# STATUS OF IRON AND MANGANESE FORMS IN SOILS OF ASSIUT

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## ABSTRACT

Six transects were taken across the Nile valley in the east-west direction in Assiut Governorate in order to determine the different forms of iron and manganese in these soils. Surface soil samples were collected from an average of 6 locations in each transect in the winter of 2003/2004. Six forms of Fe and Mn were determined, exchangeable (Exch.), carbonate bound (Carb.), Mn oxides bound (MnOx), organic bound (O-bound), poorly crystalline iron oxides bound (PCFeOx) and crystalline iron oxides bound (CFeOx) along with the total content of both elements. The residual fraction was calculated by the substraction.

Values of Fe in the carbonate form ranged from 0.00 to 11.25 mg/kg (0.007% of the total Fe). Concentrations of Fe in Mn oxide and organic bound forms represented 0.018 and 0.009% of total Fe, respectively. About 34% of the samples contained less than 1000 mg/kg of Fe bound to the poorly crystalline iron oxides, while 23.7% contained more than 2000 mg/kg. Values of Fe in the crystalline Fe oxide form ranged from 740 to 17914 mg/kg (15.52% of the total Fe). Residual Fe in soils under study had values varied between 8.36 and 94.67 g/kg with an average of 45.63 g/kg (82.11% of the total Fe). The content of the total Fe ranged from 9.73 to 105.52 g/kg with an average of 55.58 g/kg.

Levels of Mn in the soluble + exchangeable forms (Exch.) ranged between 1.20 and 13.20mg/kg (0.51% of the total Mn). Values of Mn ranged from 14.25 to 78.00 mg/kg (4.29% of the total Mn), 26.00 to 420.00 mg/kg (28.88% of total Mn) and 6.00 to 324.4 mg/kg (20.00 % of the total Mn) in the carbonate, Mn oxide and organic forms. Concentrations of Mn in the poorly crystalline Fe oxide form varied from 2.50 to 125.60 mg/kg (6.07% of the total Mn). The values of residual Mn ranged from 31.60 to 581.90 mg/kg (35.06 of the total Mn). Values of total Mn in the tested soils ranged from 149.20 to 1310.00mg/kg.

Keywords: iron, manganese, fractionation, forms, total, residual.

#### INTRODUCTION

Three forms of free metal ions were identified in the soil solution by McLean and Bledsoe (1992). Two forms of them were soluble complexes (inorganic and organic), and the third was associated with mobile inorganic and organic colloidal materials. The interaction between metals and fulvic acids produce most metal-organic complex forms (Baham et al., 1978; Boyd et al., 1979 and 1983; Sposito et al., 1979 and 1981; Bahel et al., 1983; Lake et al., 1984; Baham and Sposito, 1986; Dudley et al., 1987). Gschwend and Reynolds (1987) reported that the colloidal particles of intermediate diameter, which include iron and manganese oxides, clay minerals and organic matter that have a high capacity for metal sorption, were the most mobile particles in sandy medium.

Various studies indicated that iron in soils exists in several forms: (1) soluble iron forms such as  $Fe^{3+}$ , Fe (OH)<sup>2+</sup> and  $Fe^{2+}$ , besides some soluble organic complexes, (2) exchangable iron, (3) complexed and chelate organic

forms, (4) bound to carbonates such as siderite (FeCO<sub>3</sub>) and ferric carbonate Fe<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and bound to sulfide such as pyrite (FeS<sub>2</sub>) and ferrous mono sulfide (FeS), (5) oxide and oxyhydroxide forms such as  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>(maghemite),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(hematite), Fe<sub>3</sub>O<sub>4</sub>(magnetite),  $\alpha$ -FeOOH(goethite), and  $\gamma$ -FeOOH (lepidocrocite), and (6) occuled in primary and secondary silicate minerals (Sauchelli, 1969; Lindsay, 1979; FAO, 1983; El-Desoky, 1989; Kabata-Pendias and Pendias, 1992). Tisdale et al. (1997) indicated that the total Fe in soil ranges from 0.7 to 55% and most of it is found in the forms of primary minerals, clays, oxides and hydroxides.

Manganese exist in many chemical forms in soils: (1) dissolved in soil solution (2) exchangeable on soil particle surfaces, (3) bound to soil organic matter, (4) occluded in secondary minerals, such as MnO<sub>2</sub> (pyrolusite), Mn<sub>2</sub>O<sub>3</sub> (bixbyite),  $Mn_3O_4$  (hausmannite),  $Mn_2O_3.H_2O$  (manganite), Mn(OH)<sub>2</sub> (pyrochroite), MnCO<sub>3</sub> (rhodochriste), MnSiO<sub>3</sub> (rhodonite) and Mn<sub>2</sub>SiO<sub>4</sub> (tephroite), and (5) occluded in primary minerals, such as hornblende, biotite, olivine, garnet and augite, (Sauchelli, 1969; Sims and Patrick, 1978; Lindsay, 1979). Tisdale and Nelson (1975) reported that Mn exists in three valence states in equilibrium to each other: (1) the divalent manganese, Mn<sup>2+</sup>, which is present as an adsorbed cation or in soil solution, (2) trivalent manganese,  $Mn^{3+}$ , which is supposed to exist as a highly reactive oxide,  $Mn_2O_3$ , and (3) tetravalent manganese, Mn4+, which exists as the very inert oxide, MnO2. Baruah and Barthakur (1997) reported that available Mn includes some forms, such as water soluble, exchangeable, reducible and active forms.

