4-RESULTS AND DISCUSSTION

4.1. Physical and chemical properties of the studied soils

4.1.1. Particle size distribution:

The results of the particles size distribution of the studied soil samples, their textural class, calcium carbonate and organic matter contents are shown in Table (1). These data show that soil textural class in the different locations varies considerably from one soil to another.

For instance, the soils of Nile alluvial sediments are fine textured (clay) in the surface layers, where clay content varies from 44.1 to 60.3%.

The highest value is in the soils of El-Bagour site (No.1), while, the lowest content is in the soils of Shben El-Kom site (No.20).

With regard to the calcareous soils of Abo El-Matamer sit (No.21), El-rose Village (No.22), Ezbat El-Dekeka (No.23), El-Mosalas Village (No.24), El-Gewahy Village (No.25), El-Magd Village(No.26), El-Zafer Village (No.27), El-Nobariya (No.28), El-Ameria (No.30) and El-Banger farm (No.32),data indicat that , these soils are fine- textured soil, while those of Alex.-desert road sites (No.31 and 33) and El Nasr canal (No.34) are medium textured soils.

Table (1) also, included the particle size distribution of Ismaliya site (No.35) which indicates that this soil is coarse-textured (sand), where sand content is more than 90%.

The wide variations in the texture class in fact reflect variation in the mode of sedimentation patterns by which these soils have been formed.

4.1.2. <u>Calcium carbonate content:</u>

The data presented in Table (1) show the distribution of $CaCO_3$ content in the studied soil samples. The data indicate that the total calcium carbonate content in the alluvial soils is generally low and varies among the soils of the different sites, where it ranges from 0.4 to 3.2%. The lowest value was detected in the soil of Mahalet Marhowm (No.14), and the highest one was observed in the soil of Shben El-Kom (No.20).

With regard to the vertical distribution of total calcium carbonate content in the calcareous soils, data reveal that an increase in carbonate content was presented in the surface layers of the sites representing the calcareous soils, which ranges from 20.0 to 29.2%. The lowest value was found in the soil of El-Magd village (No.26), while the highest one characterizes the soils of El-Ameria (No.30).

Soil of Ismaliya governorate (No.35) which represent the sandy soil exhibit the lowest values of $CaCO_3$ (0.48%).

4.1.3. <u>Organic matter content:</u>

Data in Table (1) show that, values of organic matter content were relatively low, never exceeding 2.3% of soil components. It is clear that, the highest values of organic matter content are present in Nile alluvial soils which ranged from 1.1 to 2.3 % of the soil components.

As was expected, the relatively high content in all the surface layers in the Nile alluvial soils are associated with the cultivation practices.

With regard to the calcareous soils, data in Table (1) reveal that, organic matter content in the calcareous soils was very low and ranged between 0.01 and 1.09% of the soil components, while in the sandy soils which are represented by the soil sample of Ismaliya governorate (No.35), organic matter content did not exceed 0.26% of the soil components. The low content of organic matter is common feature in soils of the arid regions due to the high oxidation potential and climate conditions.

4.1.4. Soil reaction (pH):

Table (2) shows that pH values of the alluvial soils ranged from 7.27 to 7.86 indicating that the soils are neutral to slightly alkaline. The lowest value is detected in the soil of Kafr Ashma (sit No.6), whereas the highest value is found in the soil of Kafr Shobra (sit No. 2).

With regard to the calcareous soils, these soils are moderately alkaline to strongly alkaline where the pH values varied from 8.27 to 8.99, while the sandy soil of Ismaliya (sit No.35) is slightly alkaline. The higher pH values, Table (2) which indicates moderately alkaline to strongly alkaline soil reactions are true reflection of the prevailing aridity and soil chemical composition which contains appreciable amounts of soluble Na^+ and HCO_3^- ions.

4.1.5. Total salinity and soluble salts:

Saline soils occur mostly in the arid and semi arid regions due to poor rainfall and relatively high temperature which in turn, results in the accumulation of soluble salts. In the irrigated regions of these arid and semi arid zones, the process of soil salinization is more often connected with a rise of the water level and high evaporation rate. Data presented in Table (2) show that the amount of total soluble salts as expressed by the electrical conductivity (dSm^{-1}) of the soil saturation extract varies widely among the different investigated soil sites. In general, the alluvial soils are characterized by low salinity rarely 4 dSm^{-1}. This due to the effect of irrigation which exerts permanent wetting front and leaching through the soil profile. Slightly salinity levels, ranging between 4-8 dSm^{-1} are found in the site (No.6) in Kafr Ashma, site (No.14) in Mahalet Marhowm, site (No.16) in El-Giza farm and site (No.18) in Shmandal.

With regard to the calcareous soils, the soluble salt contents as measured by the electrical conductivity indicate that the soils are non saline to saline as EC_e values ranged from (1.43 to 14.21dSm^{-1}.)

Table (2) shows that the cationic composition of the soil saturaton extract in the alluvial soils is dominated by Na^+ followed by Ca^{++} and Mg^{++}, while K^+ ion is the least abundant soluble cation, except for the soils of Kafr Ashma (site No.6), Nahet Hafs (site No.8), Manshyat Esmail (site No.13) and Met Habash El-Baharya (site No.15), where Ca^{++} exceeds Na^+. The anionic composition of the soil saturation extract is dominated by $SO_4^=$ followed by Cl^-, except for few soils of sites No.4, 9, 14, 17 and 18 where Cl^- exceeds $SO_4^=$, while HCO_3^- anion is usually the least abundant soluble anion.

