

STUDY ABOUT THE COPPER REGIME FROM AGRICULTURAL ECO-MEDIUM IMPROVED BY SEWAGE SLUDGE

Nicolae IONESCU^{1,*}, Gelu MUJEA², Marilena DIACONU²,
Ana IORDĂNESCU² and Katalin IONESCU²

1 Agricultural Research and Development Station Pitești, Pitești, Romania.

2 Wastewater Treatment Plant Pitești, Pitești, Romania.

*Corresponding author: N. Ionescu, E- mail: nicolae_ionescu@yahoo.com,
contact@apacanal2000.ro

Abstract. Together with other chemical elements (macronutrients and micronutrients), copper (Cu) take active part in plant nutrition. The application of waste sludge increased Cu contents in both soil and plants. The study of heavy metal was done in terms of sludge doses increased from 0-50 t.ha⁻¹, with and without chemical fertilizers. For luvisol sensitive growth were observed with near- normal oscillations of the average concentrations of total Cu. Mobile forms of copper have seen significant growth, with indices of correlation between 0.709 for maize, the wheat (2) 0.619, 0.906 for soybean and 0.924 for wheat (4). However, copper ions (Cu²⁺) were specifically absorbed by the crop: maize, winter wheat and soybeans. The correlations obtained between Cu concentrations in plants with sludge doses, showed increases in all cases: statistically ensured in flowering period (in leaves) and insignificant in maturity period (in grains), except wheat (2) with $r = -0,507^*$.

Key words: Cu, sludge, maize, wheat, soybeans

INTRODUCTION

The existence of copper (Cu) in nature is strongly related to the contents of soil parent material originally evolved. Heavy metal accumulation in arable horizon is favored both by growing plants and the contribution of organic matter (OM) from different sources. Thus, if the lithosphere contains about 100 mg Cu, soils contain between 2 and 100 mg Cu (Yara, 2008). Our soils contain between 5 and 20 mg Cu (Bajescu & Chiriac, 1984), or between 5 and 30 mg Cu (Bajescu 1971; Ceapoiu et al. 1984). Recent estimates show content in the soil ranging between 1-37 mg Cu total forms and 3-14 mg Cu mobile ones (Davidescu & Davidescu 1981). However, the levels that are found with plant roots in the area is not the most important factor for absorption and thus to use it in normal physiological processes (Stevenson &

Ardakani 1972). Copper is found in soil in the form of ion- Cu^{2+} (highest proportions) as well as neutral insoluble salts, other water soluble components as well as mineral- rich with [copperite- Cu_2O ; asurite- $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$] (Bîlteanu 1988). The ions are absorbed on clay minerals and in a way related to organic matter. Absorption cross- Cu^{2+} in soil environment occurs depending on a number of factors. The most important are: pH, organic carbon (OC) content, presence of other metal ions, humidity etc. Positive influence on soil acidity Cu^{2+} absorption with the possibility that as the ions increases with pH values to be less active. Cu- MO complexes vary in stability over a variety of cases and is explained by the existence of different links to print the nature of trade between the mineral (Guinn & Joham 1962). In this case with be detained for such a complex, sometimes not (Mortvert et al., 1972). Instead the association with-clay has a degree of hydrolysis so that Cu^{2+} on clay is more easily absorbed by plants (Chao & Harward 1962).

In comparison with other metal ions Cu^{2+} reduces Fe and Mn availability and in turn is inhibited by Zn and Mo (Ceapoiu et al. 1984). Copper is absorbed by plants for normal functioning of normal physiological processes (Bowen 1969; Haertl 1963). Any plant that grows normally contain certain concentrations of Cu^{2+} . The control of crop plants show some states between deficiency and excess.

Deficiency occur at concentrations of 3-4 mg Cu in the leaves (Andrews 1954). The normal values are below 10 mg. From this point of view of literature data shows a relative uncertainty. The toxicity occurs when the concentration of soil and plant exceeds certain limits. An estimate of the toxicity shows that over 20 mg of plant leaves, copper becomes dangerous (Andrews 1954; Hader et al. 1957). On acid soils, but toxicity to the exchange takes place over 50 mg. Excessive concentrations of copper can be achieved by applying sewage sludge resulting from urban wastewater treatment plant (Mujea et al. 2010). Raw sludge obtained by processing and dewatering can be used as organic fertilizer only if the Cu content does not exceed legal standards (Ord. 344, 2004). Such sludge processed is used in this experiment due to high content in macro- nutrients and a moderate copper level.