This investigation aimed to evaluate the levels and forms of iron and manganese in the soils of Assiut Governorate.

# MATERIALS AND METHODS

Assiut governorate is located 325 km south of Cairo with an area about 1558 km<sup>2</sup> representing 0.15% of the total area of Egypt. Soils of Assiut governorate have an irregular relief, whereas the soil surface varies from smooth to almost flat and slightly slope toward the west (Fig. 1). The predominant climate is arid. The rainfall in the area is practically nil, except some light showers that rarely fall during winter and some unrecorded flash floods coming from the Eastern desert (Said, 1981).

Assiut Governorate was divided into 6 transects, that were taken across the Nile valley in the east-west direction. An average of 6 locations were chosen in each transect. Surface soil samples from each location were collected in the winter of 2003/2004. Most of the soils were under cultivation by wheat, faba bean, clover and rarely with other winter crops. The collected soil samples were air-dried, crushed, passed through a 2 mm sieve and kept for subsequent analysis. Some of 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). In a 1:1 of soil: water suspension, soil pH was determined using a glass electrode (Jackson, 1973). Calcium Carbonate (CaCO<sub>3</sub>) was estimated using a volumetric calcium carbonate

calcimeter (Nelson, 1982). According to Hesse (1998), electrical conductivity of the saturated soil paste (EC<sub>e</sub>) was measured using an electrical conductivity meter. 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).

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

#### Iron and Manganese Fractionation

Forms of both Fe and Mn were determined using a sequential extraction method. These forms included the soluble + exchangeable, carbonate-bound, Mn oxide-bound, organic-bound, poorly crystalline Fe oxide-bound and crystalline Fe oxide-bound as well as the residual form. The total contents of both elements were also determined.

Two grams of each surface soil sample were placed in a 50 mlcentrifuge tube to make the sequential extraction. The soluble and exchangeable form (Exch.) was extracted by using 20 ml of 1M ammonium acetate at pH 7, shaking for 2 h, centrifuging for 10 min. at 4000 rpm, and then filtrating (Kabala, 2001; Abdel salam, 2003). After collecting the previous solution, 30 ml of 1M sodium acetate at pH 5 were added to each tube, shaken for 5 h, centrifuged and filtered as in the previous step. As described

by Ahnstrom and Parker (1999), this collected solution contained the form that is bound to soil carbonates (Carb.). To extract Fe and Mn cations that are bound to Mn oxides (MnOx), 20 ml of 0.1M hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl) at pH 2 were added 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%  $H_2O_2$  were added with heating until dryness (Shuman, 1979).

| Transect | Location<br>No | рН   | ECe  | O.M<br>(%) | 0-000 | S.P.<br>(%) | Particle size   |    |       |           |
|----------|----------------|------|------|------------|-------|-------------|-----------------|----|-------|-----------|
| No       |                |      |      |            |       |             | Distribution (% |    | n (%) | Texture   |
|          |                |      |      |            | (%)   |             | S               | Si | C     | l         |
| 1        | 1              | 7.96 | 1.3  | 1.31       | 3.79  | 49.2        | 54              | 14 | 32    | S. C. L.* |
|          | 2              | 7.67 | 0.80 | 2.10       | 1.91  | 55.5        | 35              | 48 | 17    | L.        |
|          | 3              | 7.67 | 0.80 | 1.11       | 1.46  | 37.8        | 76              | 10 | 14    | S.L.      |
|          | 4              | 7.73 | 0.84 | 1.31       | 2.11  | 46.5        | 63              | 21 | 16    | S.L.      |
|          | 5              | 8.44 | 0.88 | 0.46       | 1.32  | 27.3        | 84              | 5  | 11    | L.S.      |
|          | 6              | 7.72 | 0.80 | 1.58       | 3.04  | 59.0        | 44              | 15 | 41    | C.        |
| 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              | 8.08 | 0.80 | 0.55       | 3.73  | 16.9        | 89              | 4  | 7     | L. S.     |
|          | 2              | 7.76 | 2.10 | 2.12       | 2.45  | 59.0        | 44              | 37 | 19    | C. L.     |
|          | 3              | 7.95 | 0.85 | 1.21       | 2.01  | 40.4        | 68              | 10 | 22    | S. C.L.   |
|          | 4              | 7.95 | 3.33 | 2.24       | 6.31  | 61.4        | 35              | 31 | 34    | C.L.      |
|          | 5              | 7.75 | 0.73 | 1.33       | 3.06  | 65.3        | 24              | 36 | 40    | C.        |
|          | 6              | 8.02 | 1.52 | 0.85       | 23.85 | 21.4        | 87              | 3  | 10    | L. S.     |
| 4        | 1              | 7.75 | 1.24 | 1.22       | 4.60  | 27.3        | 79              | 3  | 18    | S. L.     |
|          | 2              | 7.80 | 1.86 | 2.31       | 3.23  | 72.3        | 21              | 27 | 52    | C.        |
|          | 3              | 7.91 | 1.72 | 1.70       | 3.31  | 60.0        | 42              | 19 | 39    | C. L.     |
|          | 4              | 7.55 | 0.90 | 1.49       | 0.96  | 57.1        | 31              | 37 | 32    | C.L.      |
|          | 5              | 7.81 | 1.22 | 2.04       | 3.41  | 68.0        | 32              | 30 | 38    | C. L.     |
|          | 6              | 8.12 | 1.30 | 0.82       | 14.61 | 26.0        | 86              | 2  | 12    | L. S.     |
| 5        | 1              | 8.04 | 1.54 | 1.68       | 25.03 | 37.0        | 58              | 15 | 27    | S. C.L.   |
|          | 2              | 8.25 | 0.92 | 1.14       | 2.44  | 67.9        | 16              | 34 | 50    | С.        |
|          | 3              | 7.98 | 0.83 | 2.01       | 4.58  | 71.0        | 16              | 38 | 46    | C.        |
|          | 4              | 7.77 | 0.72 | 1.14       | 0.89  | 60.7        | 52              | 23 | 25    | S. C.L.   |
|          | 5              | 7.80 | 1.67 | 2.42       | 4.09  | 59.7        | 37              | 36 | 27    | L.        |
|          | 6              | 7.84 | 0.90 | 2.01       | 2.89  | 86.4        | 11              | 33 | 56    | C.        |
|          | 7              | 7.52 | 1.84 | 1.61       | 5.54  | 76.0        | 28              | 20 | 52    | C.        |
| 6        | 1              | 7.60 | 1.30 | 2.21       | 3.07  | 67.7        | 32              | 36 | 32    | C. L.     |
|          | 2              | 7.83 | 0.75 | 2.01       | 2.95  | 71.5        | 23              | 35 | 42    | C.        |
|          | 3              | 7.73 | 0.83 | 1.48       | 2.80  | 61.6        | 66              | 16 | 18    | S. L.     |
|          | 4              | 7.90 | 0.72 | 1.34       | 2.56  | 54.7        | 53              | 28 | 19    | S. L      |
|          | 5              | 7.90 | 0.95 | 2.80       | 1.32  | 67.2        | 31              | 35 | 34    | C.L.      |
|          | 6              | 7.74 | 0.81 | 1.71       | 3.42  | 60.2        | 43              | 25 | 32    | C.L.      |
|          | 7              | 7.90 | 1.10 | 1.71       | 16.63 | 27.6        | 78              | 10 | 12    | S.L.      |