It can be concluded from the above discussion that the amount and type of salt accumulation differ, according to the environment and irrigation and fertilization practices.

4.2. <u>Total and DTPA-extractable copper:</u>

4.2.1. <u>Total copper</u>

The data presented in Table (3) show that total Cu content in the alluvial soils ranges from 35 to 155 µg g^{-1}. The lowest value characterizes the soils of Shben El-Kom, while the highest value is in the soil of Kafr Shobra.

The wide range of Cu content is apparently could be associated with soil texture, $CaCO_3$ content and mineralogy of soils. The highest values are found in the soils of low content of $CaCO_3$, fairly high content of clay and dominated by smetite minerals.

With regard to the calcareous soils, data in Table (3) reveal that total Cu content in the studied calcareous soils varied widely between 13 and 97 µg g^{-1}. The lowest value is detected in the soils of El-Gewahy village, whereas the highest one is in the soil of Cairo Alx. desert road.

In this respect, **El-Demerdashe (1970)** showed that total Cu content ranged from 60 to 70 mg kg^{-1} in the alluvial soils and from 2 to 10 mg kg^{-1} in the sandy soils, while in the calcareous soils it ranged from 6.3 to 13.0 mg kg^{-1}. **Abdel Salam *et al*. (1971)** found that the values of total Cu in the calcareous soils of wadi El-Natrun ranged from 2 to 18 mg kg^{-1}. **El-Sayed (1971)** reported that values of total Cu content in some soils of Egypt ranged from 31.4 to 205.2 mg kg^{-1}. He added that the sandy and calcareous soils contained much less total Cu than the alluvial soils. Relatively high total Cu content were reported by **Wassif**

(1973) for the calcareous soils of El-Salloum (12.5mg kg^{-1}) and maryout (153.8 mg kg^{-1}).

Abdel Mottalb *et al*. (1989) showed that the values of total Cu ranged between 10 and 40 mg kg^{-1} in soils of North Tahrir, Burg El-Arab and El-Hammam.

To substantiate the role of some soil constituents on controlling total Cu content, the correlation coefficients between total Cu and each of these factors were computed, Table (4) and fig.(1). The obtained coefficients imply that the total Cu is positively and significantly correlated with clay %, OM %. In contrast, total Cu is negatively and significantly correlated with $CaCO_3$ % and EC. Here, it is worth to mention that the obtained data are in close agreement with those of **Awad *et al*.(2002), Abdel Razik (2002)** and **Grais (2006).** They found that total Cu has significant positive correlation with organic matter %, clay % and silt%. On the other hand, $CaCO_3$ is negatively and highly significant correlated with the total Cu.

Multiple regressions were also computed to determine the relationship between some soil variables and total Cu in the studied soils. The calculated multiple regression equation is as follows:

Total Cu = - 113.811 + 0.4815 clay % - 1.0892 CaCO3% + 5.0385 OM% + 19.618pH + 0.7401silt% - 2.9421EC

4.2.2. <u>DTPA-extractable Cu</u>

The chelating agent DTPA offers a great promise for assessing readily available micronutrient cations in soils. Such agent gives the most favorable combination of stability constant for simultaneous complexing of Cu. **Mawardi *et al*.(1979)** suggested that the DTPA extracting method as described by **Lindsay and Norvell (1978)** is the most suitable method for extracting micronutrients from the soils of Egypt. Therefore, this extractant has been used for extracting the readily available Cu in the soil under study.

DTPA-extractable Cu of the investigated soils is presented in Table (3). Data reveal that the alluvial soils contain the highest amounts of extractable Cu (ranged from 3.71 to 9.68 µg g^{-1}). The lowest value was detected in the soils of Manshyat Esmail Amin village, while the highest value was found in the soils of Manshyat Habashy. The high values of DTPA-extractable Cu may be attributed to the relatively fine texture of the alluvial soils. Similar results were obtained by **El-Kherbawy *et al*. (1987)** who found that soil soluble and exchangeable copper ranged from 0.1 to 2.6mg/kg. **El-Sayed (1988)** found that exchangeable copper in El-Fayoum soils ranged between 0.002 and 25 mg/kg.

Regarding the calcareous soils, data in Table (3) show that DTPA-extractable Cu ranged from 0.37 to 6.17 µg g^{-1}. The highest value was detected in the soils of el-Magd village, whereas the lowest value was found in El-Banger Farm soils. In this respect, **Awad *et al*. (2002)** found that the DTPA-extractable

Cu, ranged from 0.1 to 1.0 ppm in the soils of El Nobariya. **Grais (2006)** in his study on the soils of the north western coast of Egypt found that DTPA-extractable Cu varied from 0.03 to 0.83 mg kg^{-1}.

In the sandy soils, total and DTPA-extractable Cu were 37 and 0.71 µg g^{-1}, respectively.

The correlation coefficients between some soil variables and DTPA-extractable Cu were computerized, Table (4) and Fig.(2). The obtained results show positively high significant correlation between DTPA-extractable Cu and each of clay% (r = 0.580^{**}) and OM% (r = 0.689^{**}), and negatively high significant correlation with $CaCO_3$% (r = - 0.870^{**}) and pH (r = - 0.550^{**}). Similar results were obtained by **Sadik *et al*. (2002)** who found a significant positive relationship between soil available copper and both clay% and organic matter, while **Grais (2006)** found a significant negatively correlated between DTPA-extractable Cu and soil pH.

