide in photosynthesis [5]. The lack of micronutrients is an extended nutritional imbalance constraining crop production in many cultivated lands around the world [72]. Around 1 to 3 % of cultivated land has low zinc availability levels for suitable crop production [19;4;21].

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Zn deficiency is found to be fifth among the causes of mortality and disease in developing countries [101]. It is a micronutrient disorder in cereal crops that reduces nutritional quality and yields. Worldwide, about 50% of cereal plants are cultivated on soils with low zinc availability [4]. Now, increasing zinc availability in edible plant parts is a strategic aim in agriculture [23;21;100]. The concentration of Zn in soil depends on its type. For uncontaminated soils, the amount of Zn concentration ranges from 17 ppm to 125 ppm, and the average amount is about 64 ppm in worldwide soils [43]. However, higher mean Zn concentrations have been recorded in Solonchaks, alluvial, and Rendzine soils, and lower mean Zn concentrations have been reported in light organic and mineral soils [43]. Alloway stated that soils that contain less than 10 ppm concentrations of Zn are considered to be Zn-deficient soils, and more than 200 ppm concentrations of Zn are considered to be contaminated from dissimilar sources[4]. The movement and availability of zinc from soil solution to plant roots can be evaluated through the available Zn amount, soil pH, soil texture, soil temperature and moisture, soil organic matter, soil microbial activity, root exudates, etc.

Zinc in the soil

The substance of zinc in the soil depends on the geochemical and petrochemicalweathering processes. Moreover, it also depends on the mineralogical composition of the parent material, soil mineralogy, and the total amount of Zn present in the [58], especially the concentration of quartz [50]. It is dependent on the intensity of weathering, climate, and other predominating factors during the process of soil formation. Zn is found in numerous minerals such as sphalerite (ZnS), franklinite [$ZnO(FeMn)_2O_3$], zincite (ZnO), zincosite $ZnSO_4.2H_2O$, gahnite ZnAl2O4, smithstone (ZnCO3) and calamine [$Zn_2(OH)_2SiO_3$]. Zn contents in various parent materials like crust (51 ppm), granite (50 ppm), basalt (100 ppm), sandstone (20 ppm), shale (100 ppm), and limestone (40 ppm) were reported by Allowau[4]. Zinc minerals normally contain 5–15% Zn [69].Native zinc mineral is the release of zinc due to the decomposition of organic matter due to the production of organic acid. The Zn value of the earth's crust is 80 mg kg^{-1}; a high concentration of Zn is separated in igneous rock (basalt and gabbro, 100 mg/kg). In ranged between Indian soils, total Zn contents ranged between 20 and 97 mg kg1 [67] however, in the world, it ranged between 10 and 300 mg kg^{-1} [99], and it depends upon the parent rock, weathering, organic matter, texture, and soil reaction. Different forms of Zn are found in the earth's crust, such as silica, carbonate, and sulfate minerals, and in the soil as water-soluble, exchangeable, and connected to organic matter and secondary clay minerals [4]. DTPA-extractable zinc varied from 0.12-2.80 mg kg1 in Indian soils [67] and its critical limit is 0.6 mg kg1 [46;89].The DTPA extractable Zn in different soil orders follows the following trend: Alfisols>Mollisols>Inceptisols>Entisols [84],while total zinc concentration in soil is found in orders such as oxisol (24–30 ppm), vertisol (69–76 ppm), humid and sub-humid tropical (22–74 ppm), and arid and sub-arid (20–89 ppm), as reported by [45] and the different types of moisture regimes exert a strong influence on the lowest total zinc in an aquic moisture regime, and in an ustic moisture regime there is the lowest total Zn content in soil because an aquic moisture regime with humid and sub-humid climatic regions and excessive rainfall might be favorable for Zn leaching [77;4]. The distribution of zinc decreases with an increase in sandy soils, increasing pH or lime content with depth, increasing soil moisture regime, and being low in organic matter [*44;4*;39]. Zinc availability increases with increasing soil organic matter and clay content and decreases with increasing soil pH and soluble P content in soil [63]. It was also found that there was an opposite relationship between Zn solubility and pH but a proportional relationship between DTPA-Zinc and the organic substance content of soils [30;37]. The total Zn content in soils is usually inferior in light-textured soils and superior in heavy-textured soils [32]. Generally, the extractable Zn concentration of the subsurface soil is lower than that of the surface soil.