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

S = Sand, L = Loam, Si = Silt and C = Clay

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. This collected extract contained the form that is bound to the organic matter (O-bound).

| Transect | Location No | DTPA-extractable       |       |      |      |  |  |
|----------|-------------|------------------------|-------|------|------|--|--|
| No       |             | Micronutrients (mg/kg) |       |      |      |  |  |
|          |             | Fe                     | Mn    | Zn   | Cu   |  |  |
| 1        | 1           | 16.14                  | 30.16 | 0.87 | 2.97 |  |  |
|          | 2           | 35.01                  | 41.02 | 0.95 | 4.02 |  |  |
|          | 3           | 34.30                  | 35.74 | 0.94 | 1.65 |  |  |
|          | 4           | 29.87                  | 35.08 | 0.91 | 2.83 |  |  |
|          | 5           | 31.25                  | 17.62 | 0.48 | 0.95 |  |  |
|          | 6           | 46.22                  | 37.78 | 0.73 | 4.58 |  |  |
| 2        | 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 |  |  |
| 3        | 1           | 7.70                   | 14.50 | 0.55 | 0.78 |  |  |
|          | 2           | 16.10                  | 36.76 | 1.12 | 3.49 |  |  |
|          | 3           | 18.04                  | 35.24 | 0.71 | 2.10 |  |  |
|          | 4           | 15.25                  | 50.86 | 1.30 | 4.67 |  |  |
|          | 5           | 12.13                  | 38.57 | 0.57 | 3.85 |  |  |
|          | 6           | 13.47                  | 11.76 | 0.47 | 0.47 |  |  |
| 4        | 1           | 13.84                  | 33.88 | 0.77 | 1.05 |  |  |
|          | 2           | 13.21                  | 87.74 | 1.00 | 3.68 |  |  |
|          | 3           | 10.20                  | 12.60 | 0.85 | 3.25 |  |  |
|          | 4           | 13.04                  | 24.42 | 0.62 | 2.74 |  |  |
|          | 5           | 30.19                  | 8.06  | 0.85 | 0.84 |  |  |
|          | 6           | 12.73                  | 22.02 | 0.60 | 3.60 |  |  |
| 5        | 1           | 17.22                  | 46.70 | 0.83 | 3.32 |  |  |
|          | 2           | 27.85                  | 77.62 | 0.34 | 4.15 |  |  |
|          | 3           | 14.67                  | 84.16 | 1.47 | 4.13 |  |  |
|          | 4           | 27.40                  | 24.90 | 0.37 | 3.48 |  |  |
|          | 5           | 20.29                  | 41.22 | 1.50 | 4.10 |  |  |
|          | 6           | 21.51                  | 98.88 | 0.69 | 4.18 |  |  |
|          | 7           | 27.73                  | 76.32 | 1.04 | 3.47 |  |  |
| 6        | 1           | 14.15                  | 19.48 | 0.44 | 3.02 |  |  |
|          | 2           | 15.62                  | 20.20 | 0.38 | 3.33 |  |  |
|          | 3           | 19.38                  | 24.40 | 0.46 | 3.08 |  |  |
|          | 4           | 35.45                  | 18.44 | 0.38 | 1.20 |  |  |
|          | 5           | 20.90                  | 25.78 | 0.40 | 2.78 |  |  |
|          | 6           | 17.03                  | 29.18 | 0.72 | 3.18 |  |  |
|          | 7           | 18.80                  | 20.86 | 0.65 | 2.59 |  |  |