Multiple regression analysis was computed to determine the relationships between some soil variables and DTPA-extractable Cu. The multiple regression equation is

DTPA-extractable Cu= 26.4521+0.06227clay%- 0.2577$CaCO_3$% +0.4556OM%+3.6076pH+0.0895silt%+0.0045 EC

4.3. Distribution of soil copper fractions in the studied soils:

Amounts and percentages of total copper extracted from the tested soils by the reagents in the fractionation scheme are given in Table (5). These results are presented in the following:

4.3.1. Total copper:

Data presented in Table (5) show that the values of total Cu content in the alluvial soils were varying from 35 to 155 µg g^{-1}. The lowest value was detected in the soils of Shben El-Kome, whereas the highest contents characterized the soils of Kafr Shobra. These results are in good agreement with those (**El-Sayad, 1988 and Abdel Kareim, 1995**) who found that total Cu fluctuated between 17 and 149 µg g^{-1} in the alluvial soils.

With regard to the calcareous soils, data presented in Table (5) reveal that total Cu content ranged from 23 µg g^{-1} in the soils of El-Gewahy village, and 97 µg g^{-1} in Alex-Cairo desert road.

Variations in the total copper content are due to variations in soil texture and organic matter content. It seems that the finer the texture; the higher organic matter content the higher total copper content of the soil.

4.3.2. <u>Copper fractions in some tested soils:</u>

Studies on the speciation of heavy metals in soils usig sequential extraction techniques have increased in recent years, because these simple techniques provides knowledge about metal affinity to the soil components and the strength with which they are bound to the matrix (***Narwal et al .,1999***). Unlike the single extraction technique, sequential extraction gives information about both mobile and stable fractions of metals in soil, which evaluates the actual and potential mobility of metals .Numerous fractionation techniques have been used for sequential extraction of heavy metals in soils (***Tessier et al.,1979;Spostito et al.,1982***; ***Shuman,1985***).The technique varies in the number of fractions extracted, as well as the order and kind of reagents used . In general, the fractionation schemes start with the weakest extractants and end with the strongest, most aggressive and separate five to seven metal fractions.

4.3.2.1. <u>Soluble copper:</u>

Data presented in Table (5) show that the values of soluble Cu extracted by water in the Nile alluvial soils are ranging from 0.8 to 1.6 µg g^{-1} corresponding to about 2.94 % of the total. The lowest content was found in the Kafr Shobra soil, while the highest value was detected in the soils of El-Bagour.

In the calcareous soils, data in Table (5) reveal that the contents of water soluble Cu ranged between 0.01 and forming from 0.04 to 6.95% of total Cu. The lowest content characterized the soils of El-Nasr canal, while the highest content was associated with the soils of El-Maged village.

It is clear that, the water soluble Cu was presented in very small amounts showing an average of were 1.34 and 0.89 µg g^{-1} in the alluvial and calcareous soils, respectively.

These may be due to that water does not extract sufficient copper to represent adequately the labile nutrient available to plant roots, because copper is strongly bound to specific sites on the surface of clay and organic matter constituents.

4.3.2.2. Exchangeable copper:

Table (5) reveals that, exchangeable copper in the Nile alluvial soils ranges from 0.6 to 1.8 µg g^{-1} coresponding to 0.7 and 4.5% of total copper. The lowest value has been recorded at Nahyat Saft El-Horya village, while the highest occured in the soils of Markaz El-Shohada.

These results are in agreement with those obtained by **Mc Laren and Crawford (1973) and Aboulroos *et al*.(1991).**

Regarding the calcareous soils, data presented in the Table (5) show that exchangeable copper fluctuates between 0.2 and 2.0µg g^{-1}, being from 0.37 to 3.6% of total copper. The highest content was recorded in the soils of Alex.-Cairo desert road, whereas the lowest content was detected in the soils of El-Dekeka village.

Generally, higher values of exchangeable copper were shown by the alluvial soils than by sandy and calcareous ones.

The average values of the alluvial and calcareous soils were 1.4 and 0.94 µg g^{-1}, respectively. Theses values are in agreement with those reported by **El-Damaty *et al*. (1973), Sabet *et al*.(1975)** and **El-Sokkary and Mesherf (1984).** The amount of exchangeable copper seems to be related to the soil constituents which have high ability to cation exchange, i.e. clay and organic matter fractions.

4.3.2.3. Copper bound by calcium carbonate:

Data presented in Table (5) show that the values of copper bound to calcium carbonate in the Nile alluvial soils are ranging from 0.0 to 2.4 µg g^{-1} making from 0.0 to 3.67% of total copper in the tested soils. The lowest values were found in the soils of Kafr Shobra village, while the highest value was in the soils of El-Shohada.

With regard to the calcareous soils, data presented in Table (5) reveal that the values of copper bound to calcium carbonate in the calcareous soils varied widely from 0.8 to 3.6 µg g^{-1} corseponding to 1.48% and 9.5% of total copper. The highest value was in the soil of El-Maged village, while the lowest value in the soils of El-Dekeka village.

These values are slightly higher than those obtained by **El-Kherbawy *et al*. (1987)**, who found that such fraction varied between 1.0 and 2.5 µg g^{-1} in north Tahrir calcareous soils.

It is clear from the average values that, the calcareous soils possessed the highest average content of copper bounded to calcium carbonate. This may be explained on the ground that the calcareous soils have relatively higher $CaCO_3$ content than in the Nile alluvial or sandy soils.

