

## STUDY ABOUT SLUDGE DOSES INFLUENCE UPON ZINC, COPPER AND MANGANESE CONTENTS FROM SOIL-WHEAT ECO-SYSTEM

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### ABSTRACT

*Contents of Zn, Cu and Mn both in soil and wheat plants were observed depending on the doses of sludge: 0-50 t.ha<sup>-1</sup>, with and without chemical fertilizers (type NP). Wheat plants absorbed ions Zn<sup>2+</sup>, Cu<sup>2+</sup> and Mn<sup>2+</sup> in specific amounts. Zinc was absorbed in 25 to 40 mg.kg<sup>-1</sup> d.w. at flowering and 70 mg.kg<sup>-1</sup> at maturity. Copper has been used in wheat 6-7 mg.kg<sup>-1</sup> d.w. both in flower and maturity, and plant manganese was present in a concentration of 130 mg.kg<sup>-1</sup> d.w. at flowering and around 100 mg.kg<sup>-1</sup> d.w. at maturity. Correlations obtained between total biomass and contents of Zn, Cu and Mn in leaves showing obvious increases only for zinc ( $r = 0,515^*$ ) and minor for copper ( $r = -0,037$ ) and manganese ( $r = -0,047$ ). Grain yields were correlated with Zn, Cu and Mn from kernels marginally positive in the zinc ( $r = 0,079$ ) and marginally negative with copper ( $r = -0,254$ ) and manganese ( $r = -0,236$ ).*

### INTRODUCTION

Generally soils containing varying amounts of zinc (Zn), copper (Cu) and manganese (Mn). Earth is estimated at 10-300 mg.kg<sup>-1</sup> media content from a d.w. Zn, 2-100 mg.kg<sup>-1</sup> d.w. Cu and 175-1820 mg.kg<sup>-1</sup> d.w. Mn. The presence of three chemical elements in soil is not a criterion for the availability to plants (Tisdale, 1975). White luvisoil containing Zn, Cu and Mn evolved in various forms, associated with the mineral and organic parts. Solubility and their availability varies from soluble forms to the highly retained (Băjescu, 1971, 1984). Into the soil Zn, Cu and Mn are absorbed in the form of ions Zn<sup>2+</sup>, Cu<sup>2+</sup> and Mn<sup>2+</sup>. Like other heavy metals, Zn, Cu and Mn are in octahedral positions by partial replacement of other chemical elements (Al, Fe) in clay mineral structure. Zinc and copper can be incorporated in the Fe and Mn hydrated oxides in specific existing small balls (bobovines), or film on the surface of clay minerals. Regime Zn, Cu and Mn in soil, has a strong complex character, due to many factors, depending on which crops can absorb and use, or not. The most important are: soil reaction, redox potential, organic matter, rainfall regime, microbiological activity, mineralogical composition (Hera, 1988). In soils with a pH between 5.0 and 6.5 become available to plants these heavy metals (Wear, 1956). From this point of view white luvisoil best meets the accessibility of Zn, Cu and Mn for plants. Specific microbial activity here is quite low, leading to a true conservation of Zn<sup>2+</sup>, Cu<sup>2+</sup> and Mn<sup>2+</sup> available. Organic matter (OM) affects the mobility of these ions, both through lower affinity compared to other heavy metals, making it readily available and the specific degree of decomposition. However, the eco-environment that has experienced white luvisoil with sludge waste show the existence of the total forms, and those mobile ones (Giunn, 1962), and broad opportunities to be absorbed and used in many biological processes involving (Davidescu, 1981, Bîlteanu, 1988). A reliable source is the zonal agricultural OM is anaerobic digestion and dehydrated sludge from waste water treatment plant in Pitești. This material comparable in quality to manure (Mihalache, 2006), sludge is processed as a new source, so macro-nutrients (MACRO<sub>n</sub>) for agricultural plants: nitrogen, phosphorus, potassium, calcium and micro-nutrients (MICRO<sub>n</sub>), including Zn, Cu and Mn where concentrations are relatively high. However, using different doses of sludge waste, it is possible that this favorable

environment with high availability for Zn, Cu and Mn occur some excesses, which induce phytotoxic phenomena of field plants. In the present study bring some results on how the wheat plants were grown and developed in terms of progressive processed sludge dose rich in Zn, Cu and Mn.

