

Factors affecting content in soil and its availability to plant

Khososy.A.M

The objectives of this research were: (i) to investigate the distribution of native and added Cu in some soils of Egypt with diverse soil properties, (ii) to evaluate the plant availability of the various Cu fractions, and examine the effect of soil properties on the distribution and plant availability of the soil different Cu fractions, and (iii) to examine the effect of incubation periods on availability of copper in soils. To reach these objectives, a green house and laboratory studies were conducted. The soils in these experiments were selected to have wide variations in physical and chemical properties. Wheat plants were planted in soil samples representing Nile alluvial soils (El-Giza Farm), calcareous soils (El-Nobariya) and sandy soils (Ismaliya). Sequential fractionations were conducted to partition total soil Cu into water soluble, exchangeable, carbonate, occluded, organically bound, and residual forms. Simple correlations were calculated between the various properties of the studied soils and Cu fractions to evaluate the properties most effective on the distribution of soil total Cu and the above mentioned fractions as well. The obtained results could be summarized as follows:

- 1- Chemical and physical properties
 - 1.1. Nile alluvial soils: Textural class of the alluvial soils is clay. The clay content varied from 44.1 to 60.3%. total calcium carbonate is very low and varied from 1.1 to 2.3%. The analytical data show that soil reaction of the Nile alluvial soils varied from pH 7.23 to 7.86 indicating that the soils are neutral to slightly alkaline. The amounts of total soluble salts as expressed by the electrical conductivity (dSm') of the soil saturation extract varied from 0.74 to 6.49 dSm-l indicating that these soils are none saline to slightly saline. The cationic composition of the soil saturation extract is dominated by Na⁺ followed by Ca⁺⁺ and Mg⁺⁺, while K⁺ ion is the least abundant soluble cation. Soluble anions is dominated by SO₄⁼ followed by Cl⁻ and HCO₃⁻.
 - 1.2. Calcareous soils: Textural class varied from sandy clay to clay. CaCO₃ content ranged from 20.0 to 29.2% with an increase in carbonate content in the surface layers, while organic matter content is very low and ranged from 0.01 to 1.09%. Soil reaction (pH) varied from 8.27 to 8.99 indicating that those soils are moderately alkaline to strongly alkaline. EC, values varied from 1.43 to 14.21 dSm' indicating that the soils are none saline to moderately saline. Soluble cations in the calcareous soils is dominated by Na⁺ followed by Ca⁺⁺ and Mg⁺⁺ while K⁺ ion is the least, while soluble anions is dominated by Cl⁻ and/or SO₄⁼ and HCO₃⁻ is the least abundant soluble anion.
 - 1.3. Sand soils: Sandy soils are classified as coarse textured soil where sand content is more than 90% CaCO₃ content is very low (0.48%). Organic matter content is very low and not exceeding 0.26%. Soils are slightly alkaline and none saline. Soluble cations are dominated by Na⁺ followed by Ca⁺⁺ and Mg⁺⁺ while K⁺ ion is the least abundant cation. Soluble anions is generally dominated by CF and/or SO₄ followed by HCO₃⁻.
- 2.1. Total copper: In the alluvial soils of Egypt total copper content varied from 35 to 155 µg g⁻¹, while in the calcareous soils it ranged between 13 and 971. µg g⁻¹. Sandy soils have 371.1 µg g⁻¹ total Cu content. It may be noticed that the total copper content in the studied soils followed the order Alluvial soils > calcareous soils > sandy soils. Computation of the correlation coefficients dictates that the total copper is significant and positively correlated with clay% and organic matter content. In contrast, total copper is significant negatively correlated with CaCO₃ and ECe. Multiple regression equation is: $\text{Total Cu} = -113.811 + 0.482 \text{ clay\%} - 1.089 \text{ CaCO}_3\% + 5.039 \text{ OM\%} + 19.62 \text{ pH} + 0.74 \text{ silt\%} - 2.942 \text{ EC}$
- 2.2. DTPA-extractable copper: DTPA-extractable Cu varied from 3.71 to 9.68, 0.37 to 6.17 µg g⁻¹ in the Nile alluvial and calcareous soils respectively,