4.3.2.4. <u>Occluded copper:</u>

The distribution and levels of occluded copper in the Nile alluvial soils are presented in Table (5). Data show that occluded copper ranged from 1.0 to 2.4 µg g^{-1}, being within the range of 1.42-5.7% of total copper in the studied soils. Soil of berket El-Sabe, showed the lowest content of occluded Cu while, the highest value was in the soils of El-Shohada.

Regarding the calcareous soils, data presented in Table (5) reveal that occluded copper varies from 0.8 µg g^{-1} in the soils of El-Dekeka village, and 6.0 µg g^{-1} in the soils of Cairo-Alex.desert road, and fell within the range of 1.48-10% of total copper in the soils of the studied sites. These results are relatively lower than those obtained by **El-Kherbawy *et al*.(1987) and Aboulroos *et al*.(1991)** who reported that occluded copper was varying from 3.1 to 17 $mgkg^{-1}$ in soils of Egypt.

4.3.2.5. <u>Copper bound by organic sites</u>:

The organically bound fraction was one of the smallest fractions in the surface layers of all studied soils.

Values of copper bounded to organic sites are presented in Table (5). Data show that these values in the Nile alluvial soils ranged from 2.2 to 5.6 µg g^{-1}, being within the range of 3.23 to 11.42% of total copper. The lowest value is found in the soils of El-Roda Barkat El-Saba, while the highest value is in the soils of S.W.and E.Rese.Inst. Regarding the calcareous soils, data in Table (5) show that copper bound by organic sites ranged from 3 µg g^{-1} in the soils of El-Dekeka village 6.4 µg g^{-1} in the soils of El-Nasr canal. These values fell within the range of 3.91 and 24.61% of total copper. These results are in accordance with those of **El-Kherbawy *et al*.(1987)** who found that such fraction of Cu varied from 17.1 to 48 µg g^{-1} in soils of Egypt.

It is clear that, the average value of organically bound form of copper was 4.40 and 4.71 µg g^{-1} in the alluvial and calcareous soils, respectively. The proportion of the organically pound form decreased along with an increase in that of the precipitated form in the higher pH soils. **(Alva *et al*., 2000).**

4.3.2.6. Residual copper:

Table (5) reveals that residual copper content in the Nile alluvial soils varied widely from 17.1 to 80 µg g^{-1} and fell within the range of 42.55 to 75.0% of total copper. The lowest value was detected in the soils of Shben El-Kom, while the highest value was associated with the soils of Kafr Shobra. The result could be due to the high content of total Cu and relatively low values of other Cu fractions.

With regard to the calcareous soils of Egypt, data in Table (5) reveal that the values of residual copper ranged from 10.2 to 37.4 µg g^{-1} being within the range of 15.05 and 70.51% of total copper. The lowest value was in the soils of El-Gazaer village, whereas the highest value was in the soils of El-Nobariya.

Based on the above mentioned results, it is clear that the residual copper fraction was very much higher than the available fractions found in the soils of this study. The highest amounts of residual copper 48.99µg g^{-1} was detected in the contaminated Nile alluvial soils, while the relatively low amount of this element 21.07 µg g^{-1} was found in the calcareous soils.

Based on the results obtained in this study, Cu fractions in the Nile alluvial soils can be arranged in the order:

Residual > organic > occluded > carbonate > exchangeable > water soluble.

The order of fractions in the calcareous soils is slightly different being: residual > organic> occluded> carbonate> exchangeable>water soluble.

These results agree with those obtained by ***Liang et al.(1990)*** who found that most of the total Cu was present in the residual fraction.

4.4. Relation ship between some soil characteristics and Cu fractions in soils:-

4.4.1. Alluvial soils:

Concerning the relationship between Cu status in the studied soils and some soil characteristics, it is clear from Table (6) and Fig (3) that water soluble Cu was positively correlated with clay% (r= 0.526*) and negatively correlated with total Cu (r =-0.551*). Also, a negative significant correlation Table (6) and Fig (4) was found between exchangeable Cu and EC (r = -0.680*). These results agree with those obtained by **Perveen *et al*.(1993), Maji *et al*.(1993) and Dhane and Shukla(1995)**.

With regard to the occluded-Cu, data in Table (6) and Fig (5) show that there was a positively significant correlation between occluded Cu and pH (r = 0.508*), but, negative correlation was found between occluded Cu and EC (r = -0.720*). A positively significant correlation was found between organic Cu and silt %(r = 0.678*) Fig (6). Also, a positive significant correlation was found between residual Cu and each of clay% (r = 0.610*) and organic matter content (r =0.870*). Also a highly significant positive correlation between total Cu (r = 0.900*) and residual Cu fraction. While a negative correlation was found between residual Cu and $CaCO_3$ content (r= -0.708*). Fig (7). These results are in agreement with those obtained by **Kabata-Pendias and Pendias (1992).**

The multiple regression analysis was carried out to determine the relationship between Cu fractions and some soil variables of the alluvial soils, the multiple regression equations are:

Water soluble Cu = $-3.7486 – 0.01324clay\% - 0.01181Silt\% + 1.2665OM\% + 0.6019pH – 0.0522EC - 0.01161Total\ Cu$

Exch-Cu = $-1.7894 + 0.0068clay\% + 0.048silt\% + 0.5982CaCO_3\% + 1.2029OM\% - 0.2847EC - 0.0298total\ Cu$

Carbo-Cu = $0.0881 - 0.0257clay\% + 0.0445silt\% - 0.1561CaCO_3\% + 2.0163OM\% - 0.1898EC - 0.0298total\ Cu$