### MATERIAL AND METHODS

Field experiment with waste sludge doses was initiated in 2004. Its basic features included: achieving a 4-year rotation with the structure: 1.maize- 2.wheat- 3.soybean- 4.wheat, and complexation with chemical fertilizers. The data in this paper refer to the winter wheat crop in the second year of research. In its normal cultivation technology intervened on two factors and, namely a) factor with graduation sludge doses: 0, 5, 10, 25 and 50 t.ha<sup>-1</sup> repeated after an initial application to wheat and maize and b) factor, chemical fertilizers: N<sub>0</sub>P<sub>0</sub>, N<sub>60</sub>P<sub>40</sub> and N<sub>120</sub>P<sub>80</sub>. Winter wheat has received such a double dose application of sludge waste. Experiment was subdivided plot type with variants of 100 m<sup>2</sup> surface and were repeated for three times. Soil sampling was performed by agrochemical tests of arable horizon (0-20 cm) in the period between flowering and maturity of plants. Leaf samples were collected during the flowering season- specific wheat and last three leaves including standard leaf (or flag leaf). Grain samples were collected and analyzed after ripening wheat. Chemical analysis were by European and modern methodologies, namely: Zn, Cu, Mn total forms of soil and leaves by ISO 11047-99, and mobile forms of soil by ISO 14870-99. Waste sludge using suffered anaerobic fermentation (digesting process) and dehydration in sewage treatment station Pitești. The chemical composition of sludge and cultural characteristics of soil were specific (Table 1). The data in table show that all three heavy metals from waste sludge and the cultivated soil, which was applies bio-solid (term fermented and dehydrated sludge accepted as the present one), is below the legal limits, which allows them to recommend the use of wheat crop (Nicholson, 1996). In these circumstances it can hope to obtain favorable results, expressed both by the formation of total biomass, grain biomass and the reduced content of wheat leaves and berries heavy metals: Zn, Cu and Mn. Statistical data processing was performed by analysis of variance (Anova test) and with correlations and regressions.

**Table 1**  
**Heavy metals – Zn, Cu, Mn content of sewage sludge and cultivation soil**

Specific environment		Zn, mg/kg	Cu, mg/kg	Mn, mg/kg
Sewage sludge	Values	1372	134	351
	MAL*	2000	500	-
Cultivation soil	Values	126	27	833
	MAL	300	100	-

MAL\* - maximal admissible limits (legal)

### RESULTS AND DISCUSSIONS

The contents of Zn, Cu and Mn in cross- cultural environment (white luvicsoil)

Cultural soils are known and currently know of content changes in three heavy metals: zinc, copper and manganese. Of periodic investigations and zinc values were found between some units and 300 mg, of copper values from a few units and 200 mg, and manganese values between 280 and 3200 mg, total forms, and about 100 mg Zn, 20 mg Cu and 300 mg Mn mobile forms (Swain, 1955, 1977 quoted by Davidescu, 1981). Following soil determined by the contents of Zn, Cu and Mn show the existence of heavy metals, both total and forms through mobile forms (Table 2).

**Table 2**

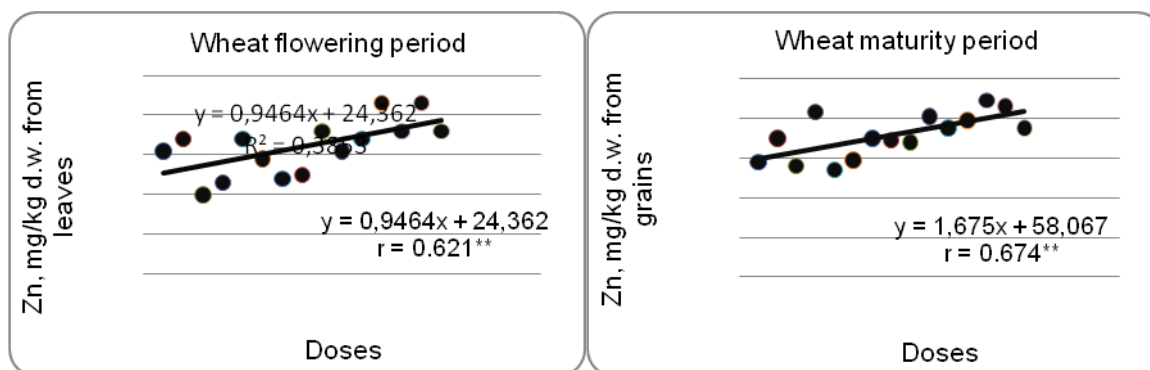
**Zn, Cu and Mn contents (mg.kg<sup>-1</sup> d.w.- total forms and mobile forms) in cultivated soil**

