FACTORS AFFECTING CERTAIN MICRONUTRIENTS AVAILABILITY IN SOILS

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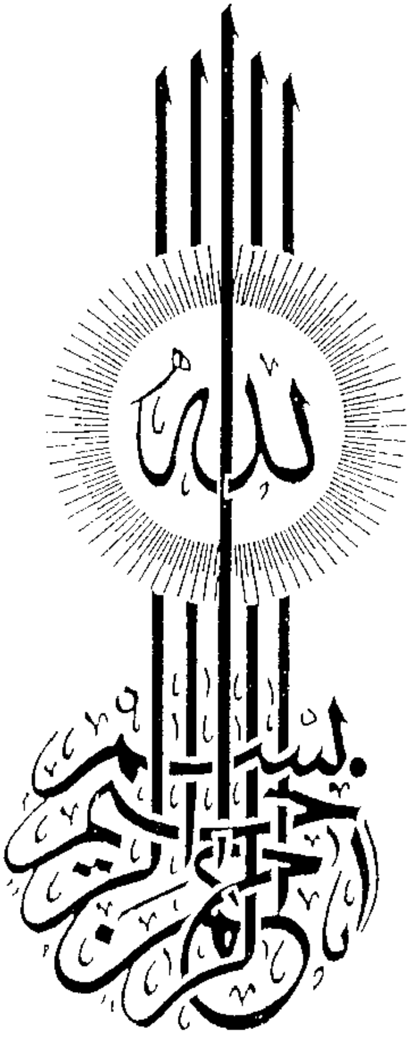

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1. INTRODUCTION

One of the most interesting subjects for study is that the problem connected with micronutrients in the soils of Egypt.

As a matter of fact, the establishment of fertility in these soils is now a serious problem because of the scarcity of information pertinent to micronutrients. Zinc is one of which that has to be supplied to the soil for normal crop production.

Although Zn had been recognized as an essential element for plants for many years, yet no consideration, so far, has been given to the evaluation of its status and chemical behaviour as well as the factors affecting its availability in Egyptian soils. For these resons, Zn as an essential micronutrient has been chosen as the object of the present study.

The experiments embodied in the current investigation are an attempt to give an idea about the status of Zn in Egyptian soils. Moreover, the estimation of plant-available Zn either chemically by different extractants, or biologically by plant analysis was undertaken for the evaluation of the performance extractants. If an extractant gave the highest

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correlation with plant Zn , it is considered, however, to be the extractant of choice. Also a special regard had been focussed on the evaluation of plant-available Zn as an index to Zn fertilization.

Furthermore, the present study was meant to illustrate the mobility, retention and release of Zn in soils and other controlled systems ,i.e., pure clay minerals, pure $CaCO_3$ in clay fraction and cation exchange resin (Dowex 1-X 50). In addition a contribution is accomplished to study the uptake and translocation of retained Zn in the plant. In these connections the tracer technique was applied using radioactive Zn^{65}.

It was also hoped that some light might be thrown on the mechanism of Zn fixation, characteristics of retained forms and the factors affecting availability in calcareous soils.

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2. REVIEW OF LITERATURE

2.1. Zn. in soil :

Zn is common and rather widely difused element. It occurs in soils in Known or postulated bonding that includes true solution in ionic, complexed, or chelated form, weakly exchangeable bonding with monovalent cation exchangers such as NH_4^+ and K^+, specific absorption such as the displacement of Zn^{++} with Co^{++} or Cu^{++}, "chelated" crystalline bonds in primary minerals, clays, and fertilizer granules; and bonding in amorphous precipitates. Hodgson (1963) , described five types of bonding of Zn by the soil in slightly different terms and emphasized the difficulties of defining the type of bonding, the adsorption surface, and the difference between adsorption and precipitation reactions. These forms are probably in equilibrium, but the rates of reestablishing equilibrium may be very slow when the equilibrium is disturbed by fertilization or crop removal.