MATERIALS AND METHODS

In the period 2004- 2007 a complex experiment was initiated. During this experiment plants were cultivated by the structure: 1.- maize, 2.- winter wheat, 3.- soybeans and 4.- winter wheat. In normal cultivation technologies these plants were

fertilized with different doses of organic- mineral. Thus, these doses were applied to sewage sludge: 0 t.ha⁻¹, 5 t.ha⁻¹, 10 t.ha⁻¹, 25 t.ha⁻¹ and 50 t.ha⁻¹.

The sewage sludge suffered an anaerobic digesting followed by dewatering within Pitesti Wastewater Treatment Plant. Chemical fertilizers were differentiated on three levels: unfertilized, needs to ½ of normal and total doses (1/1). Plants have received such N₅₀P₅₀/maize, N₆₀P₄₀/wheat, N₃₀P₃₀/soybeans and N₄₀P₄₀/wheat for doses ½ and N₁₂₀P₈₀/maize, N₁₂₀P₈₀/wheat, N₆₀P₆₀/soybeans and N₈₀P₈₀/wheat for the 1/1 doses. Sludge doses were applied in the same quantities in the first two years- from maize and wheat in year two, following that soybeans and wheat in the past year to receive their residual effect.

The experiment with the lot divided had the A factor- sludge doses and the B factor- chemical fertilizers doses. Each variant had a surface of 100 m² each and was rehearsed (replicated) for three times. Leaves samples were taken during flowering period: at maize the leaves located at cob level, at winter wheat the last 3 leaves including the standard leaf and the soybeans the leaves in the central area of the plant but also with bean- pods in formation process. Soil samples were collected with the agrochemical sampling device of arable horizon 0-20 cm, between flowering to maturity period.

Chemical analysis were performed according to the latest European standards and methodologies: copper leaves (Cu_{LV}), grains (Cu_G) and ground (Cu_{TF}) forms total- SR ISO 11047-99, mobile forms of ground (Cu_{MF})- SR ISO 14870-99, both over sludge an-aerobically digested and over soil and plants. The data were statistically processed by analysis of the variant (Anova test) and with the help of correlations and regressions.

RESULTS AND DISCUSSIONS

Cu contents in the cultivation environment (soil).

Ground measurements performed revealed heavy metal forms both by total and by mobile forms. Total soil copper values ranged from average to be considered good (Table 1). Thus, in the four years Cu_{TF} ranged between 14-15 mg.kg⁻¹ d.w. as minimum and 25-28 mg.kg⁻¹ d.w. the maximum value.

Table 1. The copper contents from soil (mg.kg⁻¹ d.w.), total forms.

Heavy metal	Maize	Wheat	Soybean	Wheat	Toxic limit
Cu, limits media	20 – 28 23	19 – 25 21	15 – 19 17	14 – 24 19	80 (100 ³⁴⁴)