Abbreviations: Zn-Zinc, Fe- iron, Al- aluminium, Soil pH-Soil pH is a measure of the acidity and alkalinity in soils. Soil pH levels range from 0 to 14.

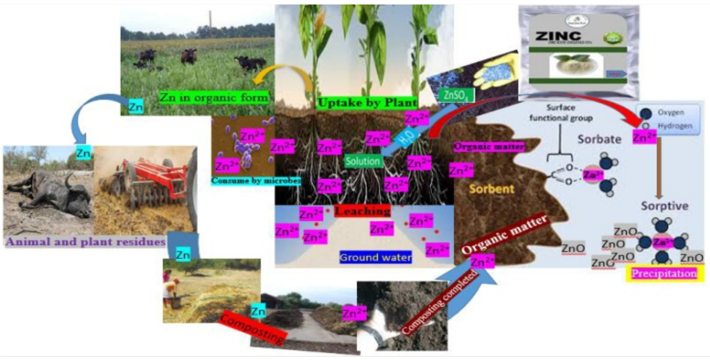

Figure-1: Graphical abstract

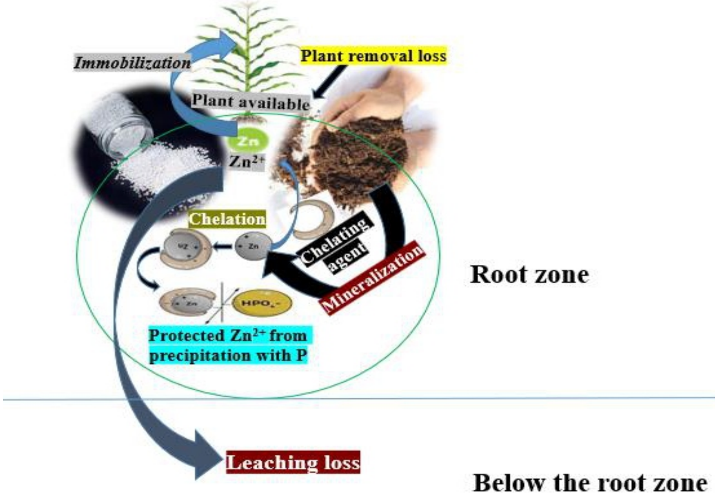

Figure: 2. Zinc (Zn) in soil

(Zinc is needed in very small amounts by plants. The normal concentration of Zn in most plants is between 20 to 100 ppm. Removal in the harvested portion of most crops is less than 0.5ppm. Zinc, like all plant nutrients, must be dissolved in water before it can be taken up by roots. Zinc exists in the soil solution as the di-valent cation Zn^{2+}, and precipitates in an excess concentration of phosphorus, iron etc.)

Different forms of Zn in soil

Total Zn is distributed over five pools in soils [95], 1. Water soluble-Present in the soil solution, 2. Easily exchangeable ion bound to soil particles by electrical charge, 3. Organically bound pool, 4. Chelated, 5. Adsorbed or complexed held in primary minerals and associated with secondary minerals. The contribution of these different pools towards Zn availability to the plants depends on dynamic equilibrium and fraction of zinc. It is absorbed by the plant through roots mostly in divalent ionic

