

## **STUDIES ON SOIL ZINC AND COPPER FORMS OF ASSIUT GOVERNORATE**

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### **ABSTRACT**

Assiut Governorate, Egypt, was divided using five transects across the Nile valley in the east-west direction in order to assess the various forms of Cu and Mn. Surface soil samples were collected from an average of six locations for each transect. Soil zinc and copper forms including soluble + exchangeable, carbonate-bound, Mn oxide-bound, organic-bound, poorly crystalline Fe oxide-bound and crystalline Fe oxide-bound forms of the studied samples were determined in a sequential extraction. The total contents of Zn and Cu in these samples were also determined.

Concentrations of soil Zn in these forms decreased in the order of: Residual > PCFeOx > CFeOx > O-bound > Carb. > Mn Ox > Exch.form. Levels of Zn in these respective forms represented 91.86, 3.81, 2.76, 0.59, 0.42, 0.37 and 0.22% of the total soil Zn.

The mean levels of soil Cu bound to the residual, crystalline Fe oxide, poorly crystalline Fe oxide, organic matter, Mn oxide, carbonate and exchangeable forms were 43.62 (82.69% of total Cu), 1.35 (2.56% of total Cu), 5.06 (9.59% of total Cu), 0.94 (1.78% of total Cu), 0.33 (0.63% of total Cu), 0.82 (1.55% of total Cu) and 0.63 mg/kg (1.19% of total Cu), respectively. The total Zn content of these soils had an average value of 52.75 mg/kg.

**Key words:** Zinc, copper, fractionation, forms, total, residual.

### **INTRODUCTION**

Soil micronutrients were categorized into different forms including (1) soluble in soil solution, (2) exchanged and/or specifically adsorbed on inorganic soil particles, (3) contributed with insoluble biological residues, (4) precipitated in the form of pure or mixed compounds, (5) occluded in primary and /or secondary minerals (Shuman, 1991), and (6) present in the bodies of soil living organisms (Hodgson, 1963; McLaren and Crawford, 1973).

The soil metal cations were classified into the readily labile, potentially labile, and non-labile groups (Han and Banin, 2000; Han et al., 2001). Usman (2004) reported that the metals in the exchangeable form are readily labile, whereas those bound to carbonates, easily reducible oxides, and organic matter are potentially labile. He also reported that the metals occluded in oxides such as poorly crystalline and crystalline iron oxides are considered non-labile.

Zinc occurs in soils as (1) soluble in soil solution, (2) adsorbed on the soil colloids by chemisorptions or cation exchange processes, (3) associated with organic matter in soluble or insoluble forms, (4) minerals such as ZnO

(zincite),  $\text{Zn}(\text{OH})_2$ ,  $\text{ZnCO}_3$  (smithsonite),  $\text{ZnFe}_2\text{O}_4$  (franklinite),  $\text{Zn}_2\text{SiO}_4$  (willemite), and (5) primary minerals as ferromagnesian minerals such as hornblende, biotite and augite (Sims and Patrick, 1978; Lindsay, 1979; FAO, 1983).

The exchangeable Zn ranged from 0.07 to 1.54 mg/kg in some soils of southeastern USA (Liang et al., 1990), 1.10 to 2.02 mg/kg in some soils of the Western area of Nile Delta (Abdel Salam, 2003). The values of Zn in the organic form varied from 0.16 to 1.92 mg/kg in some soils of southeastern USA (Liang et al., 1990), 0.30 to 39.30 mg/kg in the unpolluted North American soils (Nielsen et al., 1986). In some soils of southeastern US, Shuman (1985) found that the concentration of Zn bound to poorly crystalline Fe oxide and crystalline Fe oxides forms varied from 0.00 to 4.83 and 0.75 to 18.58 mg/kg, respectively. Total Zn varied from 18.00 to 180.00 mg/kg in some soils of Upper Egypt (Ghoneim et al., 1984a), 10.00 to 300.00 mg/kg in the unpolluted North American soils (Nielsen et al., 1986). The highest amount of Zn was found in the residual fraction (Iyengar et al. (1981). Narwal et al. (1999) reported that 98% of the total content was in the form of residual Zn.