100³⁴⁴ : Ord. 344/2004

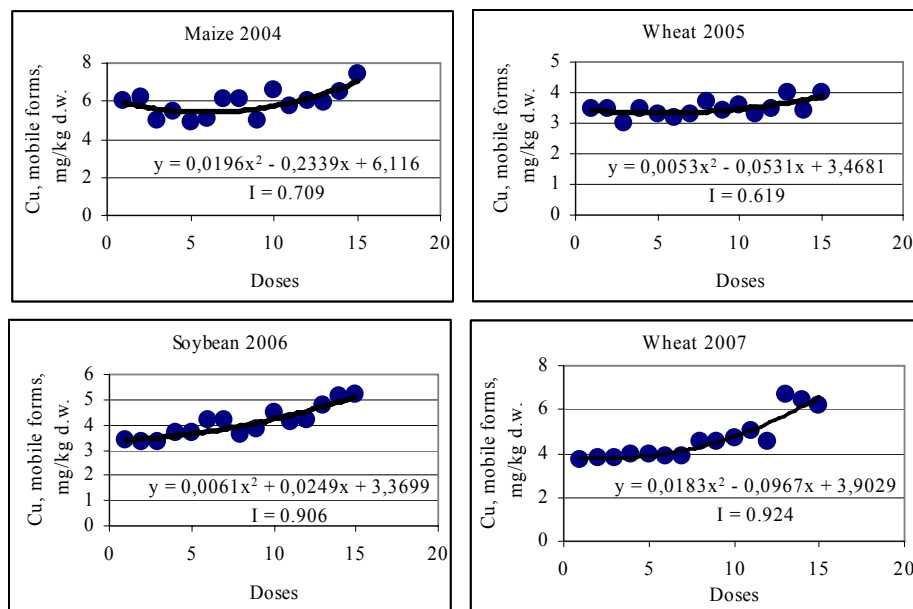


Figure 1. Correlations between Cu concentrations, mobile forms (Cu_{MF}), and sludge & chemical doses used

Due to the positive effect of waste sludge introduced into the soil, copper Cu_{MF} has evolved highly significant positive (Fig. 1). Depending on the dosage used Cu_{MF} evolved from 5-6 $mg \cdot kg^{-1}$ d.w. of control at 7 $mg \cdot kg^{-1}$ d.w. in large doses for maize, between 3.5-4.0 $mg \cdot kg^{-1}$ d.w. for wheat from second year, between 3.5-5 $mg \cdot kg^{-1}$ d.w. for soybeans, and between 4-6 $mg \cdot kg^{-1}$ d.w. the wheat from last year.

Influence of experimental factors on the content of Cu in leaves and grains

Given the favorable conditions in the cultivation soil, field plants absorbed Cu in the vegetative organs. Copper is considered an essential micro-nutrient. The average concentration of plants would be the situation in general between 5 and 20 mg (Băjescu & Chiriac 1984). Between 4 and 5 mg with the leaves is considered a danger zone that begins with Cu deficiency. Given the limits of this deficiency and heavy metal excess, plant analysis highlighted moderate concentrations of copper. The correlations obtained between the doses used and concentrations of Cu in the three plants show very significant increases in insurance and statistically significant (Fig. 2).

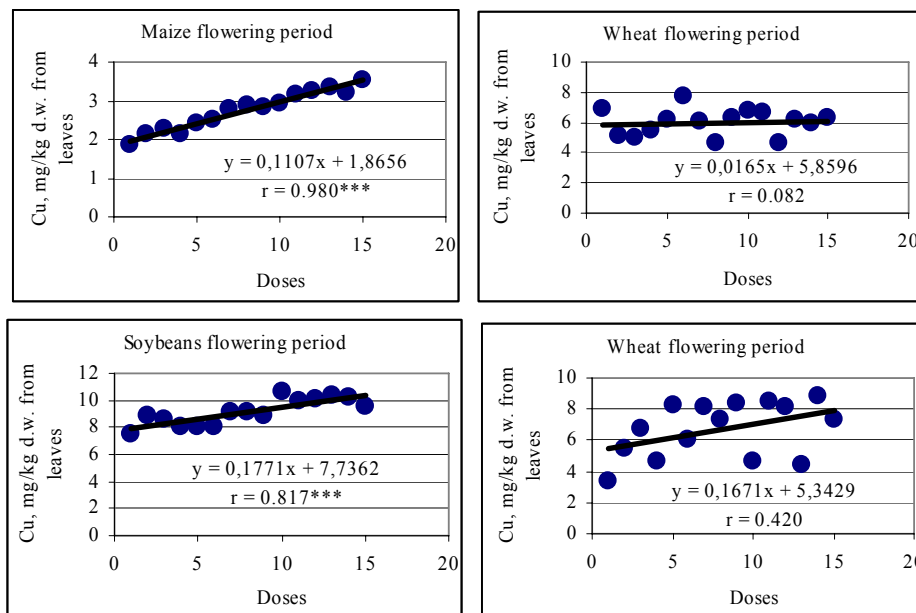


Figure 2. Correlations between Cu concentrations from plant leaves (Cu_{LV}), and sludge & chemical doses used