With respect to the total Zn content in soils, Holmes (1943) found an average of 24 ppm. of Zn in 70 soils near Kinston North Carolina, U.S.A. Twelve-soils from the area have Zn content varied between 34 and 105 ppm. On the other hand, Swain (1955) found that the values varied between 10 and 300 ppm. Masev (1964) found that calcareous soils

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had a medium supply of total Zn (30-90 ppm.) and added that the soils developed over calcareous parent rock contained more Zn than soils developed on loess . He also found that exchangeable Zn was lacking or very low, and the water soluble Zn was not found in most soils. Hibbard (1940) , Kanehiro (1964) and Kruglova (1964) reported that Zn is usually more concentrated in soil surface than in subsurface.

2.2. Factors affecting Zn availability :

Although the total Zn content in the soils is quite low, plants need such small quantities so that Zn deficiences would be rare if total soil Zn was even moderately available to plants. "Plants are generally adequately supplied with Zn in nutrient solutions containing 0.1 ppm. or more, Hewitt (1966)". The availability of Zn is particularly sensitive to changes in the soil environment. Some effects of these changes are directly related to the performance of the root system in exploring the soil volume for this nonmobile element and some of the effects are on the "pools" or bonding of the element in soil.

The environments which may affect Zn availability, are the soil pH , precipitation by phosphates and adsorption reaction on clay minerals, $CaCO_3$ and organic matter.

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2.2.1. Soil pH :

Zn like several other metals, forms a hydroxide with ability to act as a base or weak acid. In this respect Zn has two different ionic forms depending on the pH of the liquid environment. The formations of negatively charged zincates was suggested by Camp (1945) as being significant in soils more alkaline than pH 7.85. He also added that Zn availability declined as the pH of the soil rised and the critical level was found between the pH range of 5.5 to 6.5 . Shaw and Dean (1952) and Woltz et al.(1953) confirmed the findings of Camp (1945), and found that Zn deficienoes usually occurs on soils of pH 6 or higher.

For further supports regarding the effect of pH on Zn solubility, Jurinak and Thorne (1955) reported titration curves by titrating clay suspensions, containing Zn, with NaOH and $Ca(OH)_2$. They found an increase in the solubility of Zn with NaOH additions as the pH exceeded 6.5. This was taken as evidence of formation of soluble Zincate ions. An absence of increased Zn solubility in the alkali range with $Ca(OH)_2$ additions is consistent with low solubility of calcium zincate. Since under conditions favourable for plant growth, Ca is a major cation constituent of soil solutions, for that reason,

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the authers found that the above results indicated that zinoate formation is probably not an important factor in increasing Zn availability in nonalakli soils within the alkalinity range favourable for plant growth. It could be detected from the foregoing reports that the predominant occurence of Zn deficiences in the pH range of 6.0 to 8.0 is governed by the conditions of minimum Zn solubility.

2.2.2. Precipitation by phosphates:

Through the investigations of Leggett (1952), Bingham and Martin (1956), Ellis *et al.* (1964) and Olson *et al.* (1965), it was found that heavy dosages or prelonged use of phosphate fertilizers have been shown on many soils to decrease Zn uptake, and even to bring Zn deficiency for various crops.

On the other hand, Boawn *et al.* (1954), Thorne (1957) and Seatz *et al.* (1959), reported that the degree of the effect of P on Zn avialability varied with the soils and crops involved and the levels of avialable Zn and phosphours in the soils.

2.2.3. Adsorption reactions:

The adsorption reactions can reduce Zn solubility to deficiency levels. Such adsorption reactions can occur on many types of surfaces including organic matter, lime

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and clay minerals.

Organic matter effect : Baughman (1956) reported that organic matter was found to be a major soil factor in Zn fixation and the Zn fixing power of the soil was in the order of its organic content. He found that the mechanism of Zn fixation by organic matter was designated as chelated and complexed, the former reactions may also be a significant factor in reducing Zn availability in soils. It was found also by DeMumbrum and Jackson (1956) that peat may hold Zn and Cu by chelation type reaction. Their evidence was based on infrared absorption studies which showed considerable shifts in the double bond region of peat sorbing Zn or Cu which were not apparent when sorbing Ca and related strong basic cations.