Sims and Patrick (1978), Lindsay (1979) and FAO (1983) reported that soil copper occurs in several forms, such as (1) dissolved in soil solution, (2) exchanged on soil colloids, (3) occluded with organic matter, (4) minerals as  $\text{CuO}$  (tenorite),  $\text{Cu}_2\text{O}$  (cuprite),  $\text{Cu}(\text{OH})_2$ ,  $\text{CuCO}_3$ ,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  (malachite),  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$  (azurite),  $\alpha\text{-CuFe}_2\text{O}_4$  (cupric ferrite),  $\text{CuSO}_4$  (chalcocyanite) and  $\text{Cu}_3(\text{PO}_4)_2$ , and (5) crystal lattices of primary and secondary silicate minerals. The concentration of Cu in soil solution ranged between  $10^{-8}$  and  $10^{-6}$  M at pH >7 (Tisdale et al., 1997).

The average content of the total Cu was 33.00 mg/kg in Sohag Governorate (Ibrahim et al., 2001), 53.60 mg/kg in soils of Assiut Governorate (Ghoneim et al., 1984b). In Saskatchewan soil, Liang et al. (1991) found that the content of the exchangeable Cu ranged between 0.30 and 0.80 mg/kg. Abdel Salam (2003) found that the levels of Cu in the carbonate form ranged between 1.60 and 4.38 mg/kg in some soils of the Western area of Nile Delta. Elkhatib et al. (1994) found that the concentration of Cu in the Carb. form varied between 0.32 and 0.71 mg/kg in Edku lake sediments. Shuman (1985) found that the values of Cu bound with poorly crystalline iron oxides and crystalline iron oxide varied from 0.17 to 4.83 and 0.50 to 20.50 mg/kg. Liang et al. (1991) reported that the values of Cu in Mn oxide and organic forms range from 0.60 to 1.70 and 0.33 to 2.43 mg/kg, respectively.

The objective of this study is to assess the status of various soil Zn and Cu forms of Assiut, Egypt.

## **MATERIALS AND METHODS**

Five transects were taken across the Nile valley in the east-west direction in Assiut Governorate, Egypt. Surface soil samples were collected from an average of 6 locations from each transect in the winter of 2003/2004.

Most of the studied soils at that time were cultivated by wheat, faba bean and clover. The collected soil samples were air-dried, crushed, passed through a 2 mm sieve and kept for subsequent analysis. Some of the soil characterizations of these samples are present in Tables 1 and 2.

Particle-size distribution was measured using the pipette method according to Piper (1950). Organic matter (OM) was determined using the Walkley-Black method (Jackson, 1973). Soil pH was determined in a 1:1 of soil: water suspension using a glass electrode (Jackson, 1973). Calcium Carbonate ( $\text{CaCO}_3$ ) was estimated using a volumetric calcium carbonate calcimeter (Nelson, 1982). Electrical conductivity ( $\text{EC}_e$ ) was measured in the saturated soil paste extract using an electrical conductivity meter (Hesse, 1998). Available micronutrient cations (Fe, Mn, Zn and Cu) were extracted using 0.005 M DTPA (diethylene triamine penta-acetic acid), at pH 7.3 according to Lindsay and Norvell (1978), and then determined by atomic absorption spectrophotometer (GBC 906 AA).