while in the sandy soil it was 0.71ggDTPA-extractable Cu is positively and highly significant correlated with clay% and OM% but negatively and highly significant correlated with CaCO₃% and pH. Multiple regression equation is $DTPA-Cu = -26.452 + 0.062 \text{ clay\%} - 0.258 \text{ CaCO}_3\% + 0.456 \text{ OM\%} + 3.608 \text{ pH} + 0.0895 \text{ silt\%} + 0.005 \text{ EC}$. Content of copper fraction in the studied soils

3.1. Total copper

Total copper content in the Nile alluvial soil varied from 35 to 155 $\mu\text{g g}^{-1}$ with an average 81.86 $\mu\text{g g}^{-1}$, while calcareous soils showed a total copper content that ranged between 23 and 97 $\mu\text{g g}^{-1}$ with an average of 49.7 $\mu\text{g g}^{-1}$. Variations in the total Cu content are due to variation in soil texture and organic matter content.

3.1.1. Soluble copper

Soluble Cu extracted by water in the Nile alluvial soils ranged from 0.8 to 1.6 $\mu\text{g g}^{-1}$ being about 0.52-1.6 % of the total, while in the calcareous soils, soluble Cu varied from 0.01 to 1.8 $\mu\text{g g}^{-1}$ with about 0.04-3.6 % of total Cu.

3.1.2. Exchangeable copper

Exchangeable Cu content in the Nile alluvial soils ranges from 0.6 to 2.0 $\mu\text{g g}^{-1}$ representing from 0.7 to 2.9 % of total Cu while in the calcareous soils, exchangeable Cu fluctuates between 0.2 and 2.0 $\mu\text{g g}^{-1}$ making 0.37 and 2.08 % of total copper.

3.1.3. Copper bound by CaCO₃

The values of Cu bound to CaCO₃ in the Nile alluvial soils are varying from 0.0 to 2.4 $\mu\text{g g}^{-1}$ respectively 0.0 and 2.40 % of total Cu. In the calcareous soils copper bound by CaCO₃ varied from 0.8 to 3.61 $\mu\text{g g}^{-1}$ making 1.48 and 7.20 % of total Cu. The calcareous soils possessed the highest average content of copper bounded by CaCO₃.

3.1.4. Occluded copper

The distribution of occluded copper in the Nile alluvial soils ranged from 1.0 to 2.4 $\mu\text{g g}^{-1}$ constituting 1.47 and 2.40% of total Cu. In the calcareous soils the occluded copper varies from 0.8 to 6.0 $\mu\text{g g}^{-1}$ being within the range of 1.48 and 6.18 % of total Cu.

3.1.5. Copper bounded by organic sites

Values of bound to organic sites in the Nile alluvial soils ranged from 2.2 to 5.6 $\mu\text{g g}^{-1}$ and fell within the range of 3.24 to 8.92% of total Cu, while in the calcareous soils copper bound by organic sites ranged from 3 to 6.4 $\mu\text{g g}^{-1}$ and fell within the range of 5.55 and 24.61% of total Cu.

3.1.6. Residual copper

Residual copper content in the Nile alluvial soils varied widely from 17.1 to 80.0 $\mu\text{g g}^{-1}$ and fell within the average of 48.85 to 51.61% of total Cu. In the calcareous soils, the residual Cu values ranged from 10.2 and 44.9 $\mu\text{g g}^{-1}$ being within the average of 15.05 and 69.25% of total Cu. On the basis of results obtained in this study the Cu fractions in the alluvial soils were in the order: Residual > organic > occluded > carbonate > water soluble > exchangeable. In the calcareous soils the order of fraction as: Residual > organic > occluded > carbonate > exchangeable > water soluble.