Occl-Cu = $1.1836 + 0.0121clay\% + 0.0608silt\% + 0.3430CaCO_3\% - 3.3767OM\% - 0.2723EC + 0.0041total\ Cu$

Organ-Cu = $4.0961 + 0.0605clay\% + 0.1831silt\% + 0.3321CaCO_3\% - 3.3767OM\% - 0.2723EC + 0.0041\ total\ Cu$

Resid-Cu = $-140.593 + 0.5921clay\% - 0.244silt\% \quad 13.6731CaCO_3\% \quad 60.221OM\% - 0.6421EC + 0.3772total\ Cu$

As the multiple regression equation of Resid-Cu mean that an increase of one precent of organic matter increase the resid-Cu by 60.22µg g^{-1}.

4.4.2. Calcareous soils:

To evaluate the role of soil variables in affecting Cu fractions in the soils representing the calcareous ones , correlation coefficients were computed and recorded in Table (7).

The data in Table (7) and Fig (8) indicate that the amounts of water soluble Cu were positively and significantly correlated with clay% ($r = 0.536^{*}$). The amounts of exchangeable Cu were negatively and significantly correlated with each of OM% ($r = -0.719^{*}$) and EC ($r = -0.575^{*}$), while it was positively correlated with total Cu ($r = 0.610^{*}$).Fig(9).

Also, the amounts of occluded Cu were not significantly related to any of the soil variables. There is a negatively significant correlation between carbonatic Cu and organic matter content ($r = -0.84^{*}$), Fig (10).

The organically bound Cu fraction was negatively and significantly correlated with clay% ($r = -0.68^{*}$) but positively correlated with EC ($r = 0.54^{*}$) Fig (1). Moreover, positively significant correlations have been established between residual Cu and each of clay% ($r = 0.61^{*}$) and silt %($r = 0.717^{*}$) and being highly and significantly correlated with total Cu. On the other hand, pH displays a significant negative correlation ($r = 0.640^{*}$) with residual Cu Fig (12). This result confirmed the finding of both **Choa (1972) and Miller *et al*.(1986).**

The multiple regression analysis was carried out to determine the relationship between Cu fractions and some soil variables in the calcareous soils of Egypt, the multiple regression equations are:

Water soluble Cu = -0.0773 + 0.01166clay% -0.0894Silt% +0.1088$CaCO_3$%-2.4982OM%–0.0943EC-0.03489total Cu

Exch-Cu = 1.3054+0.0054clay%- 0.03316silt%+ 0.1031$CaCO_3$% -0.2847EC- 1.6754OM% -0.01134total Cu

Carbo-Cu=3.3689+0.05863clay%-0.0917silt%+0.1506$CaCO_3$%-0.1614EC – 3.5580OM% -0.0388total Cu

Occl-Cu = 9.6258+0.1129clay% - 0.3395silt% + 0.2365$CaCO_3$% -6.1191OM% - 0.4677EC+ 0.0714total Cu

Organ-Cu= 7.8944 + 0.184clay% + 0.0174silt% + 0.1585$CaCO_3$% -0.1178OM% + 0.0121EC-0.0285 total Cu

Resid-Cu=-54.9166 + 0.0087clay% + 2.0321silt% - 0.7026$CaCO_3$% + 31.4684OM% - 0.6267EC + 0.5846total Cu

4.4.3. Fractionation of Cu prior to cultivation:

Data of total and fractions of Cu in the studied soil samples before cultivation are presented in Table (8). In the alluvial soil, the amounts of Cu as water soluble, exchangeable, carbonate, occluded, organically bound and residual fractions were 1.2, 2.0, 1.8, 1.8, 5.6 and 44.9 µg g^{-1} and constituted 1.74, 2.9, 2.6, 2.6, 8.12 and 65.07% of total Cu, respectively.

With regard to the calcareous soil, the amounts of water soluble, exchangeable, carbonate, occluded, organically and residual fractions were 0.85, 1.0, 3.0, 1.2, 5.0 and 27.50 µg g^{-1} and constituted 2.05, 2.65, 8.69, 3.07, 12.82 and 70.51% of total Cu, respectively.

In the sandy soil, the corresponding fractions of Cu were 0.8, 1.4, 2.4, 1.2, 3.0, 18.1 µg g^{-1} and constituted 2.16, 3.78, 3.48, 3.24, 8.11 and 48.92% of total Cu, respectively.

It is clear that the water soluble Cu fraction constituted the least amounts of Cu in the Nile alluvial and sandy soils which corresponded to about 1.76 and 2.16% of the total. This can be considered a symptom of low lability of copper in these soils .Similar results were reported by ***Kabala et al.,(2001)***.

Residual and organically Cu constituted the highest portion of soil Cu (65.07, 70.51, and 48.92%) and (8.12, 12.82, 8.11%) in the alluvial, calcareous and sandy soils, respectively. These two fractions can be considered as the primary form of native copper in the investigated soils.Also, the high percent of residual Cu may be due to the amount held within silicate mineral structure where more than half of total soil Cu was present in mineral lattices **(Mc Laren and Crawford, 1973, Shuman1979, Miller *et al*.,1986 and Liang *et al*., 1991).** Almost similar results were obtained by **El-Sokkary and Meshref (1984)** in alluvial, calcareous and sandy soils of Egypt.