**Table (1): Some soil characterizations of the studied soils.**

| Transect No | Location No | pH (1:1) | $\text{EC}_e$ (dS/m) | O.M (%) | $\text{CaCO}_3$ (%) | S.P. (%) | Particle-size Distribution (%) |    |    | Texture |
|-------------|-------------|----------|----------------------|---------|---------------------|----------|--------------------------------|----|----|---------|
|             |             |          |                      |         |                     |          | S                              | Si | C  |         |
| 1           | 1           | 7.60     | 1.60                 | 0.68    | 4.74                | 20.7     | 88                             | 2  | 10 | L. S*   |
|             | 2           | 7.70     | 2.60                 | 1.59    | 3.56                | 59.4     | 44                             | 34 | 22 | L.      |
|             | 3           | 7.61     | 1.27                 | 1.23    | 2.32                | 57.0     | 35                             | 36 | 29 | C. L.   |
|             | 4           | 7.60     | 0.72                 | 1.77    | 1.22                | 56.3     | 42                             | 36 | 22 | L.      |
|             | 5           | 7.90     | 0.70                 | 0.80    | 3.37                | 51.9     | 35                             | 45 | 20 | L.      |
| 2           | 1           | 7.93     | 1.38                 | 1.04    | 4.87                | 30.0     | 80                             | 7  | 13 | S.L.    |
|             | 2           | 7.80     | 1.15                 | 1.41    | 3.00                | 59.1     | 40                             | 21 | 39 | C.L.    |
|             | 3           | 8.51     | 6.10                 | 0.98    | 4.13                | 49.5     | 62                             | 17 | 21 | S. C.L. |
|             | 4           | 7.82     | 1.83                 | 1.89    | 2.60                | 51.3     | 44                             | 32 | 24 | L.      |
|             | 5           | 8.03     | 0.93                 | 0.45    | 1.16                | 19.8     | 86                             | 4  | 10 | L. S.   |
|             | 6           | 7.70     | 0.84                 | 1.60    | 3.53                | 48.5     | 53                             | 19 | 28 | S. C.L. |
| 3           | 1           | 8.00     | 0.68                 | 1.09    | 3.37                | 63.5     | 25                             | 23 | 52 | C.      |
|             | 2           | 8.15     | 1.33                 | 0.79    | 2.87                | 67.9     | 14                             | 35 | 51 | C.      |
|             | 3           | 8.07     | 1.24                 | 1.03    | 2.60                | 45.2     | 65                             | 17 | 18 | S. L.   |
|             | 4           | 7.90     | 0.70                 | 1.33    | 2.87                | 52.8     | 55                             | 26 | 19 | S.L.    |
|             | 5           | 8.07     | 0.94                 | 1.25    | 3.08                | 52.0     | 53                             | 21 | 26 | S.C.L.  |
|             | 6           | 8.53     | 3.02                 | 0.97    | 13.10               | 30.3     | 75                             | 6  | 19 | S.L.    |
| 4           | 1           | 7.80     | 1.90                 | 2.25    | 7.59                | 75.4     | 21                             | 20 | 59 | C.      |
|             | 2           | 7.67     | 0.76                 | 1.90    | 3.23                | 74.3     | 15                             | 26 | 59 | C.      |
|             | 3           | 7.71     | 0.83                 | 2.30    | 2.20                | 67.5     | 25                             | 27 | 48 | C.      |
|             | 4           | 7.93     | 0.88                 | 1.98    | 2.90                | 62.6     | 34                             | 29 | 37 | C. L.   |
|             | 5           | 7.98     | 1.02                 | 1.45    | 3.59                | 61.7     | 43                             | 15 | 42 | C.      |
|             | 6           | 8.15     | 1.00                 | 1.21    | 17.00               | 25.3     | 85                             | 5  | 10 | L.S.    |
| 5           | 1           | 7.75     | 1.89                 | 2.15    | 7.50                | 77.3     | 20                             | 27 | 53 | C.      |
|             | 2           | 7.87     | 0.91                 | 1.34    | 2.42                | 69.9     | 30                             | 25 | 45 | C.      |
|             | 3           | 8.12     | 0.80                 | 1.27    | 2.49                | 31.5     | 81                             | 8  | 11 | S.L.    |
|             | 4           | 7.76     | 0.72                 | 1.81    | 2.42                | 63.0     | 37                             | 34 | 29 | C.L.    |
|             | 5           | 7.62     | 1.14                 | 2.28    | 2.35                | 64.4     | 46                             | 35 | 19 | L.      |
|             | 6           | 7.80     | 1.07                 | 2.68    | 5.42                | 82.1     | 25                             | 38 | 37 | C.L.    |

\* S = Sand, L = Loam, Si = Silt and C = Clay.