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

The form of Fe and Mn cations that is bound to the poorly crystalline Fe oxides (PCFeOx) was extracted according to Shuman (1979) by adding 20 ml of a solution containing 0.2M ammonium oxalate  $[(NH_4)_2C_2O_4]$  and

0.2M oxalic acid ( $H_2C_2O_4$ ) at pH 3 to the remained soil sample in each tube, shaked for 4h in dark, centrifuged and filtrated. To extract the form of that is bound to the crystalline Fe oxides (CFeOx), 20 ml of citrate buffer solution (Na citrate dihydrate+NaHCO<sub>3</sub>+ NaCl) adjusted at pH 7.3 (Kittrich and Hope, 1963) were added 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 (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) 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 Fe and Mn in each surface soil sample was obtained by digesting 0.5 g soil sample with concentrated acids of HF, HNO<sub>3</sub> and HCl in sequence (Shuman, 1979). Iron and manganese 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 contents (Usman, 2004).

## **RESULTS AND DISCUSSION**

# 1- Iron

Table (3) shows that in all studied sites, the soluble + exchangeable (Exch.) form of iron was not detectable. Shuman (1985) found that iron in the exchangeable form was negligible compared to the amounts found in the crystalline iron oxide and residual forms. Abollino et al. (2002) also reported that the values of exchangeable Fe ranged from 0.001 to 0.178% of the total.

The carbonate bound form of Fe of the studied soils ranged from 0.00 to 11.25 mg/kg with an average of 2.1 mg/kg (0.007% of the total). A value as high as 61.38 mg/kg was found in the sandy soil of T6/L4. Most of the soil samples (87% of the samples) had values less than 5mg/kg. Abollino et al. (2002) found that Fe bound to the carbonate varied from 0.103 to 0.899% of total Fe.

Iron bound to Mn oxide ranged from 0.60 (T5/L1) to 35.30 mg/kg (T1/L5) with an average of 8.34 mg/kg (0.018% of the total Fe). However, only one sample (T6/L4) contained a highest value of 64.80 mg/kg. More than half of the samples (68.4%) contained less than 5mg/kg of this form, while only 5 samples (13.2%) contained more than 20mg/kg (Table 3). The concentration of Fe in MnOx form in some soils of southeastern USA ranged between 14.50 and 1029.00 mg/kg (Shuman, 1985). Amounts of the Fe in MnOx form ranged from 519 to 940 mg/kg (Sims and Patrick, 1978).

Concentrations of Fe bound to the organic fraction ranged from 0.00 to 21.40 mg/kg with an average of 5.25 mg/kg (0.009% of total Fe). The lowest values were found in (T5/L1 and T5/L5), while the highest value was found in T1/L2. Most of the samples (87%) contained less than 9 mg/kg of this form. Shuman (1985) reported that the content of Fe in organic form ranged from 0.00 to 64.45 mg/kg in some soils of southeastern US. Abollino et al. (2002) found that Fe bound to the organic fraction varied between 0.290 and 2.191% of total. Kuo et al. (1983) found that the amounts of Fe associated with organic matter were not detectable.