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form (Zn^{2+}) from the solution. The amount and rate of transformation of these pools of zinc determine the size of the labile pool of Zn. Zn in soil discrete chemical forms differ in their solubility and availability to plants [26]. High zinc buffering capacity and high pH of soils resulted in a low amount of water-soluble and exchangeable Zn while the availability of zinc gets reduced and attributed to the formation of zinc hydroxides [27; 50]. The solubility of zinc is greatly dependent on pH, increasing by 100 folds for each unit decrease in soil pH (inverse relationship). In general, the solubility of zinc is maximum in the pH range of 4.5 to 6.0 in the organic soils and 5 to 7 in the mineral soils. Soil reaction (pH) and organic matter level markedly regulate the behavior of Zn between the plant available pools [2]. The formation of soluble organo-metal complexes and stable metaloorganic complexes through the organic matter plays an important role in the availability of zinc. Natural complexing agents existing in the organic materials efficiently enhance the concentration of soluble zinc complexes and zinc chelate in soil solution. The equilibrium among different pools is influenced by pH, the concentration of Zn and other cations, such as Fe and Mn [55] and therefore their susceptibility to plant uptake, leaching and extractability. The amorphous sesquioxides and organically bound Zn have a higher ability to absorb Zn due to their high specific surface area [25]. The occluded Zn in the crystalline oxides of Fe will not be available to the plant due to a strong chemical bond between the heavy metals. There is an occurrence of a higher proportion of zinc in the amorphous than in the crystalline sesquioxide fraction, the amount of applied Zn in different fractions particularly exchangeable Zn (EX-Zn), water-soluble Zn (WS-Zn) and organically bound Zn (ORG-Zn) were slightly lower and the WS-Zn and EX-Zn forms characterize the most mobile and immediately bioavailable fractions. The Zn fractions were in the following order: Total-Zn >RES-Zn (residual zinc)>CRY-Zn (crystalline oxide bound zinc)> ORG-Zn (organically bound Zn)>COM-Zn (complexed zinc)> AMO-Zn (carbonate and amorphous oxide zinc)> WS+EX-Zn (water-soluble and exchangeable zinc) [48]. Soil factors that influence the availability of Zn to the plants are: the total Zn, clay colloids, calcium carbonate, redox conditions and microbial activity in the rhizosphere, soil moisture status, concentration of other trace elements, concentration of macro-nutrients, concentration of phosphorus and climate [4].

Behavior of Zn in soil

The native and added Zn behaves differently based on soil types, root rhizosphere, climate etc. In general, the adsorption of Zn is enhanced with increasing of initial concentration of Zn at adsorbent [28].Adsorption and desorption are the critical processes in soil that regulates the behavior of Zn in soil and act as division between the solution and solid phases [25].The adsorption of Zn increased when Zn concentrations increased in the contact solution [96].The zinc is released from soil minerals or added through organic and inorganic fertilizers and equilibrium reactions become operative between solution and exchangeable phase of soil. The application of organic amendment will result in a decreased leaching potential risk[14].The adsorption, desorption and equilibrium behavior of zinc in the soil is influenced by soil pH, clay content, organic matter (OM), cation exchange capacity (CEC) and Fe/Al oxides. The high soil pH, higher amount of $CaCO_3$ and clay directly correlated to the Zn sorption and inversely related to zinc desorption [28;12;73;86].

Increasing soil pH affects the Zn hydrolysis, which would be preferentially sorbed on the soil surface [12;77]. Usually there are two main forms of sorbed ions: a) Non-specifically sorbed ions:Its outer surface complex in which involves electrostatically bonding, the readily exchangeable form of Zn. b) Specifically sorbed ions: Inner surface complex which involves ionic and covalent bonds, non-exchangeable form of Zn. In sorption capacity, Zn can be sorbed in clay minerals [70;76;90]. The clay colloids of soil have high organic matter content and it had greater adsorptive capacity and bonding energies for Zn. Zn sorption and release behavior of applied Zn dependent on its efficiency of fertilization. Its process based on the force acting between the sorbent and the sorbate, these forces included Van der Waals, coulomb and lewis acid base interaction. The Freundlich and Langmuir adsorption isotherms have been successfully applied to zinc adsorption and desorption in soils [36;38;9;42]. The absorption Zn on surfaces of hydrated Fe and MnO_2 in the oxygenated rhizosphere of rice roots is most likely decreasing the concentration and mobility of Zn in the rhizosphere of flooded rice [80].

In general, adsorption is fitted to the Freundlich isotherm only while desorption is fitted to both Freundlich isotherms and Langmuir isotherm. Soil parameters such as pH and soil organic carbon (SOC) have been identified as the most important factors governing the adsorption and desorption processes. The available Zn to plants is that present in the soil solution, it is adsorbed in a labile form. The soil factors affecting the availability of Zn to the plants are those that control the amount of Zn in the soil solution. Factors include the total Zn content, clay content, calcium carbonate content, redox conditions, especially phosphorus and climate, microbial activity in the rhizosphere, soil moisture status, concentration of macro-nutrients and trace elements, [4].The most probable reasons for the widespread Zn deficiency in may be attributed to the high rate of Zn adsorption with little desorption. Hence, in areas where the soil has high adsorption capacity, high application rates of Zn fertilizer are needed while soils with low adsorption will need lower rates of Zn fertilizers, which would minimize the expense and accumulation of Zn. The Langmuir and Freundlich models will help to quantify the amount of potentially available soil Zn for crop uptake and can be used to devise stratified Zn fertilizer recommendations for these sites and different landscape positions [28].