**Table (2): Levels of the DTPA- extractable Fe, Mn, Zn and Cu.**

| Transect No | Location No | DTPA-extractable Micronutrients (mg/kg) |       |      |      |
|-------------|-------------|---|-------|------|------|
|             |             | Fe                                      | Mn    | Zn   | Cu   |
| <b>1</b>    | 1           | 16.07                                   | 22.46 | 0.74 | 1.15 |
|             | 2           | 13.08                                   | 31.06 | 0.80 | 3.60 |
|             | 3           | 17.27                                   | 35.10 | 0.66 | 3.55 |
|             | 4           | 17.85                                   | 37.08 | 0.78 | 3.78 |
|             | 5           | 13.71                                   | 13.12 | 0.55 | 2.72 |
| <b>2</b>    | 1           | 11.65                                   | 23.20 | 0.63 | 1.09 |
|             | 2           | 13.62                                   | 27.02 | 0.88 | 2.73 |
|             | 3           | 14.88                                   | 46.88 | 0.65 | 2.98 |
|             | 4           | 11.62                                   | 27.12 | 1.05 | 3.00 |
|             | 5           | 39.63                                   | 34.20 | 0.43 | 1.20 |
|             | 6           | 32.42                                   | 37.34 | 0.98 | 3.34 |
| <b>3</b>    | 1           | 19.06                                   | 35.12 | 0.87 | 4.31 |
|             | 2           | 14.04                                   | 29.50 | 0.70 | 3.25 |
|             | 3           | 13.75                                   | 41.44 | 1.12 | 3.02 |
|             | 4           | 14.03                                   | 67.70 | 0.63 | 2.85 |
|             | 5           | 12.37                                   | 32.62 | 0.47 | 2.54 |
|             | 6           | 17.00                                   | 24.44 | 0.80 | 0.47 |
| <b>4</b>    | 1           | 11.37                                   | 74.72 | 1.25 | 3.54 |
|             | 2           | 21.80                                   | 55.34 | 1.06 | 4.14 |
|             | 3           | 15.72                                   | 60.82 | 1.00 | 4.09 |
|             | 4           | 37.14                                   | 83.10 | 2.04 | 5.10 |
|             | 5           | 15.52                                   | 70.26 | 0.69 | 2.85 |
|             | 6           | 14.24                                   | 3.96  | 0.37 | 0.60 |
| <b>5</b>    | 1           | 16.27                                   | 77.72 | 0.50 | 3.35 |
|             | 2           | 30.61                                   | 39.50 | 0.41 | 4.05 |
|             | 3           | 14.28                                   | 34.28 | 0.78 | 1.60 |
|             | 4           | 28.47                                   | 42.10 | 0.58 | 3.38 |
|             | 5           | 22.00                                   | 33.08 | 0.80 | 3.13 |
|             | 6           | 25.57                                   | 70.20 | 1.16 | 4.39 |

#### ■ Zinc and Copper Fractionation

Sequential extractions were prepared by placing two grams of each surface soil sample in a 50 ml centrifuge tube. To extract the soluble and exchangeable form (Exch.), 20 ml of 1M ammonium acetate at pH 7 were added, shaken for 2 h, centrifuged for 10 min. at 4000 rpm, and then filtrated (Kabala, 2001; Abdel salam, 2003). After collecting the previous solution, the form that is bound to soil carbonates (Carb.) was extracted by adding 30 ml of 1M sodium acetate at pH 5, added to each tube, shakeing for 5 h, centrifuging and filtering as in the previous step (Ahnstrom and Parker, 1999). Forms of Zn and Cu that bound to Mn oxides (Mn Ox) were collected by adding 20 ml of 0.1M hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) at pH 2 to each tube, shaking for 30 min, centrifuging and filtering as shown by Sims (1986). After collecting the supernatant, 4 ml of distilled water and 2 ml of hydrogen peroxide (30%) were added to the soil sample in each tube and then evaporated on a steam bath to the original suspension level; additional 2 ml of 30% H<sub>2</sub>O<sub>2</sub> were added with heating until dryness (Shuman, 1979). The