Lime minerals effect : Canals (1950) showed that Zn was adsorbed from solution by calcium carbonate at 57°C, the adsorption of Zn was slightly less at 20° C, but when the temprature was raised to 90°C and 100°C, the adsorption of Zn by $CaCO_3$ was greatly increased. Leeper (1958) postulated that, in calcareous soils, $CaCO_3$ may be an important adsorbent of heavy metals. Woltz et al. (1953) obtained a decreasing uptake of Zn in soybeans with increasing rates of lime stone. They recognized that lime minerals

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may constitute a potential adsorptive phase for Zn element. Jurinak and Bauer (1956) studied Zn adsorption on calcite, dolomite and magnesite by applying the isotopic tracer technique. They found that the Ca- magnesite showed a somewhat greater affinity for adsorption Zn ions than calcite, while dolomite is intermediate. Relatively recent, Berger _et al._ (1961) and Berger (1962) confirmed the effect of lime on adsorption of Zn and added that Zn deficiency is commonly found in calcareous soils.

Adsorption on clay minerals : The adsorption of Zn on some clay minerals was studied by El-Gabaly (1943, 1950), who found that the amounts of Zn adsorbed is not all exchangeable. In Kaolinite, biotite, bentonite, muscovite and pyrophyllite, Zn is adsorbed and is not readily replaced by other cations and decreased the ammonium adsorption capacity. This was interpreted as the Zn being adsorbed in unfilled holes in the octahedral layer of alluminosilicates. In clays containing-Mg including Mg-bentonite, vermiculite and brucite, Zn fixation did not decrease the ammonia adsorption capacity. The latter results was interpreted as Zn replacing Mg ions in the exposed lattices of the clay particle surfaces. The fixation of Zn on clay lattices was further supported by the investigations of Nelson and Melsted (1955), DeMumbrum and Jackson(1956)

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and Jurinak and Bauer (1956), who found also that the strongest adsorption of Zn on crystal Lattices is associated with surfaces containing-Mg ions.

2.3. Estimation of plant-avialable Zn :

Many attempts have been made to stimulate the solvent power of the plant root system by extracting the soil with different chemical agents.

The chemists , in their attempts to extract a measurable amount of the element to correlate with the uptake by plants, have resorted to stronger extractants than the soil solution or water, such as KCl and acitic acid; Hibbard (1940), NH_4OAC.; Lyman and Dean(1942), 1N NH_4OAc + 0.1% dithizone in CCl_4. Shaw and Dean (1952), EDTA , Viro (1955), and HCl, Nelson et al. (1959).

The efficiency of the extractant to extract a measurable amount of Zn was found to depend on its ability to make different bits or chemical fractions into the total Zn content in the soil. These chemical fractions represent discrete forms of chemical bonding in the soil or probably a mixture of forms with some forms dominating when a given extractant is used.

The successful use of a chemical extractant technique

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for assessing plant - available Zn depends upon the efficacy of the method in extracting the corresponding element from those compounds in the soil which can be considered to participate in the supply of Zn to plants.

The efficiency of the Zn extractants were reexamined by Boawn *et al.* (1957), Massey (1957) and later by Bauer and Lindsay (1965), who found high correlation between extraction of Zn with NH_4OAc + , dithizone and plant Zn uptake. Thereby they considered under well controlled conditions, that 1N NH_4OAC + 0.1% dithizone in CCl_4 is the best extractant for the estimation of plant-available Zn.

2.4. Soil tests as indices of changing Zn availability in the Soil :

Changing in the test should reflect quantitatively or at least be correlated with the changing nutrient status of the soil resulting from fertilization or crop removal. Boawn *et al.* (1960) showed that only 10 pounds of 16-pounds-per-acre Spring application of Zn (as Zinc sulphate) could be extracted from the soil in July with 0.1N HCl. They reported also that the extractable Zn declined with time, but crop removal accounted for only a small part of this decline. For example, during three-years experiments ,

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