| Transect | Transect Location Iron Forms (mg/kg) |      |       |       |             |        |       |          | Total  |  |
|----------|--------------------------------------|------|-------|-------|-------------|--------|-------|----------|--------|--|
| No       | No                                   | c    |       |       |             |        |       |          |        |  |
|          |                                      |      |       |       |             |        |       |          |        |  |
|          |                                      | Exch | Carb. | MnOX  | O-<br>bound | PCFeOX | CFeOX | Res.     |        |  |
| 1        | 1                                    | n.d  | 0.45  | 2.00  | 2.00        | 1982   | 9028  | 27397.55 | 38412  |  |
|          | 2                                    | n.d  | 3.45  | 14.10 | 21.40       | 1094   | 17338 | 45936.05 | 64407  |  |
|          | 3                                    | n.d  | 5.40  | 17.80 | 14.30       | 2406   | 8058  | 11098.50 | 21600  |  |
|          | 4                                    | n.d  | 4.50  | 6.70  | 8.90        | 786    | 10788 | 93926.90 | 105521 |  |
|          | 5                                    | n.d  | 4.80  | 35.30 | 3.20        | 1454   | 5247  | 34763.70 | 41508  |  |
|          | 6                                    | n.d  | 9.30  | 24.90 | 19.70       | 2794   | 16917 | 50235.10 | 70000  |  |
| 2        | 1                                    | n.d  | 3.00  | 4.60  | 3.90        | 618    | 4048  | 10945.50 | 15623  |  |
|          | 2                                    | n.d  | 1.20  | 3.20  | 3.30        | 1154   | 9258  | 39086.30 | 49506  |  |
|          | 3                                    | n.d  | 2.10  | 2.20  | 1.90        | 1442   | 9198  | 40065.80 | 50712  |  |
|          | 4                                    | n.d  | 0.30  | 6.10  | 8.10        | 2354   | 16198 | 38333.50 | 56900  |  |
|          | 5                                    | n.d  | 11.25 | 30.90 | 3.00        | 1400   | 5138  | 10133.85 | 16717  |  |
|          | 6                                    | n.d  | 2.55  | 12.70 | 3.70        | 1582   | 10707 | 33707.05 | 46015  |  |
| 3        | 1                                    | n.d  | 0.45  | 2.90  | 1.00        | 344    | 740   | 9216.65  | 10305  |  |
|          | 2                                    | n.d  | 0.45  | 1.70  | 15.40       | 1210   | 13698 | 41576.45 | 56502  |  |
|          | 3                                    | n.d  | 3.30  | 18.90 | 7.60        | 298    | 5480  | 48929.20 | 54737  |  |
|          | 4                                    | n.d  | n.d   | 1.00  | 1.60        | 1058   | 6180  | 45080.40 | 52321  |  |
|          | 5                                    | n.d  | n.d   | 4.90  | 2.40        | 810    | 8478  | 56216.70 | 65512  |  |
|          | 6                                    | n.d  | 5.85  | 3.00  | 0.40        | 178    | 1181  | 8360.75  | 9729   |  |
| 4        | 1                                    | n.d  | 1.80  | 2.60  | 3.00        | 226    | 2258  | 11235.60 | 13727  |  |
|          | 2                                    | n.d  | 0.15  | 2.60  | 3.90        | 602    | 4438  | 56561.35 | 61608  |  |
|          | 3                                    | n.d  | 0.45  | 3.10  | 6.30        | 1010   | 4038  | 43842.15 | 48900  |  |
|          | 4                                    | n.d  | 3.45  | 23.40 | 14.90       | 1498   | 10740 | 56431.25 | 68711  |  |
|          | 5                                    | n.d  | 1.20  | 2.10  | 3.80        | 290    | 5540  | 55392.90 | 61230  |  |
|          | 6                                    | n.d  | 2.70  | 1.40  | 0.70        | 234    | 2420  | 10962.20 | 13621  |  |
| 5        | 1                                    | n.d  | n.d   | 0.60  | n.d         | 194    | 2681  | 42634.40 | 45510  |  |
|          | 2                                    | n.d  | 0.90  | 14.50 | 1.30        | 610    | 5118  | 51076.30 | 56821  |  |
|          | 3                                    | n.d  | 0.15  | 3.00  | 3.00        | 882    | 4539  | 94674.85 | 100102 |  |
|          | 4                                    | n.d  | 1.35  | 8.20  | 6.10        | 1906   | 3980  | 92014.35 | 97916  |  |
|          | 5                                    | n.d  | 2.10  | 5.60  | n.d         | 2495   | 14124 | 64187.30 | 80814  |  |
|          | 6                                    | n.d  | 0.90  | 5.60  | 4.20        | 1090   | 8580  | 77027.90 | 86708  |  |
|          | 7                                    | n.d  | 1.35  | 4.40  | 0.90        | 1294   | 11701 | 42409.35 | 55411  |  |
| 6        | 1                                    | n.d  | n.d   | 4.80  | 3.00        | 2228   | 17914 | 49661.20 | 69811  |  |
|          | 2                                    | n.d  | n.d   | 4.30  | 3.10        | 1370   | 14318 | 72529.6  | 88225  |  |
|          | 3                                    | n.d  | 2.25  | 10.00 | 3.90        | 2159   | 14684 | 43841.9  | 60701  |  |
|          | 4                                    | n.d  | 61.38 | 64.80 | 1.40        | 2195   | 6626  | 48567.4  | 57516  |  |
|          | 5                                    | n.d  | 2.55  | 17.10 | 6.50        | 2137   | 13318 | 57220.9  | 72702  |  |
|          | 6                                    | n.d  | n.d   | 3.80  | 8.60        | 2083   | 11870 | 62156.6  | 76122  |  |
|          | 7                                    | n.d  | n.d   | 6.90  | 3.20        | 1961   | 11182 | 56677.9  | 69831  |  |

 Table (3): Concentrations of Fe in various forms as well as its total content in the surface soil samples of Assiut Governorate.

Iron levels in the poorly crystalline Fe oxide form of the studied soils ranged between 178 (T3/L6) and 2794 mg/kg (T1/L6) with an average of 1291.7 mg/kg (2.34% of the average of total Fe). About 34% of the samples contained less than 1000 mg/kg of this form, while 23.7% contained more than 2000 mg/kg (Table 3). Shuman (1985) found that the values of Fe in PCFeOx form ranged from 18 to 9350 mg/kg in some soils of southeastern USA. Kuo et al. (1983) found that the amounts of Fe in PCFeOx form were varied from 7.7 to 20.5% of total Fe.

The Fe content of the crystalline Fe oxide form of the soils under study ranged from 740 to 17914 mg/kg with an average of 8624.97 mg/kg representing 15.52% of the total Fe (Table 3). The lowest value of Fe in this form was found in the sandy soil (T3/L1), while the highest one was in the loamy soil (T6/L1). About 61% of the samples had a level of CFeOx bound Fe less than 10 g/kg, while only one of them had less than 1 g/kg (0.74 g/kg in T3/L1). The concentration of Fe in CFeOx form in some soils of southeastern US ranged between 70.0 and 51530.0 mg/kg (Shuman, 1985). Kuo et al. (1983) found that the Fe in the CFeOx form ranged from 4.3 to 20.8% of total Fe. Zhang et al. (1997) reported that the Fe in soils was present predominantly in the crystalline and poorly crystalline iron oxides at pH greater than 6.5.