soil sample in each tube was then cooled, shaken for 2h with 20 ml of 1M ammonium acetate at pH 7, centrifuged and filtrated. The collected extract contains the form that is bound to the organic matter (O-bound).

**Fig. 1. Locations of the studied soils**

To extract the form of Zn and Cu cations that is bound to the poorly crystalline Fe oxides (PCFeOx) according to Shuman (1979), 20 ml of a solution containing 0.2M ammonium oxalate  $[(\text{NH}_4)_2\text{C}_2\text{O}_4]$  and 0.2M oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) at pH 3 were added to the remained soil sample in each tube, shaken for 4h in dark, centrifuged and filtrated. The forms of Zn and Cu that is bound to the crystalline Fe oxides (CFeOx) were extracted by adding 20 ml of citrate buffer solution (Na citrate dihydrate+ $\text{NaHCO}_3$ + NaCl) adjusted at pH

7.3 (Kittrich and Hope, 1963) to the remained soil sample in each tube. Then, each sample was placed in a water bath at 80°C and 1gm of sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) was added to each sample with stirring for 15 min. Each sample was left to cool up, centrifuged and filtered. The supernatant was collected in a 50 ml volumetric flask, completed with distilled water.

The total content of Zn and Cu in each surface soil sample was obtained by digesting 0.5 g soil sample with concentrated acids of HF,  $\text{HNO}_3$  and HCl in sequence (Shuman, 1979). Zinc and copper in each extract were determined using a GBC 906 atomic absorption spectrophotometer. The residual form (Res.) was obtained by subtracting the sum of extracted forms from the total content (Usman, 2004).

## RESULTS AND DISCUSSION

The mean Zn levels of the investigated forms of the studied soil samples were 0.21, 0.40, 0.35, 0.57, 3.65, 2.65 and 88.08 mg/kg for the exchangeable, carbonate bound, Mn oxide, organically bound, poorly crystalline iron oxide, crystalline iron oxide and residual forms, respectively. Levels of the total Zn in these soils changed from 24.20 to 167.00 mg/kg with an average of 95.89 mg/kg. The concentration of Zn in these forms decreased in the order of: residual > PCFeOx > CFeOx > organically bound > carbonate bound > Mn Ox > exchangeable form. These respective forms represented 91.86, 3.81, 2.76, 0.59, 0.42, 0.37 and 0.22% of the total Zn in the soil samples. The total Zn content of some soils of upper Egypt was reported to vary from 18.00 to 180.00 mg/kg (Ghoneim et al., 1984a). Liang et al., (1990) found that Zn bound to the organic fraction in some soils of southeastern USA ranged from 0.16 to 1.92 mg/kg. As it is clear in the investigated soil samples, Iyengar et al. (1981) also reported that the highest levels of Zn were recorded in the residual fraction.

The distribution of Cu in its forms followed the same trend as Zn with the exception that Mn oxide bound Cu was lower than the exchangeable one. The mean concentration of Cu in the residual, crystalline iron oxide, poorly crystalline iron oxide, organically bound, Mn oxide, carbonate bound and exchangeable form was 43.62 (82.69% of the total Cu), 1.35 (2.56% of the total Cu), 5.06 (9.59% of the total Cu), 0.94 (1.78% of the total Cu), 0.33 (0.63% of the total Cu), 0.82 (1.55% of the total Cu) and 0.63 mg/kg (1.19% of the total Cu), respectively. The amount of the total Cu in these studied soils varied between 8.25 and 80.20 mg/kg with an average level of 52.75 mg/kg. Ghoneim et al. (1984b) reported that the total Cu in soils of Assiut Governorate ranged between 14.30 and 102.80 mg/kg with an average level of 53.60 mg/kg. In Sohag Governorate soils, Ibrahim et al. (2001) found that the total Cu content ranged between 0.80 and 53.00 mg/kg with an average value of 33.00 mg/kg.