Heavy metals	Zn		Cu		Mn	
	TF	MF	TF	MF	TF	MF
Limits	52-120	1.7-11.3	18.7-24.7	3.0-4.0	704-861	372-464
Media	79.1	4.2	20.8	3.5	765.9	421.8

The data obtained show that each of the three chemical elements were present in amounts considered average to good. Thus, the total forms were included in total between 52 and 120 mg zinc like the limits, and 79.1 mg.kg<sup>-1</sup> d.w. annual average. The copper limits were between 18.7 and 24.7 mg and average of 20.8 mg.kg<sup>-1</sup> d.w. Manganese varied between 704 and 861 mg with an average of 765.9 mg.kg<sup>-1</sup> d.w. Mobile forms, slightly increasing, have oscillated between 1.7 and 11.3 mg with an average of 4.2 mg.kg<sup>-1</sup> d.w. zinc, between 3.0 and 4.0 mg with an average of 3.5 mg.kg<sup>-1</sup> d.w. copper, and between 372 and 464 mg, with an average of 421.8 mg.kg<sup>-1</sup> d.w. to manganese. Given the critical limits of Zn, Cu and Mn, it is considered that the data obtained here demonstrate the provision of conditions for absorbing and translocation of these chemicals, very important in plant growth and development (Thorne, 1949, Davidescu, 1975). Compared with natural reserves of luvosoil, sludge waste has increased its contribution to Zn, Cu and Mn, in particular by mobile forms (Bowen, 1969). In general it appears that eco-environment of luvosoil, which were applied different doses of sludge processed along with doses of chemical fertilizers, suffered slight increases in the heavy metal content, both in total, less obvious forms as chosen by mobile- stressed forms for zinc and manganese less obvious in the case, copper has remained relatively constant over the 15 experimental variants.

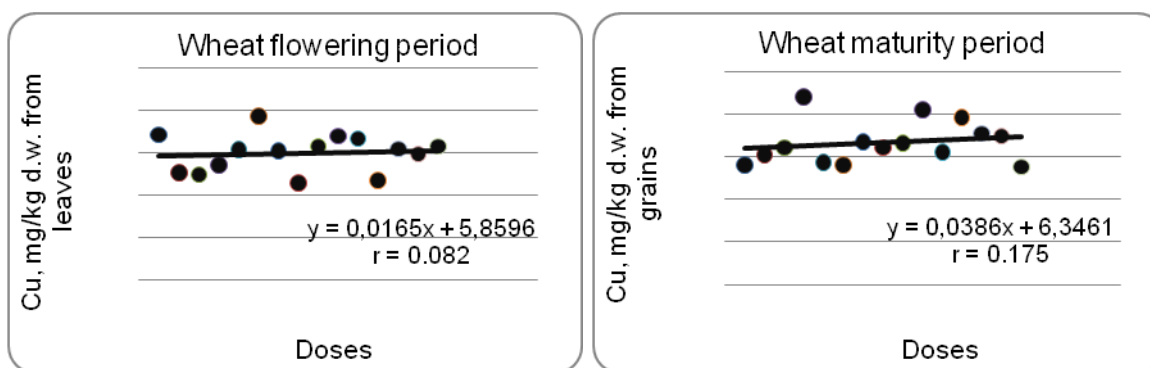
Correlations between contents of Zn, Cu and Mn in plants and total biomass produced

