

EFFECT OF CALCIUM CARBONATE ON
THE MOVEMENT AND FIXATION OF
CERTAIN MICRONUTRIENTS

By

YEHIA NOUR ELDEEN ABDALLAH

THESIS

Submitted in Partial Fulfilment of the
Requirements For the Degree of

MASTER OF SCIENCE

in

Soil Science

Approved by:

A. H. El-Samary

F. L. Hegazy

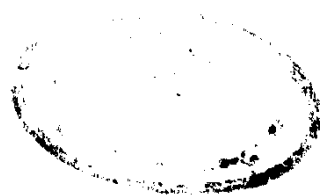
Committee in Charge

Date: 2 / 10 / 1973



5272

Soil Department
Faculty of Agriculture
University of Ain Shams



1973

(31-411)
Y.N.

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Dr. Abd el Menaim El Galla, Assistant Professor of Soil Chemistry, Soil Department, Faculty of Agriculture, Ain Shams University, for his supervision and constructive criticism.

Thanks are also to Dr. Saad el Sherief, Professor of Plant Nutrition, Soil Department, Faculty of Agriculture, Ain Shams University, for his help in this investigation. The writer is most grateful to Mr. Aly Abd el Rasik, Research Assistant, Soil and Water Research institute, Ministry of Agriculture.

—•••••—

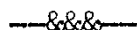


LIST OF TABLES

	Page
1 Effect of varying concentrations of $ZnSO_4$ on the amounts and the percentages of Zn retained on soil materials.....	45
2 Effect of varying concentrations of Zn-EDDHA added on amounts and percentages of retained Zn on soil materials.....	48
3 Effect of the time of contact on the amount and percentage of retained Zn added as $ZnSO_4$ on certain soil materials.....	55
4 Effect of time of contact on the amount and percentage of retained Zn added as Zn-EDDHA on certain soil materials.....	56
Effect of PH of the media on Zn retention added as $ZnSO_4$ on certain soil materials.....	63
5 Effect of pH of the media on Zn retention added as Zn-EDDHA on certain soil materials.....	66
7 The effect of varying concentration of ferrous ammonium sulfate on the amounts and percentage of Fe retained on soil materials.....	77
8 The effect of varying concentration of Fe-EDDH solution on the retention of Fe on soil materials.....	79
Effect of time of contact on the amount and percentage of Fe retention from ferrous ammonium sulfate on certain soil materials....	84
9 Effect of time of contact on the amount and percentage of Fe retention from Fe-EDDHA on certain soil materials.....	86
1 Effect of pH of the media on retention of Fe added as ferrous ammonium sulfate by certain soil materials.....	90
2 Amounts of Zn in the leachate of the inorganic and chelated treatments and affected by organic matter and calcium carbonate level	98
3 Percentages of Zn remaining water soluble from $ZnSO_4$ in the successive depths of the soil treated with $CaCO_3$ and organic matter..	101
4 Percentages of Zn remaining water soluble from Zn-EDDHA in the successive depths of the soil treated with $CaCO_3$ or $CaCO_3$ and organic Matter..	103
5 Percentagen of chemically available Zn % remained from Zn added as $ZnSO_4$ in the successive depths of the soils treated with $CaCO_3$ or $CaCO$ and organic matter.....	106
6 Percentages of the different Zn forms in the soil treated with zinc sulfate as affected by $CaCO_3$ or $CaCO_3$ and organic matter.....	108

C O N T E N T S

	Page
INTRODUCTION	1
REVIEW OF LITERATURE.....	3
The Adsorption Reaction of Zinc and Iron with Soil Materials.....	3
Reactions of Zinc and Iron chelates with Soil Materials.....	16
Release of Retained Zn and Fe.....	21
Movement of Zinc and Iron through Soil Columns.....	28
MATERIALS AND METHODS.....	31
RESULTS AND DISCUSSION.....	42
Retention and release of Zn.....	42
Retention and release of Fe.....	76
The Movement of Zinc and Iron in Soil Columns.....	97
SUMMARY	118
LITERATURE CITED	122
ARABIC SUMMARY:	