The residual Fe in the soils under study had values varied between 8.36 and 94.67 g/kg with an average of 45.63 g/kg (82.11% of total Fe). The lowest Fe content of this form was found in T3/L6 and highest content was found in T5/L3. Only 2 samples contained less than 10 g/kg (T3/L1 and T3/L6), while 60.53 % of the samples contained less than 50.0 g/kg. Miller et al. (1986) found that the levels of residual Fe in some soils ranged from 14.6 to 48.8 % of the total Fe. Abollino et al. (2002) found that most of total Fe was associated with the residual Fe was ranged between 57.50 and 88.36% of the total Fe.

The content of total Fe in the studied soils varied from 9.73 to 105.52 g/kg with an average of 55.58 g/kg (Table 3). The lowest content was in the sandy soil of T3/L6, while, the highest content was in the loamy soil of T1/L4. About 34% of the samples contained less than 50 g/kg, while only 8 samples (21% of the samples) were higher than 70 g/kg. Many workers reported that the concentration of total Fe in some soils of Egypt ranged from 1.70 to 12.90% in various types of soils (Abd EI-Kader and Abu-Ghalwa, 1973), from 2.80 to 13.80 % in the Nile valley soils (Metwally and Abdellah, 1978) and from 0.46 to 5.88 % with an average 3.74 % in the upper Egypt soils (Abd EIRazek et al., 1984). Moreover, EI-Gala and Hendawy (1972) found that the lowest content of total Fe in some soils of Egypt was in calcareous soils and the highest one was in the alluvial soils.

### 2- Manganese

The concentration of Mn in the soluble + exchangeable (Exch.) form of the soils under study ranged between 1.20 (T6/L1) and 13.20 mg/kg (T1/L6) with an average of 4.50 mg/kg representing 0.51% of the total Mn (Table 4). About 68% of the samples contained exchangeable Mn less than 5.00 ppm, while only 3 samples (T1/L6, T5/L4 and T6/L4) contained more than 10 ppm of exchangeable Mn. Shuman (1985) found that the levels of the exchangeable Mn ranged from 0.20 to 145.5 mg/kg in some soils of southeastern USA. Abdel Salam (2003) found that the values of Mn in the Exch. Form of alluvial and calcareous soils ranged from 7.00 to 8.50 and 1.50 to 3.70 mg/kg, respectively.