The Langmuir adsorption isotherm model can be used to evaluate the adsorption maxima and the bonding energies for Zn in the soil, and the Freundlich adsorption isotherm is an empirical equation that can also be used for straight line and linear expansion.

Langmuir Model: the Langmuir model was applied to investigate Zn adsorption in the soil by relating the bonding energy (k) and adsorption maximum (b) with the regression equation and it's a linear model.

$$\frac{ce}{x/m} = \frac{1}{kb} + \frac{ce}{b}$$

Where,

x/m = Amount of Zn adsorbed per unit weight of soil (mg kg^{-1})
C_e = Equilibrium Zn concentration in soil solution (mg L^{-1})
k = bonding energy of Zn to the soil.
b = maximum adsorption capacity of the soil.

Freundlich Model: The Freundlich equation is one of the simplest nonlinear sorption models (Freundlich, 1909).

$$x/m = kCe^{1/n}$$

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$\log x/m = \log K + 1/n \log Ce$

Where, X/m = Amount of Zn adsorbed per unit weight of soil (mg kg^{-1})

Ce= Equilibrium Zn concentration in soil solution (mg L^{-1})

K and n are imperial constants where 1/n can be obtained from the slope and K from

the antilogarithm value of the intercept.

Zinc mobility in soil

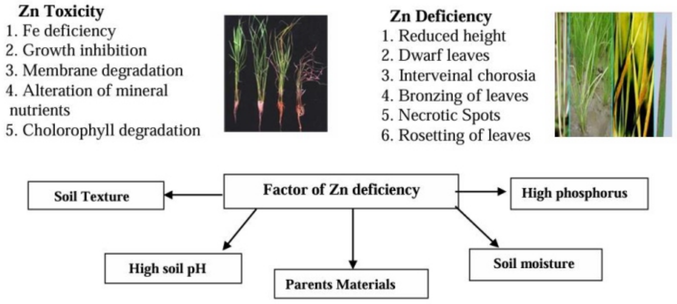
Upon application of zinc to the soil, it migrates to depth and distributes in different soil columns. Many factors able to influence the movement of zinc in soil profile, Zn concentrations, organic ligands, and a drop in pH may increase the solubility of metal and contribute to Zn mobility in soils. The transformations of Zn retained by soils may be generally related to the structure of the surface of sesquioxide and the porosity of soil components. The movement of dissolved nutrients in the water is related to the structure of the soil profile to its granulometric distribution, mobility and extractability in a column experiment [1]. Zinc is not mobile in the soil. Plant roots therefore have to grow to the zinc, rather than have the zinc move in the soil solution to the root. Zinc chelates are relatively mobile in the soil and can move with soil water, provided water is available to distribute the zinc and transformation of zinc added to soil depends on soil reaction. In the low pH soil, the application of the organic zinc complexes produces minute migration and tiny leaching of Zn in the soil profile [7]. The labile Zn Fraction has the highest leaching potential and may be a risk to groundwater quality and the migration of Zinc through the soil profiles [49]. The Zinc distribution, mobility and leachability in soil columns depend on the soil type and the organic chelates used. The leaching of Zn causes changes in the most labile forms of Zn due to the migration of the micronutrient through the soil profiles. The sources of Zn with little mobility and moderate stability could behave like a stock of micronutrients as the wate-soluble plus exchangeable and organically complexed fractions increased in the upper zones of the soil profiles.