The concentrations of Zn in the Exch., Carb., MnOx and O-bound were very low in all the locations of transect 1 with values less than 1.00 mg/kg (Fig. 2). However, both PCFeOx and CFeOx forms had higher values reaching 5.20 and 2.80 mg/kg, respectively. The first location of this transect had lowest levels of both residual and total Zn (20.00 and 24.20 mg/kg,

respectively), while the third location contained the highest ones (106.25 and 112.60 mg/kg, respectively). Concentrations of the exchangeable Zn in some soils of southeastern USA ranged from 0.07 to 1.54 mg/kg (Liang et al., 1990). Moreover, Shuman (1985) found that the values of Zn in CFeOx in some soils of southeastern USA ranged from 0.75 to 18.58 mg/kg.

The values of Cu in the exchangeable, Mn oxides and organically bound forms of transect 1 soils were less than 1 mg/kg. They were somewhat higher than 1 mg/kg in the carbonate and crystalline iron forms (Fig. 2). Copper in the poorly crystalline iron oxide in the soils of this transect was higher than that of the other forms reaching 5.40 mg/kg. The residual Cu had the highest level in all locations of this transect, reaching a value of 46.25 mg/kg. However, it was as low as 2.75 mg/kg in the first location. Liang et al. (1991) found that the exchangeable Cu in Saskatchewan soils ranged between 0.30 and 0.80 mg/kg. In addition, Abdel Salam (2003) found that levels of Cu in the carbonate form in some soils of the western area of the Nile Delta varied from 1.60 to 4.38 mg/kg.

Four forms (Exch., Carb., MnOx and O-bound) of most tested soil samples of transect 2 were very low in Zn (Fig. 3). Zinc concentration in the PCFeOx form was always higher than that of the crystalline iron oxide one. Most of the total Zn in the soils of this transect was found in the residual form. Location 4 contained the highest Zn values in most studied forms. Abdel Salam (2003) found that the exchangeable Zn in some soils of the western area of the Nile Delta ranged between 1.10 and 2.02 mg/kg. In some northern American soils, Neilsen et al. (1986) found that the concentration of Zn in MnOx form varied from 4.30 to 42.40 mg/kg with an average level of 13.10 mg/kg.

The average contents of Cu in the Exch., Carb., MnOx, O-bound and CFeOx forms in the soils of transect 2 was as low as 0.70, 1.28, 0.47, 1.00 and 1.67 mg/kg, respectively, while it was higher (5.17 mg/kg) in the PCFeOx form (Fig. 3). It is obvious that the total and residual Cu in this transect were very low in locations no. 1 (18.00 and 10.55 mg/kg, respectively) and no.5 (22.20 and 13.35 mg/kg, respectively). However, in location no. 4, they were as high as 67.40 and 55.70 mg/kg, respectively. Elkhatab et al. (1994) found that the concentration of Cu in the carbonate form of Edku lake sediments varied between 0.32 and 0.71 mg/kg. Moreover, Abdel Salam (2003) reported that the average values of total Cu in alluvial soils of Egypt (28.50 mg/kg) were higher than those of calcareous soils (12.80 mg/kg).