LIST OF FIGURES

- 2) Fig. (1): Effect of different conc. of $ZnSO_4$ on amount of Zn retained on: A- $CaCO_3$ B-clay fractions..... /43
- Fig. (2): Effect of different conc. of Zn-EDDHA on Zn retained on : A- $CaCO_3$ B-Clay Fraction..... /43
- 3) Fig. (3): Effect of time of contact on Zn retention, added as $ZnSO_4$ on : A- $CaCO_3$ B-Clay fractions..... /54
- 4) Fig. (4): Effect of time of contact on Zn retention, added as Zn-EDDHA on: A- $CaCO_3$ B-Clay fraction..... /54
- 5) Fig. (5): Effect of pH of the media on Zn retention, Zn added as $ZnSO_4$ on: A- $CaCO_3$ B-Clay fraction..... /63
- Fig. (6): Effect of pH of the media on Zn retention, Zn added as Zn-EDDHA on: A- $CaCO_3$ B-Clay fractions..... /63
- 6) Fig. (7) The release of retained Zn from $ZnSO_4$ by EDTA, HCL & KCL on: 1- $CaCO_3$ clay size 2-Na-clay fraction 3-Ca-clay fraction 4-Nakaolinite 5-Ca-Kaolinite..... /71
- 7) Fig. (8): The release of retained Zn from Zn-EDDHA by EDTA, HCL & KCL on: 1- $CaCO_3$ clay size. 2-Na-Clay fraction 3-Ca-clay fraction. 4-Na-kaolinite. 5-Ca-kaolinite..... /71
- 8) Fig. (9): Effect of different concentrations of Fe. added as ferrousamm. sulfate on amount of Fe retained on: A- $CaCO_3$ B-Clay fractions..... /76
- 9) Fig. (10): Effect of time of contact on the Fe retention, added as ferrous ammonium sulfate on: (A) $CaCO_3$ (B) Clay fraction.. /84
- 10) Fig. (11): Effect of pH of the media on Fe retention, added as ferrous ammonium sulfate on: (A) $CaCO_3$ (B) Clay fration..... /90

INTRODUCTION

Zn and Fe are recognized as essential elements for normal plant growth and crop production.

The chelation phenomena have long been recognized as a very important chemical and biological reaction in soil. Naturally occurring chelates of heavy metals is thought to be important sources for these elements in the soils. Currently, synthetic chelates are widely used as a mean for supplying micronutrients especially iron and zinc to plant.

In calcareous soils, supplying of Zn and Fe in inorganic forms to plants represents a problem because of the complicated reactions occurring in such soils. These reactions affect the availability of zinc and iron due to precipitation, fixation and or retention on different soil components.

The application of synthetic chelates to soils as a means for supplying Zn and Fe to plants is increasing as a field practise. Although some success has been obtained in correcting chlorosis and other symptoms on plants with

LITERATURE REVIEW

The chemistry of micronutrient cations appears to be regulated largely by reaction with mineral and organic surfaces in soils. Coulombic forces giving rise to base exchange reactions certainly attract heavy metals as they do with all soil cations, but the interactions of Cu, Co, and Zn with organic and clay surfaces involve additional forces of attraction. Fe and Mn under conditions of satisfactory aeration are bound in most soil principally as precipitates of oxides and phosphates. In this way oxides of these metals respond to changes in pH, oxidation potential, and the presence of soluble complexing agents that form the most part that governs the movement and availability of these elements to plants.

The Adsorption Reaction of Zinc and Iron with Soil Materials

The adsorption reaction in soils can ~~be~~ reduce Zn and Fe solubility to deficiency levels. Such adsorption reaction can occur on many types of surfaces including lime, clay minerals and organic matter. Besides, the adsorption

reaction may also be affected by some factors such as pH, time of contact, concentration and ion properties.

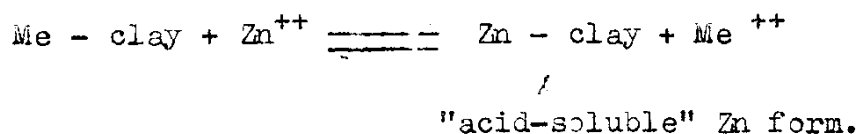
Soil materials and adsorption reaction:

The adsorption reactions on different soil materials will be discussed in the following sections:-

a- Clay minerals:

Jenny & Elgabaly (1943) and Elgabaly (1950) found in their studies of zinc salts with clay minerals, that the amounts of Zn adsorbed was not all in an exchangeable form. In kaolinite, biotite, bentonite, muscovite and pyrophyllite, Zn was adsorbed but it was not readily replaced by other cations and the ammonium adsorption capacity of the clay minerals was also decreased. This was interpreted as the Zn being adsorbed in unfilled holes in the octahedral layer of aluminosilicates. Brown (1950) found that the sorption of Zn by clay differ from that for Ca and Mg.

Nelson & Melsted (1955) suggested that the reaction of Zn and clay is in the following form



Sharpless et al (1969) reported that the main factor that accounted for the extent of Zn retention on clays is cation exchange capacity.

Most of the earlier work dealing with heavy metals in soils was carried out at relatively high concentrations of the reacting ion. De Mumbrum and Jackson (1956), in attempting to repeat some of these conditions, found that precipitation was a serious factor. While precipitation should be a major concern in laboratory investigations, it is an unlikely^{of} natural occurrence in acid soils with Zn at least. Even with Fe^{+++} , adsorption is apparently favored over precipitation as evidenced by the way iron oxides become distributed over soil surfaces. Whitting and Page (1961) have shown experimentally that adsorption of Fe^{+++} by montmorillonite will precede precipitation over a range of pH values.

b- Calcium carbonate:

 ^{et al}
Canals (1950) showed that Zn was adsorbed from solution by calcium carbonate at 57°C and the adsorption was slightly less at 20°C.