Zn interaction on climate

Climate change will result in more extreme weather events including an increased frequency of severe droughts and extreme rainfall [97]. The recent Intergovernmental Panel on Climate Change (IPCC, 2013) assessment report V indicated that climate scenarios predict an increase of annual mean temperatures by 1.5 – 4°C by the end of 21st century. As a consequence of climate change, plants may be more often subjected to high temperatures and low soil moisture during the growing season in spring and summer [47]. Nutrient concentrations vary between soil horizons depending on the temperature and soil moisture. Soil temperature has effects on root attributes like growth, morphology, respiration, longevity and membrane fluidity to control the nutrient acquisition efficiency in plants [13].Climate change involves rising temperatures [91;35] and altered precipitation patterns, which also increase the probability of summer droughts [16; 53 71] distribution and mobility of Zinc in soil influenced by these altered abiotic conditions [79]. Zinc deficiencies are generally reported in cool, wet climates in early spring time when there is slow root due to low soil temperature and inadequately drained soils may also show zinc deficiency. Soil temperature has a significant influence on Zn availability and the highest values were recorded in the mesic temperature regime and the lowest values were found in the thermic temperature regime [59].

Zinc deficiency in soil

Zn is highly reactive and gets fixed to the soil therefore it is an immobile nutrient, and its characteristics deficiency is found in middle leaves. Zinc deficiency is higher in the state of Rajasthan (75.3%) Madhya Pradesh (66.9%), Tamil Nadu (65.5%), Maharashtra (54.0%), Bihar (44.0 %), Uttar Pradesh (33.1%) and lower deficiency is recorded in the state of Uttarakhand (9.6%), reported by shukla *et. al.* [74]. Zinc deficient soil is also reported in different countries [4] particularly in Java [55], Turkey [20], Australia [78], China [52], and India [87; 81; 15]. Generally, the most deficient Zn is found in high pH calcareous and sandy acid soils [68; 51;45]. Zinc is an essential micronutrient that helps in the growth and reproduction of plants [64]. It plays an important role in plant hormone balance, auxin metabolism, pollen formation and regulatory co-factor of a wide range of different enzymes [10;66;4]. The different enzymes of zinc are essential for biochemical pathways concerned with photosynthesis, carbohydrate metabolism, and the conversion of sugars to starch. In India, analysis of 14,863 soil samples from all over the country showed that 49% of soils were potentially deficient in Zn, 33% in B, 12% in Fe, 11% in Mo, 5% in Mn and 3% in Cu [82]. Also these soils are alkaline and calcareous. The combination of high pH, $CaCO_3$ together with low organic matter was discussed as major factors lowering Zn availability to plant roots [22]. Zinc deficiency is common throughout the arid and semi-arid regions of the world [87] due to low Zn solubility and high Zn fixation under such conditions [29]. A significant amount of Zn is present in the soil matrix, but only a small fraction of that is available to plants [67]. Several soil factors and conditions may render soils deficient in total and available Zn. Weathered parent material, nature of clay minerals, alkaline pH, sandy texture, high salt concentrations, calcareousness, waterlogging or flooding, organic matter content, high magnesium and/or bicarbonate concentrations (also in irrigation water), more nutrient uptake than application, intensive cultivation and the use of high analysis fertilizers are considered to be the major factors associated with the occurrence of Zn deficiency [6]. Zinc deficiency is very common in Rice-wheat cropping system in the globe especially in continent of Asia [61]. Severe zinc deficiency has been reported in more than 29 percent soils of the earth [4]. According to Ullah *et al*. [92] alkaline soils of Pakistan have maximum zinc scarcity to after nitrogen and phosphorus. Most of the soils of Pakistan are calcareous [56] and are directly connected to the deficiency of zinc [34]. Zinc is much less mobile within the plant, so deficiency symptoms first appear on the younger leaves.



Conclusion

Plant nutrition is affected by various factors directly and indirectly through weather changes. Most of the research reviewed regarding the nature of micronutrient deficiency in

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India. Zinc deficiency is widespread in India, and appears to affect 20 to 50% of the cultivated lands, and even more in Terai, where the major part of the country's rice production. Zinc is essential element required for the proper growth and development of plants and its deficiency often leads to decreased crop production.

Future scope

This article finds following research gaps:

- More investigations are required to explore the real zinc interaction with other essential nutrients under variety of plant rhizospheres.
- It is not still clear the matter on optimum, deficiency and excess levels of zinc under varied rhizosphere effect.
- Prediction of bioavailability of zinc in different soil environment under dynamic nature of soil ecosystem and varied climate are difficult to understand, therefore more research is needed to explore this aspect.

Conflict of interest:

The authors declare that the review article was made with absence of any kind of financial as well as commercial relationships that could be produced as a conflict of interest.

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