**Fig.2: Zinc and Cu forms (mg/kg) in the studied soils of Transect 1.**

**Fig.3: Zinc and Cu forms (mg/kg) in the studied soils of Transect 2.**



In half of the locations of transect 3, the exchangeable Zn was not detectable (Fig. 4). Zinc levels in most of the Carb., MnOx and O-bound forms of the soils of this transect were lower than 1.00 mg/kg. On the other hand, Zn in the PCFeOx form was always higher than that of the CFeOx one except in soil of location no. 6. The residual and total Zn in this transect ranged from 93.3 to 136.20 mg/kg and from 100.80 to 142.80 mg/kg, respectively, except in location 6 where they had much lower contents (48.25 and 56.50 mg/kg, respectively). Neilsen et al. (1986) reported that the concentration of Zn in the organic fraction varied from 0.30 to 39.30 mg/kg. Shuman (1985) found that levels of Zn in the poorly crystalline Fe oxides of some soils of southeastern US ranged from 0.00 to 4.83 mg/kg.

Regarding Cu levels in the soils of transect 3, they varied from 0.1 to 0.60 mg/kg for Exch., from 0.6 to 1.50 mg/kg for Carb., from 0.20 to 0.70 mg/kg for MnOx, from 0.20 to 1.3 mg/kg for O-bound, from 4.30 to 6.90 mg/kg for PCFeOx, from 0.25 to 2.00 mg/kg for CFeOx and from 19.50 to 70.75 mg/kg for residual form as well as from 26.20 to 80.20 mg/kg for the total Cu. The mean values of Cu in the CFeOx form of these soils were in clay > loamy > sandy soils. Content of Cu in the CFeOx form in some soils ranged between 0.50 and 20.50 mg/kg (Shuman, 1985). Qian et al. (2003) reported that the residual Cu was strongly held within silicate minerals structure.

**Fig.4: Zinc and Cu forms (mg/kg) in the soils of Transect 3.**

In soils of transect 4 (Fig.5), zinc levels were almost the same in the exchangeable, carbonate bound, Mn oxide and organically bound forms. Moreover, Zn bound to both PCFeOx and CFeOx were also about the same. The results illustrated in Fig. 5 showed that the soil of location 6 contained the lowest Zn values in the residual, organically bound and crystalline iron oxide forms (48.25, 0.10 and 2.05 mg/kg, respectively) as well as in the total content (56.50 mg/kg), however it contained the highest Zn level (1.80 mg/kg) of carbonate form. Neilsen et al. (1986) reported that the total content of Zn in unpolluted north American soils ranged from 10.00 to 300.00 mg/kg. Zinc was shown to be strongly bound in the residual fraction even up to 98% of its total content (Narwal et al., 1999).

The lowest Cu values in the studied soil forms of this transect were found in those of location 6 (Fig. 5). Zinc in the organically bound form had the highest level (2.00 mg/kg) in the soil of location 4 of this transect. The highest Zn levels in both CFeOx and PCFeOx forms (3.50 and 8.80 mg/kg, respectively) were shown in the soil samples of location 2. The concentration of Cu in MnOx form of Saskatchewan soils ranged from 0.60 to 1.70 mg/kg (Liang et al., 1991). The results of (Shuman, 1979) showed that the concentration of Cu in the organic form ranged between 0.62 and 5.23 mg/kg. Abdel Salam (2003) found that the total Zn was from 91.76 to 74.42 mg/kg in the alluvial soils and from 45.41 to 84.04 mg/kg in the calcareous soils of Egypt with mean values in the alluvial soils greater than in calcareous ones.

**Fig.5: Zinc and Cu forms (mg/kg) in the studied soils of Transect 4.**

Zn levels in the exchangeable and carbonate forms in most of the locations of transect 5 were not detectable, whereas, in the organically bound and Mn oxide ones, they were almost the same (Fig 6). Zinc bound to the poorly crystalline iron oxide in the soils of this transect was always higher than that bound to the crystalline iron oxides; it ranged from 2.90 to 4.10 mg/kg in PCFeOx and 1.80 to 2.55 mg/kg in CFeOx. Values of residual and total Zn were much lower in this transect than in all other transects with an average values of 47.27 and 54.20 mg/kg, respectively, except those of the first location that contained 23.70 and 130.25 mg/kg, respectively. Neilsen et al. (1986) found that the content of residual Zn ranged from 42.30 to 132.3 mg/kg and comprised from 45.6 to 92.0 % of total soil Zn. Abdel Salam (2003) found that the total Zn was from 91.76 to 74.42 mg/kg in the alluvial soils of Egypt and from 45.41 to 84.04 mg/kg in the calcareous ones with mean values of alluvial soils greater than calcareous ones.