In the flowering stage of crop plants the content of Cu was in various concentrations. Cu in maize leaves was between 2.0 and 3.5 $mg.kg^{-1}$ d.w. in the big doses used: 50 $t.ha^{-1}$ sludge and $N_{120}P_{80}$. The increase is highly significant ($r=0.980^{***}$). In the second year of wheat leaves Cu varied around 6.0 $mg.kg^{-1}$ d.w. and $r=0,082$. Cu content in soybean leaves was between 8.0 to 10.0 $mg.kg^{-1}$ d.w. ($r=0,817^{***}$). Last year, wheat leaves had 5.5-8.0 $mg.kg^{-1}$ d.w. Cu ($r=0,420$). All these concentrations demonstrates that plants have absorbed different quantities of Cu (as species). Chemical analysis showed that three plants were used Cu at all stages of the vegetation period, after which they were stored in the grains, as a final product. In the final phase- at maturity there was noticed that the plants have deposited Cu in grains. Representing one of the constitutive plants' element, Cu was initially absorbed, transposed through xylem and phloem, and contributed to a better enzymes regime functioning, in the synthesis of chlorophyll and fruition, then Cu deposited into grains. Thus a Cu export phenomenon took place, from the cultivation environment into the grains. The common ways of each crop plants are specific (Fig. 3). Cu concentrations of grains were specifically framed between: 2.0-1.5 $mg.kg^{-1}$

d.w. for maize, 6.0-7.0 mg.kg⁻¹ d.w. for wheat (year 2), 17.0-15.0 mg.kg⁻¹ d.w. for soybean and 5.0-3.7 mg.kg⁻¹ d.w. for wheat (last year). These figures show the amounts of Cu that were exported with the harvest grains. This demonstrates on one side that at maturity plants no longer need Cu, and their value was relatively variable compared with the grains production. With higher values of copper from grain were determined in soybeans, the lowest in maize and winter wheat was intermediate.

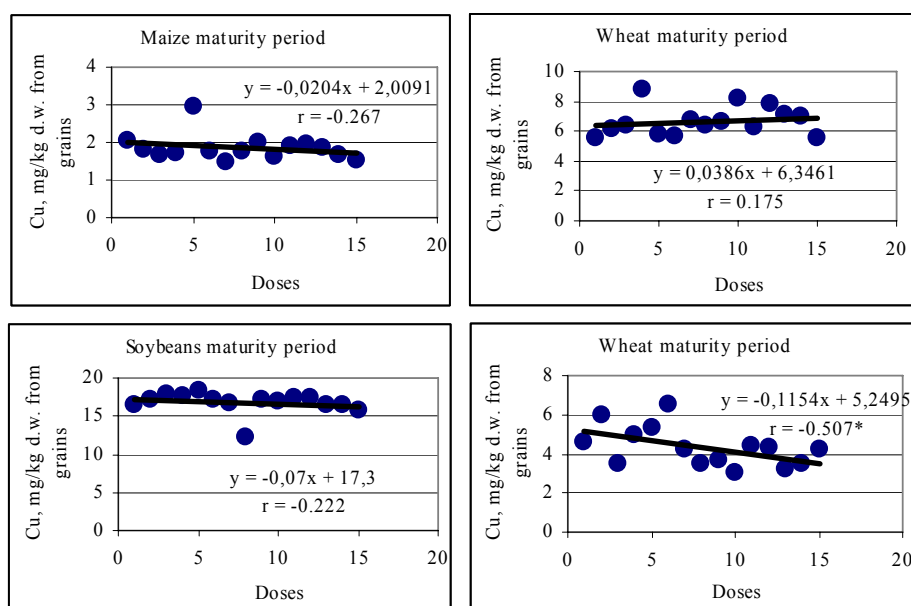


Figure 3. Correlations between Cu concentrations from plant grains (Cu_{GR}), and sludge & chemical doses used

CONCLUSIONS

Domestic sludge interfered in the Cu regime from agricultural ecosystem. Depending on doses used, with and without chemical fertilizers, Cu contents had increased as follows: moderate for total forms (Cu_{TF}) and significant for mobile forms (Cu_{MF}). Compared to the normal limit contained within 3-14 mg.kg⁻¹ d.w. Cu_{MF} , in the experiment there were obtained values between 3.5-7.7 mg.kg⁻¹ d.w. Cu_{MF} .