4. Effect of some soil characteristics on Cu fractions in soils

4.1. Nile alluvial soils

Water soluble Cu was positively correlated with clay% ($r = 0.526$) and negatively correlated with total Cu ($r = -0.551$). Exchangeable Cu was negatively and significantly correlated with EC, ($r = -0.680$). Occluded Cu was positively and significantly correlated with pH ($r = 0.508^*$) and negatively correlated with EC ($r = -0.720^*$). Organic Cu was positively and significantly correlated with silt% ($r = 0.678^*$). Residual Cu was positively and significantly correlated with each of clay% ($r = 0.610^*$) and OM% ($r = 0.870^*$) and highly and significantly correlated with total Cu ($r = 0.900^*$) and negatively correlating is found between residual and CaCO₃ % ($r = 0.708^*$). The multiple regression equations are: Water soluble Cu = $-3.749 - 0.013 \text{ clay\%} - 0.012 \text{ silt\%} + 1.267 \text{ OM\%} + 0.602 \text{ pH} - 0.052 \text{ EC} - 0.012 \text{ total Cu}$. Exchangeable-Cu = $-1.789 + 0.007 \text{ Clay\%} + 0.005 \text{ silt\%} + 0.598 \text{ CaCO}_3\% + 1.203 \text{ OM\%} - 0.285 \text{ EC} - 0.01 \text{ total Cu}$. Carbonate-Cu = $1.19 - 0.026 \text{ clay\%} + 0.045 \text{ silt\%} - 0.156 \text{ CaCO}_3\% + 2.016 \text{ OM\%} - 0.189 \text{ EC} - 0.029 \text{ total Cu}$. Occluded-Cu = $1.184 + 0.012 \text{ clay\%} + 0.061 \text{ silt\%} + 0.343 \text{ CaCO}_3\% - 0.526 \text{ OM\%} - 0.383 \text{ EC} + 0.002 \text{ total Cu}$. Organic-Cu = $4.096 + 0.061 \text{ clay\%} + 0.183 \text{ silt\%} + 0.332 \text{ CaCO}_3\% - 3.377 \text{ OM\%} - 0.272 \text{ EC} + 0.004 \text{ total Cu}$. Residual-Cu = $-0.324 \text{ silt\%} + 2.10 \text{ OM\%} - 4.2$.

4.2. Calcareous soils

Water soluble Cu was positively and correlated with clay% ($r = 0.526$). Exchangeable-Cu was negatively and correlated with each of OM% ($r = -0.719$) 0.575), while positively correlated with total Cu ($r = 0.610^*$). Occluded Cu was not significantly related to any of the variables. Carbonate Cu was negatively and significantly correlated with OM% ($r = -0.840$). Organic Cu showed a negative and significant correlation with clay% ($r = -0.680$) and positively correlated with total Cu ($r = 0.540$). Residual Cu was positively and significantly correlated with each of clay% ($r = 0.610$) and silt% ($r = 0.610$) and on the other hand pH displayed a significant correlation with residual Cu ($r = 0.640^*$) and significantly correlated with EC ($r = 0.717^*$). On the other hand, Residual-Cu = $-140.543 + 0.592 \text{ clay\%} + 13.673 \text{ CaCO}_3\% + 60.064 \text{ EC} + 0.337 \text{ total Cu}$. The multiple regression equations are: Water soluble Cu = $-1.305 + 0.117 \text{ clay\%} - 0.089 \text{ silt\%} + 0.109 \text{ CaCO}_3\% - 0.094 \text{ EC} - 2.498 \text{ OM\%} - 0.012 \text{ total Cu}$. Exchangeable-Cu = $-1.305 + 0.005 \text{ Clay\%} - 0.033 \text{ silt\%} + 0.103 \text{ CaCO}_3\% - 1.675 \text{ OM\%}$.