A half of the locations of this transect contained non-detectable Cu values in both organically bound and Mn oxide bound forms (Fig 6). The concentration of Cu in the exchangeable and organically bound forms of the soils of this transect ranged from 0.30 to 1.40 mg/kg and from 0.30 to 1.70 mg/kg, respectively. Levels of Cu in the poorly crystalline iron oxide form in all locations was about twice those bound to the crystalline iron oxides except those of location 2 which contained 0.90 and 2.25 mg/kg, respectively. The soils of location 3 contained the lowest values of residual and total Cu (27.15 and 32.00 mg/kg, respectively), while that of location 1 had the highest ones (58.95 and 68.50 mg/kg, respectively). Liang et al. (1991) reported that the values of Cu in the organic form ranged from 0.33 to 2.43 mg/kg. Copper in the residual fraction was about 88 and 97 % of total Cu in the silty and clay loamy soils, respectively (Kabala and Singh, 2001). In Egyptian soils, Abdel Salam (2003) found that the mean values of Cu in the organic form of the alluvial soils were higher than those of the calcareous ones. Shuman (1985) showed that the Cu levels in the poorly crystalline Fe oxides ranged from 0.17 to 4.83 mg/kg.

**Fig.6: Zinc and Cu forms (mg/kg) in the studied soils of Transect 5.**

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دراسات على صور الزنك و النحاس فى أراضي محافظة أسيوط  
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تم تقسيم محافظة أسيوط بواسطة خمسة محاور عبر وادى النيل فى إتجاه من الشرق إلى الغرب وذلك لتحديد الصور المختلفه من الحديد و المنجنيز فى هذه الاراضى. تم جمع عينات سطحيه من متوسط ستة مواقع فى كل محور. تم تقدير ستة صور من الزنك و النحاس وهى : الصور المتبادله، المرتبطه بالكربونات، المرتبطه بأكاسيد المنجنيز، المرتبطه بالماده العضويه، المرتبطه بأكاسيد الحديد ضعيفة التبلور، المرتبطه بأكاسيد الحديد المتبلوره بالإضافة إلى الكميه الكليه لكل عنصر. تم حساب الصوره المتبقية بواسطة عملية الطرح.

تناقص تركيز الصور المختلفه من الزنك بالترتيب الآتى: متبقى < مرتبط بأكاسيد حديد ضعيفة التبلور < مرتبط بأكاسيد حديد متبلوره < مرتبط بالماده العضويه < مرتبط بالكربونات < مرتبط بأكاسيد المنجنيز < متبادل. هذه الكميات المتتاليه كانت تمثل 91.86 , 3.81 , 2.76 , 0.59 , 0.42 , 0.37 و 0.22 % من الزنك الكلى. متوسط محتوى التربيه من النحاس المتبقى , المرتبط بأكاسيد الحديد المتبلوره , المرتبط بأكاسيد الحديد ضعيفة التبلور , المرتبط بالماده العضويه , المرتبط بأكاسيد المنجنيز , المرتبط بالكربونات و المتبادل كان 43.62 (82.69% من النحاس الكلى) , 1.35 (2.56% من النحاس الكلى) , 5.06 (9.59% من النحاس الكلى) , 0.94 (1.78% من النحاس الكلى) , 0.33 (0.63% من النحاس الكلى) , 0.82 (1.55% من النحاس الكلى) و 0.63 مللجم/كجم ( 1.19% من النحاس الكلى) على التوالى. كان متوسط الكميه الكليه من النحاس فى هذه الاراضى تساوى 52.75 مللجم/كجم.