4.5. <u>Dry matter, copper concentration and uptake:</u>

The coupling of soil testing with plant analysis, results in the effective application of nutrients to avoid deficiencies and toxicities. The utility of a soil test depends upon to what extent it predicts whether a crop will respond to fertilizer application to the soil being tested. Calibration studies have to be conducted with a large number of soils that range from low to high in the amount of nutrient being studied.

Most calibration studies are initially made in the greenhouse, as they are much faster and more economically than field studies. A number of different approaches i.e. 1) dry matter; 2) copper concentration and 3) copper uptake have been used.

4.5.1. Dry matter

The results obtained for dry matter yield of wheat plants (shoots and roots), copper concentration and copper uptake at 0.0, 0.5, 1 and 2 µg g^{-1} of added copper are given in Table (9 and 10). It is clear that the addition of 2 µg g^{-1} copper led to an increase in the dry weight of(shoots and roots) of wheat plants (g/plot) in the alluvial soil which on the average being 17.07 and 2.32 (g/pot), respectively.

With regard to the dry matter yield of (shoots and roots) of wheat plants grown in calcareous soil, the data show that the addition of 0.5 µg g^{-1} copper led to an increase in the dry weight (shoots and roots) of wheat plants with an average of 4.60 and 0.5 (g/pot), respectively.

The data show the dry matter yield of (shoots and roots) of wheat plants grown in sandy soil , the addition of 2 µg g^{-1} Cu led to increase the dry weight of (shoots) which on the average was 14.31(g/plot).Where the addition of 1.0µg g^{-1} copper led to increase the dry weight of (roots) to an average of 7.33(g/plot).

It is clear that, the dry matter yield of wheat plants grown on the alluvial soil was higher than the dry matter yield of the plants grown on the calcareous soil this may be due to the effect of soil properties such as soil texture, pH, EC and available copper as well as fertility status which enhance plant growth in the alluvial soils. These results are in agreement with those obtained by **Abou-Hussien (1985)** who found that dry matter yield of barley grown on different soils, was at the following order:

Alluvial> alkali> sandy>calcareous soils.

Also, **El-Shafie (1994)** found that dry matter weight of broad bean grown on alluvial soils was higher than that of the plants grown on calcareous soils.

4.5.2.<u>Copper concentration in the grown plants:</u>

Soil applications of Cu significantly increased the Cu concentration in all plant parts of wheat plants, Table (9 and 10). However, the effect varied among the different studied soils. Application of 2.0 µg g^{-1} resulted in proportionally higher increase in the Cu concentration in wheat plants grown on the alluvial soil compared to the other soils. **Payne *et al*. (1988)** also found that neither corn grain and silage yields nor Cu concentration were affected by Cu addition. Even though the cumulative amounts of added Cu greatly exceeded the maximum allowed loading rate (250 kg ha^{-1}) Some plants have a relatively high tolerance to increased concentration of Cu and can accumulate extremely high amounts of this metal in their tissue, the phytotoxic level is often considered to be 20 µg g^{-1}, but the majority of plant species can accumulate much more Cu (**Kabata Pendias *et al*., 1984**).

Regarding Cu content in wheat plants (shoots), grown in alluvial, calcareous and sandy soils, data in Table (9) show that the addition 2.0 µg g^{-1} copper led to an increase the concentration of Cu in shoots of wheat plants with an average of 16.0, 14.0 and 11.67 µg g^{-1}, respectively. The highest value was recorded for those plants grown on the alluvial soil, while the lowest value was obtained for those plants grown on the sandy soil, similar result were obtained by ***Tadros(1997) and Kabala and Singh(2001)***.

Data in Table (10) represent the values of Cu content in the wheat plants (roots) grown in the studied soils at copper additions of 0.0, 0.5, 1.0, 2.0 µg g^{-1}. Copper content in plant roots varied from 18 to 21.33, 8 to 15.66 and 24.33 to 43 µg g^{-1} in the alluvial, calcareous and sandy soils, respectively.

The obtained data reveal that the application of Cu significantly increased Cu concentration in both plant parts (shoots and roots) of wheat. Application rate of 1 and 2 µg g^{-1} resulted in proportionally high increase in the Cu concentration of wheat plants grown on alluvial and calcareous soils than sandy soil. The results obtained are in line with those of **Stevenson (1986) and Romheld and Marschner(1991)**

4.5.3. Copper uptake in the grown plants:

The values of copper uptake in wheat plants tissues (shoots and roots) are given in Table (9 and 10). The results obtained indicate that the application of copper significantly increased the Cu uptake by plant (shoots and roots). However, the effect varied from one soil to another. Application rate of 2 $\mu g g^{-1}$ resulted in proportionally high increase in the Cu uptake by wheat plant (shoots) grown in the alluvial soils than it did with the sandy and calcareous soils.

Concerning copper uptake by wheat plant (shoots), data in Table (9) show that the highest values were 55.52 and 166.66µg /pot in the calcareous and sandy soils, at Cu application rate of 0.5 and 2.0 $\mu g\ g^{-1}$, respectively. The highest uptake of Cu in the calcareous soil was detected with adding 0.5 $\mu g\ g^{-1}$ Cu, while the highest uptake of Cu in the sandy soils was obtained with adding 2.0 $\mu g\ g^{-1}$Cu.