| Transect | Location | ation Manganese Forms (mg/kg) |       |        |         |        |       |         | Total   |
|----------|----------|-------------------------------|-------|--------|---------|--------|-------|---------|---------|
| No       | No       |                               |       |        |         |        |       |         |         |
|          |          |                               |       |        |         |        |       |         |         |
|          |          | Exch.                         | Carb. | MnOx   | O-bound | PCFeOx | CFeOx | Res.    |         |
| 1        | 1        | 2.00                          | 31.35 | 188.00 | 261.00  | 23.20  | 31.50 | 135.45  | 672.50  |
|          | 2        | 1.30                          | 30.15 | 367.00 | 214.00  | 75.80  | 48.50 | 308.25  | 1045.00 |
|          | 3        | 4.80                          | 23.85 | 258.00 | 95.00   | 23.60  | 21.00 | 250.00  | 676.25  |
|          | 4        | 2.20                          | 21.75 | 331.00 | 112.00  | 33.00  | 31.25 | 332.55  | 863.75  |
|          | 5        | 5.90                          | 14.40 | 114.00 | 30.20   | 10.90  | 16.50 | 242.5   | 434.40  |
|          | 6        | 13.20                         | 78.00 | 302.00 | 220.00  | 43.10  | 48.00 | 489.70  | 1194.00 |
| 2        | 1        | 4.60                          | 25.05 | 107.00 | 36.90   | 11.90  | 12.00 | 68.75   | 266.20  |
|          | 2        | 3.20                          | 26.25 | 243.00 | 177.00  | 37.40  | 30.00 | 272.95  | 789.80  |
|          | 3        | 3.90                          | 43.65 | 202.00 | 105.00  | 38.90  | 30.00 | 336.55  | 760.00  |
|          | 4        | 3.20                          | 46.05 | 360.00 | 294.00  | 63.80  | 44.25 | 494.70  | 1306.00 |
|          | 5        | 5.90                          | 18.00 | 166.00 | 99.40   | 10.30  | 18.00 | 31.60   | 349.20  |
|          | 6        | 1.60                          | 29.40 | 395.00 | 254.00  | 55.80  | 53.25 | 249.95  | 1039.00 |
| 3        | 1        | 4.10                          | 14.25 | 49.00  | 12.70   | 2.50   | 7.25  | 59.40   | 149.20  |
|          | 2        | 5.30                          | 40.05 | 222.00 | 255.70  | 28.40  | 48.25 | 394.30  | 994.00  |
|          | 3        | 3.90                          | 28.20 | 223.00 | 193.80  | 19.70  | 39.25 | 507.15  | 1015.00 |
|          | 4        | 9.30                          | 183.0 | 234.00 | 256.30  | 92.50  | 62.00 | 322.90  | 1160.00 |
|          | 5        | 5.20                          | 33.75 | 276.00 | 290.90  | 36.00  | 58.75 | 466.40  | 1167.00 |
|          | 6        | 3.40                          | 24.60 | 26.00  | 6.00    | 5.40   | 10.25 | 92.55   | 168.20  |
| 4        | 1        | 7.30                          | 27.15 | 57.00  | 29.00   | 6.80   | 13.75 | 44.80   | 185.80  |
|          | 2        | 2.60                          | 46.20 | 361.00 | 324.40  | 103.40 | 71.00 | 240.40  | 1149.00 |
|          | 3        | 3.90                          | 47.55 | 227.00 | 233.00  | 31.90  | 50.00 | 577.15  | 1167.00 |
|          | 4        | 3.60                          | 27.75 | 296.00 | 288.40  | 43.10  | 69.25 | 581.90  | 1310.00 |
|          | 5        | 6.80                          | 43.95 | 400.00 | 302.10  | 42.40  | 72.00 | 62.75   | 930.00  |
|          | 6        | 2.90                          | 23.10 | 49.00  | 16.10   | 6.20   | 20.75 | 124.45  | 242.50  |
| 5        | 1        | 5.20                          | 25.20 | 309.00 | 63.20   | 30.00  | 40.25 | 89.15   | 562.00  |
|          | 2        | 2.90                          | 29.10 | 414.00 | 295.60  | 34.00  | 99.25 | 847.65  | 1722.50 |
|          | 3        | 3.00                          | 27.00 | 420.00 | 240.00  | 215.20 | 90.75 | 1126.55 | 2122.50 |
|          | 4        | 10.90                         | 28.80 | 165.00 | 251.80  | 21.40  | 42.50 | 317.10  | 837.50  |
|          | 5        | 4.60                          | 57.00 | 326.80 | 169.20  | 292.30 | 68.75 | 39.60   | 958.25  |
|          | 6        | 4.00                          | 34.50 | 388.10 | 140.80  | 125.60 | 72.00 | 253.75  | 1018.75 |
|          | 7        | 2.30                          | 41.25 | 296.90 | 85.95   | 42.60  | 55.00 | 236.75  | 760.75  |
| 6        | 1        | 1.20                          | 45.60 | 186.00 | 431.00  | 96.00  | 72.00 | 207.70  | 1039.50 |
|          | 2        | 2.30                          | 60.90 | 358.20 | 214.30  | 110.50 | 67.00 | 265.05  | 1078.25 |
|          | 3        | 6.40                          | 48.90 | 273.70 | 57.00   | 42.60  | 60.25 | 492.40  | 981.25  |
|          | 4        | 10.20                         | 29.70 | 118.90 | 215.40  | 12.60  | 20.50 | 421.70  | 829.00  |
|          | 5        | 3.90                          | 33.30 | 356.00 | 262.90  | 41.40  | 49.50 | 203.25  | 950.25  |
|          | 6        | 2.20                          | 30.30 | 376.70 | 174.50  | 68.60  | 63.25 | 248.95  | 964.50  |
|          | 7        | 1.70                          | 30.90 | 324.00 | 54.70   | 73.50  | 54.00 | 421.70  | 960.50  |

 Table (4): Concentrations of Mn in various forms as well as its total content in the surface soil samples of Assiut Governorate.

Values of Mn bound to the carbonates varied from 14.25 to 78.00 mg/kg with an average of 34.49 mg/kg representing 4.29% of the total Mn (Table 4). Only one sample (T3/L4) contained as high as 183.00 mg/kg. The lowest content was found in the sandy soils (T3/L1), while the highest one was found in the loamy soils (T1/L6). Four samples contained more than 50mg/kg Mn in the carb. form. The concentration of Mn in this form ranged between 45.00 and 73.00 mg/kg in the alluvial soils (average 59.50), 85.00 and 127.00 mg/kg with an average of 107.00 mg/kg in the calcareous soils of Egypt (Abdel Salam, 2003).

The levels of Mn bound to the Mn oxides in the investigated surface soil samples varied from 26.00 (T3/L6) to 420.00 mg/kg (T5/L3) with an average of 257.01mg/kg representing 28.88% of the total Mn (Table 4). Only T3/L1, T3/L6, T4/L1 and T4/L6 had values as low as 49.00, 26.00, 57.00 and 49.00mg/kg, respectively. About 26.3% of the samples contained more than 350mg/kg of this form. Shuman (1985) reported that the concentration of Mn in MnOx form varied between 0.00 and 680.20 mg/kg in some soils of southeastern USA.

The organic bound Mn in the soils under study ranged between 6.00 and 324.4 mg/kg with an average of 166.64 mg/kg representing 20.00 % of the total Mn (Table 4). About 31.6% of the samples contained less than 100 mg/kg. Shuman (1979) found that the content of Mn bound to the organic fraction ranged from 1.67 to 1673.00 mg/kg in some soils of southeastern USA. The lowest value was found in T3/L6, while the highest one was recorded in T4/L2. A very high value (431.00mg/kg) was found in T6/L1. Abdel Salam (2003) found that the values of Mn in the organic fraction in some Egyptian studied soils ranged from 3.30 to 29.00 mg/kg; the average values in the alluvial soils were higher than in the calcareous soils.