$-0.170EC - 0.0113\text{total Cu}.$
 $\text{Carbo-Cu} = 3.369 + 0.058\text{clay}\% - 0.092\text{silt}\% + 0.151\text{CaCO}_3\% - 3.5580\text{M}\%$
 $- 0.161EC - 0.038\text{total Cu}.$
 $\text{Occl-Cu} = 9.626 + 0.113\text{clay}\% - 0.339\text{silt}\% + 0.237\text{CaCO}_3\% - 6.1190\text{M}\%$
 $- 0.468EC - 0.071\text{total Cu}.$
 $\text{Organic-Cu} = 7.894 - 0.184\text{clay}\% + 0.017\text{silt}\% + 0.159\text{CaCO}_3\%$
 $+ 0.1180\text{M}\% + 0.012EC - 0.029\text{total Cu}.$
 $\text{Residual-Cu} = -54.917 + 0.009\text{clay}\% + 2.032\text{silt}\%$
 $- 0.703\text{CaCO}_3\% + 31.460\text{M}\% + 0.627EC + 0.585\text{total Cu}.$

5. Chemical fractionation of Cu prior to soil cultivation: In the alluvial soil, the amounts of water soluble, exchangeable, carbonate, occluded, organically bound and residual fractions were 1.2, 2.0, 1.8, 1.8, 5.6 and 44.90 $\mu\text{g/g}$ and constituted 1.74, 2.9, 2.6, 2.6, 8.12 and 65.07% of total Cu, respectively, while in the calcareous soils these fractions of Cu were 0.8, 1.0, 3.0, 1.2, 5.0 and 27.50 $\mu\text{g/g}$ and constituted 2.05, 2.65, 8.69, 3.07, 12.82 and 70.51% of total Cu. In the sandy soils, the fractions of Cu were 0.8, 1.4, 2.4, 1.2, 3.0 and 18.1 $\mu\text{g/g}$ and constituted 2.16, 3.78, 3.48, 3.24, 8.11 and 48.92% of total Cu, respectively. The data reveal that water soluble Cu constituted the least amount of Cu in the studied soils, while residual and organically Cu constituted the highest portion of soil Cu in the alluvial, calcareous and sandy soils.

6. Dry matter, copper concentration and uptake: 6.1. Dry matter: Dry matter yield of the wheat plants (shoots and roots) at 0.5, 1 and 2.0 g/g copper addition rates reveal that the addition of 2 g/g copper increased the dry weight of shoots and roots of wheat plants in the alluvial soil which on the average amounted to 17.07 and 2.32 (g/pot) and in sandy soil the addition of 2 g/g copper increased the dry weight of shoots which on the average amounted to 14.31 (g/pot). While the addition of 0.5 g/g copper increased the dry weight of roots which on the average amounted to 7.33 (g/pot). While in the calcareous soil addition of 0.5 g/g copper increased the dry weight (shoots and roots) of wheat plant being on the average 4.6 and 0.5 (g/pot), respectively.

6.2. Copper concentration: Data of copper concentration in wheat plants grown on the alluvial, calcareous and sandy soils at the additions rates of 1.0 and 2.0 g/g Cu shows that application of Cu treatment significantly increased Cu concentration in both shoots and roots of wheat plants grown on the alluvial and calcareous soils compared to those of the plants grown on the sandy soil.

6.3. Copper uptake: Copper uptake by wheat plants (shoots) grown on the alluvial soils at the application of 0.5, 1.0 and 2.0 g/g Cu varied from 240.07, 284.48 and 272.30 $\mu\text{g/pot}$, respectively, while in the calcareous soils the values were 55.52, 17.89 and 37.85 $\mu\text{g/pot}$ while in the sandy soils was 134.73, 141.89 and 166.66 $\mu\text{g/pot}$, respectively. The average of copper uptake by wheat plant (roots) grown on the alluvial, calcareous and sandy soils at the additions of 0.5, 1.0 and 2.0 g/g Cu were 49.01, 36.64 and 37.24 $\mu\text{g/pot}$ in the alluvial soils. In the calcareous soils were 7.04, 5.87 and 8.38 $\mu\text{g/pot}$; while in the sandy soils were 196.16, 168.71 and 173.32 $\mu\text{g/pot}$. It is clear that the highest values of copper uptake by wheat plant (shoots) are found in the plants grown on the alluvial soils and the lowest ones are found in plants grown on the calcareous soils, while values are recorded in the copper uptake by plant (roots), the high detected in the sandy soils and the lowest are in calcareous soils.