It is clear that, the highest values of copper uptak were found in the plants grown in the fine textured soils (alluvial) and the lowest ones were found in plants grown on the calcareous soils. These results are in accordance with those reported by **Jones (1971) and Thompson and Troeh(1982).**

With regard to the Cu uptake by wheat plants (roots), data in Table (10) reveal that the highest values of Cu uptake were 49.39, 6.62 and 203.83 µg /pot in the alluvial, calcareous and sandy soils, respectively. Increasing the rate of copper addition to 2 $\mu g\ g^{-1}$ in the alluvial soil resulted in significant increase in Cu-uptake in roots. While, the highest value of Cu uptake was with the addition rate of 0.5 $\mu g\ g^{-1}$ in the calcareous soil and 1 $\mu g\ g^{-1}$

in the sandy soil. The Cu uptake of wheat plants varied directly with the amounts of Cu in Mn oxides, organic matter, Fe oxides, total Cu and clay content. Therefore Cu associated with oxides, organic matter and total soils Cu are more important to Cu availability than Cu in other fractions. Clay content is the key soil property affecting soil Cu availability. Similar results were obtained by **Sims (1986)** and **Martens (1968)** who found that Cu uptake is significantly correlated with organic Cu, oxide-bound Cu, as well as with exchangeable Cu. The role of oxide bound Cu has generally been obtained in assessing Cu availability **(Mclaren and Crawford, 1973)**, but data in this study indicate that organic Cu as well as oxide-bound Cu tended to be the important sources of available Cu. These fractions increase as clay content in the soil increases.

4.6. Fractionations of Cu after cultivation:

Data in Table (11) show the amounts of Cu fractions in the alluvial soils under Cu addition rates of 0.0, 0.5, 1.0 and 2.0µg g^{-1} as $CuSO_4.5H_2O$ after cultivation with wheat plants. The amounts of Cu as soluble-Cu, exchangeable-Cu, carbonate-Cu, occluded-Cu, organic-Cu and residual-Cu fractions ranged from 0.0 to 0.5, 0.2 to 0.70, 0.4 to 0.6, 1.3 to 3.0, 1.0 to 1.65 and 39.05 to 41.75 µg g^{-1} Cu and constituted 0 to 0.7%, 0.28 to 0.99%, 0.51 to 0.85%, 0.87 to 4.22%, 1.45 to 2.11% and 56.14 to 58.8% of total Cu under copper application rate of 0, 0.5, 1.0 and 2.0µg g^{-1} soil as $CuSO_4.5H_2O$, respectively. Water soluble-Cu, exchangeable-Cu and occluded-Cu increase with increasing Cu addition, while the residual-Cu increased after the application of 2.0µg g^{-1}(58.8%). The high values of percentage of Cu in the residual fraction may indicate that Cu either native or added is strongly bound to soil components. Similar results were obtained by **Liang *et al*.(1990)** who found that the residual Cu ranged from 3.9 to 28.5 µg g^{-1} comprising 49.2- 78.2% of total Cu which indicates that the majority of total Cu was held within the silicate minerals structure.

With regard to the calcareous soils, data in Table (14) reveal that the amounts of water soluble Cu, exchangeable, carbonate, occluded and organically bound fractions after cultivation ranged from 0.0 to 1.0, 0.15 to 0.40, 0.6 to 1.30, 1.07 to 2.7 and 1.6 to 2.5 µg g^{-1} constituting 0.0-2.54%, 0.38-1.03%, 1.54-3.17%, 2.74- 6.59 and 5.13-6.09% of total Cu, respectively. Residual Cu ranged from 23.15 to 28.57 µg g^{-1} and comprised 56.71-72.33% of total Cu.

The calcareous soil was a special case, with a low percentage of Cu in the exchangeable and occluded fractions. This is probably a result of low clay content, **Kabala and Singh (2001).**

In the sandy soils, data in Table (15) indicate that the copper fractions content after the soil cultivated with wheat plants and application of 0.0, 0.5, 1.0 and 2.0 µg g^{-1} Cu as $CuSO_4.5H_2O$ ranged from 0.30 to 0.95; 0.4 to 1.0; 0.63 to 1.2; 1.3 to 2.0; 0.2 to 3.1 and 21.45 to 23.15 µg g^{-1} that constituted of 0.81-2.44%; 1.08-2.63; 1.71-3.08; 3.46-5.26; 0.54-8.16 and 55.9-60.53% of total Cu. The proportion of the water soluble, carbonate and organically bound forms increased with increasing Cu application. Also, the readily soluble forms (water soluble +exchangeable) varied from 0.70 to 1.65 µg g^{-1} which accounted for a small portion of the total Cu (1.89-4.23%). Several studies have shown a very low content of Cu in the readily soluble forms in sandy soil (**Saha *et al*., 1995; and Alva, *et al*., 2000).**

From the above it is quite obvious that most of the applied Cu was accumulated in OM, FeO and res**id**ual fractions .Therefore, sesquioxides and organic matter are the major components responsible for the adsorption of added Cu.

Residual Cu is the potentially available source for plants. Residual Cu in the clay mineral structures can be weathered and release Cu slowly to more readily available forms of Cu (A**ci – Cu** , MnO-Cu) during the growing season ,resulting in increases in exchangeable Cu, ***Liang et al (1990)***

4.7. Effect of copper application and incubation periods on the DTPA-extractable Cu in certain soils:

4.7.1. Alluvial soils:

Data in Table (12) and Fig (13) reveal that the amounts of DTPA-extractable Cu were progressively enhanced with increasing the rate of Cu application from 0.0 to 2.0 µg g^{-1}**.**

In the alluvial soil, the values of DTPA-extractable Cu after 3 days ranged from 1.7 to 2.06, 2.04 to 2.18, 2.71 to 3.08 and 2.8 µg g^{-1} due to the application of 0.0, 0.5, 1.0 and 2.0 µg g^{-1} treatments, respectively. After 2 weeks of incubation, the corresponding values ranged from 2.8 to 2.9, 3.04 to 3.09, 2.8 to 3.37 and 3.6 to 3.69 µg g^{-1}, respectively.