Concentrations of Mn in the poorly crystalline Fe oxide form of the soils under study ranged from 2.50 (T3/L1) to 125.60 mg/kg (T5/L6) with an average of 40.65 mg/kg (6.07 % of total Mn). Only three samples contained more than 100 mg/kg, while values as high as 215.20 and 292.30 mg/kg of Mn were found in T5/L3 and T5/L5. About 68% of the samples contained less than 50 mg/kg of Mn. The values of Mn in PCFeOx fraction in some soils of southeastern USA ranged between 0.20 and 295.00 mg/kg (Shuman, 1985).

Manganese in the crystalline Fe oxide form of the investigated soils varied between 7.25 and 99.25 mg/kg with an average of 46.36 mg/kg (5.21% of total). More than half of the samples contained less than 50 ppm (55%). The lowest Mn content of this form was found in the sandy soil (T3/L1), while the highest one was reported in the clay soil (T5/L2). Shuman (1985) found that the concentration of Mn in the CFeOx ranged from 0.90 to 333.60 mg/kg in some soils of southeastern USA.

The values of the residual Mn in the studied surface soil samples ranged from 31.60 to 581.90 mg/kg, except two clay samples which had as high as 847.65 and 1126.55 mg/kg that were found in T5/L2 and T5/L3, respectively (Table 4). The lowest and the highest values of this form were found in T2/L5 and T4/L4, respectively. The average Mn content of this form (274.6mg/kg) represented 35.06 % of the total Mn. Only 21% of the samples contained less than 100 mg/kg, while 71% of the samples had less than 400 mg/kg.

Values of the total Mn in the tested soils ranged from 149.20 mg/kg in T3/L1 to 1310.00 mg/kg in T4/L4 with an average of 918.3 mg/kg (Table 4). Values as high as 1722.50 and 2122.50 mg/kg were found in T5/L2 and T5/L3, respectively. Ibrahim et al. (2001) found that the content of the total Mn ranged between 24.0 and 1055.0 mg/kg with an average of 513.0 mg/kg in some soils of Sohag Governorate.

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حالة صور الحديد و المنجنيز فى أراضى أسيوط هالـــه حســنين جمعــه، محمــد عبــد الــرازق أحمــد، محمــد علـــى الدســوقى و أبو العيون أبوزيد أمين تسم الآراضى و المياه – كلية الزراعه – جامعة أسيوط

تم تحديد ستة محاور بمحافظة أسيوط عبر وادى النيل فى إتجاه من الشرق إلى الغرب و ذلك لتحديد الصور المختلفه من الحديد و المنجنيز فى هذه الاراضى. أخذت عينات سطحيه من متوسط ستة مواقع فى كل محور. تم تقدير ستة صور من الحديد و المنجنيز و هى : الصور المتبادله، المرتبطه بالكربونات، المرتبطه بأكاسيد المنجنيز، المرتبطه بالماده العضويه، المرتبطه بأكاسيد الحديد ضعيفة التبلور, المرتبطه بأكاسيد الحديد المتبلوره بالإضافه إلى الكميه الكليه لكل عنصر. تم حساب الصور المتبقيه بواسطة عملية الطرح.

تراوحت كميات الحديد المرتبط بالكربونات من صغر إلى 11.25 مللجم/ كجم (70.00% من الحديد الكلى). كانت نسبة الحديد المرتبط بأكاسيد المنجنيز و بالماده العضويه 20.08 و 00.00% من الحديد الكلى على التوالى. حوالى 34% من العينات إحتوت على تركيزات اقل من 1000 مللجم/ كجم حديد مرتبط بأكاسيد الحديد ضعيفة التبلوربينما احتوت (23.2% من العينات على تركيزات أعلى من 2000 ملاجم/كجم. تراوحت كميات الحديد المرتبط بأكاسيد الحديد المتبلوره بين 740 و 1791 مللجم/كجم مالجم/كجم من العديد العربينما احديد المرتبط بأكاسيد الحديد المتبلوره بين 740 و 1791 مللجم/كجم مالجم/كجم من الحديد الكلى). كانت كمية الحديد المتبقى تتراوح بين 83.6 و 94.67 جم/كجم بمتوسط 45.63 جم/كجم (20.51% من الحديد الكلى). تراوح الحديد الكلى بين 57.5 و 20.5% جم/كجم بمتوسط 55.58 جم/كجم.

تراوح محتوى التربه من المنجنيز الذائب و المتبادل بين 12.0 و 13.02 ملجم/كجم ( 5.0% من المنجنيز الكلى). كانت قيم المنجنيز المرتبط بالكربونات , بأكاسيد المنجنيز و بالماده العضويه تتراوح من 14.25 إلى 78.00 مللجم/ كجم (4.29% من المنجنيز الكلى),26.00 إلى 420.00 مللجم/كجم (29.88 % من المنجنيز الكلى) و 6.0 الى 324.4 مللجم/كجم (20.00% من المنجنيز الكلى) على التوالى. تراوحت تركيزات المنجنيز المرتبط بأكاسيد الحديد ضعيفة التبلو بين 25.0 و 125.6 مللجم/كجم (6.05% من المنجنيز الكلى). كانت كمية المنجنيز المترقوح بين 14.00 و 10.05% من الحديد الكلى) بينما كانت قيم المنجنيز الكلى تتراوح بين 14.00 و 140.05 مللجم/كجم (35.00% من الحديد الكلى) بينما كانت قيم المنجنيز الكلى تتراوح بين 14.00 و 140.05 مللجم/كجم.