Jurinak & Bauer (1956) who studied the adsorption of zinc chloride on calcite, stated that this adsorption indicate

c- Organic matter

Baughman^m (1956) reported that organic matter was found to be a major soil factor in fixing Zn in soils. He indicated that the mechanism of Zn fixation by organic matter can be designated as chelated or complexed, the former reaction may be a significant factor in reducing Zn availability under certain conditions in soils. He added that destroying the organic matter of a surface soil, allowed time to recover almost all of an added source of Zn by extracting with dithizone, recovery amounted to only 50 to 75 per cent when the organic matter was allowed to remain. De Mumbrum (1956) found also that peat may hold Zn by chelation type reaction. Thier evidence was based on infrared Adsorption studies which showed considerable shifts in the double bond region of peat sorbing Zn.

Jensen & Lamm (1961) found a correlation coefficient of 0.81 between Zn content and organic matter distribution in different soils.

Olson (1948) indicate that pH is not the only factor affecting the solubility of iron complexes with organic matter in soils, other factor such as organic matter component.

Muir et al (1964) stated that organic-acid fraction maintains Fe in solution from pH 4 to at least 9.5 and this is due to thier ability to form water soluble complexes with Fe and to stabilize ferric hydroxide sols. The water soluble complexes were formed over a wide range of pH and in the presence of Ca.

Factors Affecting Zinc and Iron Adsorption

The main factors affecting the adsorption and reaction of heavy metals on the soil materials are in general, soil pH, concentration of the element, time of contact, type of anion and replacing power of cations.

Soil pH:

Elleswarth & Dean (1952) and Wear (1956) reported that fixation of zinc was affected by soil pH. In a bentonite system and variation of pH using Zn^{65} , Jurinak & Thorne (1955) found that solubility reached a minimum in the pH 5.5 to 6.7 and as the alkalinity of the sodium and potassium systems was increased, the solubility of Zinc also increased. In calcium system, zinc solubility reached a minimum at pH 7.6, and no change in soluble zinc was noted

as the pH of the system increased. They added that the formation of insoluble calcium zincate can be postulated.

Bingham et al (1964) also showed that Cl^- system of Zn metal revealed no retention of metal below pH 5.5 to 6.5.

Smolck (1933) mentioned that the sorption of ferric ions was closely related to pH values of filtrates obtained from soil immersed in FeCl_3 solution, the higher the pH the higher was the sorption.

Kilman (1937) observed that iron may be translocated in soils in both cationic and anionic forms. He added that if the iron was in an anionic form, the iron stayed in solution even under strongly alkaline condition but if it was in the cationic form, ferrous sulfide, or hydrated ferric oxide, adsorption depends on conditions in the soil especially the soil pH.

Boischot & Durroux (1950) showed that fixation of iron occurs by chemical precipitation at pH level > 5.1 . Alinari (1954) mentioned that $\text{Fe}(\text{NO}_3)_2$ was fixed under the fixing factors of pH, CaCO_3 content and temperature.

Witting & Page (1961) pointed out that less Fe (III) was adsorbed on clay minerals as the pH decreased, because

of (a) increased competition from H^+ (b) change in ionic species of Fe (III) present in the aqueous phase as the M^+ ions concentration increased and (c) any dissolution of clay caused by increased activity of H^+ , or a combination of these factors.

Tayel (1964) showed that there was no correlation between extractable iron (II) and soil pH in the Egyptian soils. Clark (1964) found that Fe was fixed by clay at pH 5.5.

Muir et al (1964) stated that the organic-acid fractions had maximum ability to complex iron at pH 8 and the amino acid solution is inactive above pH 4.5. They added that the water soluble complexes are formed over a wide range of pH and in presence of Ca ions.

Concentration of element:

It had been generally stated that the cation exchange increased as the concentration of the solution was increased, Kelly & Cummins (1921), but not in direct proportion to concentration, Gedroiz (1922).

Bingham et al (1964) showed that by increasing the concentration of the metal, its retention increased. He

Jamison (1944) reported that the retention of Zn by soil seemed to be increased with time of contact at least up to 48 hours.

Working on kaolinite, Brown (1950) found that zinc was sorbed more slowly than other cations.

Nelson & Melsted (1955) studied the chemistry of zinc added to soil and clay as related to time of equilibrium and observed that acid form of zinc increased with increasing length of time of contact between the soil and zinc solution.

The data also indicated no changes in the forms of zinc present between the 30 minutes and the 6 months contact time, in the hydrogen system clay. They added that in calcium system the change from the unadsorbed and exchangeable forms to the acid-soluble form is quite rapid at first (first minutes), but much slower after a few weeks.

Sharpless et al (1969) found that addition of concentrated solution of Zn SO_4 to soil result in rapid adsorption of Zn, about 70 % of the added amount was in exchangeable form during the first minute.

Boischot (1950) found that fixation of iron by soil depends on time of contact.