Having available good Cu_{MF} concentrations, plants absorbed Cu^{2+} ions in specific quantities. Domestic sludge doses helped absorption in a direct

and increasing relationship with it. Thus, in the flowering phase, plants leaves were containing in average between: 2.0-3.5 mg.kg⁻¹ d.w. Cu_{LV} for maize, between 5.9-6.1 mg.kg⁻¹ d.w. Cu_{LV} for wheat, 7.8-10.2 mg.kg⁻¹ d.w. Cu_{LV} for soybean and between 5.7-8.4 mg.kg⁻¹ d.w. Cu_{LV} for the wheat in the last cultivation year.

Copper proved to be an indispensable micronutrient for plants' life. It is relatively easily absorbed from the Cu_{MF} rich soil, being trans-located in the entire plant and used in the multitude of specific bio-chemical processes. After fulfilling its specific physiological functions, Cu was stored into the grains, as final products of the plants raise-up and development processes. Cu_{GR} content into beans was specific for the three plants and obviously at different levels compared to flowering phase. Thus, Cu_{GR} oscillated between: 2.0-1.5 mg.kg⁻¹ d.w. in maize beans, 6.2-7.0 mg.kg⁻¹ d.w. in wheat grains, 17-16 mg.kg⁻¹ d.w. in soybeans and 5.0-3.6 mg.kg⁻¹ d.w. last year wheat grains. These quantities represent the Cu export from soil fertilized with sewage sludge.

REFERENCES

- Andrews, W.B. (1954): Response of Crops and Soils to Fertilizers and Manures. State College, Mississippi: W.B. Andrews.
- Bajescu, I. (1971): Repartitia microelementelor B, Mn, Co, Cu, Zn in unele soluri din Romania. Teza de Doctorat, Universitatea Bucuresti, Bucharest.
- Băjescu, I., Chiriac A. (1984): Distributia microelementelor in solurile din Romania. Implicatii in agricultura. Ed. Ceres Bucuresti, Bucharest.
- Bowen, J.E. (1969): Absorbition of copper, zinc and manganese by sugar cane tissue. Plant Physiology 44: 255-261.
- Ceapoiu, N., Bilteanu, Gh., Hera, Cr., Saulescu, N.N., Negulescu, F., Barbulescu, Al. (1984): Graul. Ed. Academiei Bucuresti, Bucharest.
- Chao, T.T., Harward, M.E. (1962): Nature of acid soil clays and relationships to ion activities and ion ratios in equilibrium solutions. Soil Science 93: 246-253.
- Davidescu, D., Davidescu, V. (1981): Agrochimia moderna. Ed. Academiei Bucuresti, Bucharest.
- Guinn, G., Joham, H.E. (1962): Effect of two chelating agents on absorption and translocation of Fe, Cu, Mn and Zn by the cotton plant. Soil Science 94: 220-229.
- Hader, R.J., Harward, M.E., Mason, D.D., Moore, D.P. (1957): An investigation of some of the relationships between Cu, Fe and Mo in the growth and nutrition of lettuce: I. Experimental design and statistical methods for characterizing the respons surface. Proceedings Soil Science Society of America 21:59-67.
- Haertl, E.J. (1963): Chelation in nutrition, metal chelates in plant nutrition. Journal of Agromony and Food Chemistry 11: 108-113.
- Mujea, G., Diaconu, M., Ionescu, N., Iordanescu, A., Ionescu, K. (2010): The sewage sludge influence upon copper content in the luvisoil-plants eco-system, Scientific Papers Series A UASVM Bucharest 53: 134- 140.

Stevenson, F.J., Ardakani, M.S. (1972): Organic matter reactions involving micronutrients in soils. *Micronutrients in Agriculture* 79-91.

***Ordinul nr. 344/708. Normele tehnice privind protectia mediului, in special a solurilor cand se utilizeaza namoluri de epurare in agricultura. *Monitorul Oficial* 959, 2004.

***Yara International ASA, *Technical Elements*, Oslo- Norge, 2008.