7. Fractionation of Cu after cultivation: 7.1. The amounts of Cu in the soluble C Carbo-Cu, Occl-Cu, organic-Cu and resid-Cu to 0.5, 0.2 to 0.7, 0.4 to 0.6, 1.3 to 3.0, 1.0 to 41.75 $\mu\text{g/g}$ Cu and constituted 0.0 to 0.99%, 0.51 to 0.85%, 0.87 to 4.22%, 1.45 to 56.14 to 58.8% of total Cu under the application of 1.0 and 2.0 g/g respectively.

7.2 In the calcareous soils, the amounts of Cu, Exchan-Cu, Carbo-Cu, Occl-Cu, Orga-Cu varied from 0.15 to 0.40, 0.60 to 1.30, 1.07 to 23.15 to 28.57 $\mu\text{g/g}$ and constituted 0.154 to 3.17%, 2.74 to 6.59%, 5.13 to 6.9% to 72.33% of total Cu under the application of 0.5 g/g Cu, respectively.

7.3. In the sandy soils, the Cu fractions cultivation and application of 0.0, 0.5, 1.0 and were 0.3 to 0.95, 0.4 to 1.0, 0.63 to 1.2, 1.3 to 21.45 to 23.15 $\mu\text{g/g}$ that constituted 0.262, 1.71-3.08, 3.46-5.26, 0.54-8.16 and 55 total Cu, respectively. Exchan-Cu, ranged from 0.65 and 39.05 $\mu\text{g/g}$, 0.28 to 2.11% and 0.0, 0.5, 1.0, 1.6 to 2.5 38 to 1.03%, and 56.71 to 1.0 and 2.0 content after 2.0 g/g Cu 0.0, 0.2 to 3.0 1-2.44, 1.08-9-60.53% of 8.

8. Effect of incubation on DTPA extractable - Cu: 8.1. Alluvial soils: In the incubation experiment, DTPA extractable-Cu was progressively and significantly increased as a result of increasing rate of Cu application from zero to 2 g/g Cu in each of the following incubation periods; 3 days, 1, 2, 4 and 6 weeks. However, it was sharply increased during the first 2 weeks of incubation then it slightly decreased during the other incubation periods.

8.2. Calcareous soils: Results show that application rate of 0.5, 1.0 and 2.0 g/g Cu as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ resulted in progressively significant increase in DTPA-extractable Cu at the one and two weeks of

incubation periods in comparison with that of the first 3 days of incubation period then slightly decreased at 4 and 6 weeks of incubation, where the values of DTPA-Cu were significantly decreased in comparison with the values at 2 weeks of the incubation. 8.3. Sandy soils: The highest DTPA-extractable Cu was obtained from the application of 2 j.tg g⁻¹Cu after 4 weeks incubation while the lowest one being obtained from the application of 0.5 jig g⁻¹Cu after 2 weeks incubation. The increase of DTPA-Cu with increasing incubation time reflects the fact that the concentration and/or bonding strength of ligands in the soil extracts changes with time due to mineralization Cu. Finally it can be concluded that: • Sesquioxides and organic matter are components responsible for the adsorption of copper. • The residual copper is the potentially available for plants. • The efficient use of copper to wheat plants can be increased if applied two weeks in the calcareous soils, and 4 weeks in sandy soils. Plants reach their most active rate of absorption of added available sources may be alluvial and it before the fixation.