With regard to the values of DTPA-extractable Cu after 6 weeks of incubation, the values ranged from 1.51 to 1.63, 1.54 to 1.62, 1.57 to 1.7 and 1.89 to 1.93 µg g^{-1} due to Cu application of 0.0, 0.5, 1.0 and 2.0 µg g^{-1}. Data reveal that DTPA-extractable Cu progressively decreased with increasing the incubation period. The values representing the average of DTPA-extractable Cu after 3 days, one week, 2 weeks, 4weeks and 6 weeks ranged from 1.89 to 2.87, 2.43 to 3.64, 2.85 to 3.72, 1.53 to 1.73 and 1.57 to 1.91 µg g^{-1}, respectively. It is clear that the amounts of

DTPA-extractable Cu were highly increased at the 3 days, one and 2 weeks of incubation periods then decreased at the four weeks incubation periods. However, at 6 weeks of incubation, the values of DTPA-extractable Cu significantly increased in comparison with the corresponding values at 4 weeks of the incubation. The mean values under 6 weeks of the incubation were 1.58, 1.57, 1.64 and 1.91µg g^{-1} due to Cu application rates of 0.0, 0.5, 1.0 and 2.0 µg g^{-1} as $CuSO_4.5H_2O$**,** respectively.

Regarding the effect of Cu treatments, the average values Of DTPA-extractable Cu due to the application of 0.0, 0.5, 1.0 and 2.0 µg g^{-1} as $CuSO_4.5H_2O$, were progressively and significantly increased in comparison with control treatment. These results agree with those obtained by **Petersen *et al*. (2004)** who found that addition of Cu increases available Cu that tended to decreased with incubation time.

4.7.2. Calcareous soil:

Data in Table (13) and fig (14) represent the values of DTPA-extractable Cu, as affected by different incubation periods and Cu treatments in calcareous soil under investigation. Results show that application Cu rate of 0.5, 1.0 and 2.0 (µg g^{-1}) as $CuSO_4.5H_2O$ resulted in progressive significant increase in DTPA-extractable Cu, at the different incubation periods in comparison with control treatment.

Regarding the effect of incubation periods, the values of DTPA-extractable Cu after 3 days were 0.82, 0.71, 1.0 and 1.53 µg g^{-1} due the application rates 0.0, 0.5, 1.0 and 2.0µg g^{-1} respectively. Under 6 weeks of incubation period, the corresponding values were 0.4, 0.50, 0.62 and 0.81 µg g^{-1}, respectively.

It is clear that the amounts of DTPA-extractable Cu were highly reduced through the first 3 days of incubation them progressively increased during the following incubation periods. However, at 4 and 6 weeks of incubation, the values of DTPA-extractable Cu were quit lower in compared with the corresponding values at 2 weeks of the incubation.

This result may be due to that the calcareous soils contain the highest amounts of carbonate in the clay fraction. These results are in agreement with those obtained by **Singh *et al*.(1999)** who found that the adsorption of copper is one of the important factors that govern its availability to plants. The capacity and strength with which it is adsorbed depend largely on soil characteristic such as pH, $CaCO_3$, CEC, organic carbon and clay content. Also, **Doula *et al*. (1999)** found that the extent of copper adsorption increases with increasing pH and with decreasing ionic strength **Pardo (2000)** found that the adsorption of copper increased with increasing solution pH and copper initial concentration.

4.7.3. Sandy soils.

Data in Table (14) and Fig (15) show that Cu application at the rate of 0.0, 0.5, 1.0 and 2.0 µg g^{-1} resulted in progressive significant increase in the amounts of Cu extracted by DTPA, at different incubation periods in comparison with control treatment. The average values of DTPA-extractable Cu after 3 days of incubation were 2.65, 2.36, 2.74 and 3.52 µg g^{-1} as a result of Cu application rate of 0.0, 0.5, 1.0 and 2.0 µg g^{-1}, respectively. After 6 weeks of incubation period, the corresponding average values were 2.02, 2.52, 2.88 and 3.10 µg g^{-1}, respectively. Data reveal that the amounts of DTPA-extractable Cu were relatively high during the first tow periods of incubation (3 days and one week)

The highest DTPA-extractable Cu was extracted from the application of 2 µg g^{-1} Cu after 4 weeks, while the lowest one being obtained from Cu application rate of 0.5µg g^{-1} after 2 weeks incubation, where the chemical available (DTPA-extractable) Cu contents were 3.83 and 2.23 µg g^{-1}, respectively. Similar results were obtained by **Petrsen *et al*. (2004)** they found that soluble Cu is distributed among several chemical forms with varying degree of bioavailability to bacteria and that the relative speciation of Cu in solution depends on the degree of Cu loading. Also, increase of DTPA-extractable Cu with the increase of incubation time reflecting the fact that the concentration and /or bonding strength of legends in the soil water extracts changes with time, while the decreases with increase incubation time might be attributed to Cu mineralization.

The study indicates that use efficiency of Cu in wheat plants may be bigger if applied at 2 weeks in alluvial and calcareous soils and at 4 weeks in sandy soil.