Depending on the biomass produced by plants of wheat, some trends were observed in the levels of zinc, copper and manganese. An average concentration of Zn in plants were generally the situation about 20 mg.kg<sup>-1</sup> d.w. (after Epstein, 1972 quoted by Davidescu, 1981). Between 20 and 100 mg of soil, the plants have ensured normal nutrition. Below this concentration (20 mg), and over 100 mg, crops show deficiency or excess. Cumulative toxicity occurs when soil concentrations are between 300 and 500 mg. Given these three possibilities, plant analysis revealed moderate concentrations of zinc (Figure 1). Thus, the total biomass produced directly correlated with increasing concentrations of Zn in leaves during flowering. Clearly positive trend demonstrates the favorable effect of waste sludge doses, chemical fertilizers and zinc content of wheat leaves at this time of maximum activity, namely physiological flourished period. In a later stage of development and maturity, it was found that wheat plants were stored Zn in grain. Representing an element of the constitution of plants, Zn was initially absorbed, translocated through the xylem and phloem, contributed to a better functioning of enzymes, photosynthesis, resistance, after which it was stored into the grains. Such a phenomenon occurs Zn export of eco-environment of the grain crop. There are some estimates that effect, but very little data (Antal, 1999). The correlation established between the production of grain so formed and Zn concentrations in grain, proved to be very slightly increasing and fluctuating data. This demonstrates, one the one hand, the mature wheat plants do not require Zn and its concentrations were relatively variable in relation to the production of grain. Zinc concentrations in wheat leaves within the theoretical (the right correlation) between about 27 and 39 mg Zn, while the grains were deposited between 70 and 71 mg Zn. The two correlations are news for nutrition regime of wheat grown on luvosoil.



**Fig. 1. Correlations between Zn concentrations from plant leaves and grains with sludge & chemical doses used**

The second chemical element- copper was absorbed by plants and translocated in wheat, vegetable parts. To the plant Cu is also considered an essential micronutrient. An average concentration of Cu in the plant would be between 5 and 10 mg. During intense growth, wheat leaves should contain between 2 and 7 mg Cu. A normal nutrition occurs when the soil is found between 3 and 100 mg Cu (Tisdale, 1975), and over 100 mg appear specific toxicity phenomena. Tests have revealed the existence of different total correlations between the two phases (Figure 2). Thus, of flowering the wheat plants correlated less obvious, even with negative contents of leaves. Regression slope is unstressed, employment revealed values between about 6.0 from check plot to 5.9 mg from bigger biomass. In the final stage of maturity, copper was negatively correlated with grain yield. Theoretical values were classified as between 7 mg in unfertilized variant and decreased to about 6.2 mg to the highest wheat yields. And if copper plant tests have demonstrated the need for micronutrient copper, especially in very young stages and both flowering, at the end in maturity, this chemical element still was not necessary.



**Fig. 2. Correlations between Cu concentrations from plant leaves and grains with sludge & chemical doses used**

Periodic investigations revealed that soils are quite important in manganese content. Crops require about 30-50 mg Mn in their vegetation period. Since the absorption of manganese in the soil occurs in a particular selective excess symptoms rarely occur, but not exclusive. If this third element, manganese, two different correlations were similar. Thus, in flowering period, wheat required more Mn- around of 130 mg.kg<sup>-1</sup> d.w. and relatively low on training more consistent measure of total biomass. Regression is less clear, less obvious and weak statistical assurance (r = -0,047)- Figure 3.

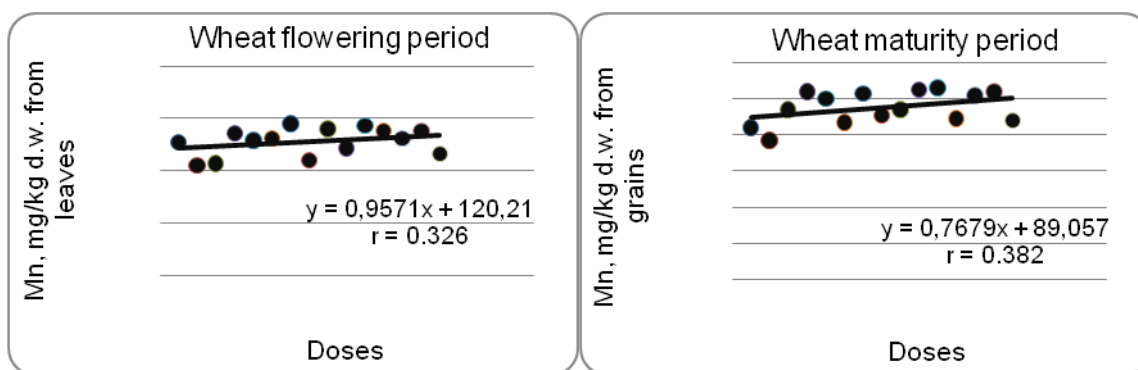


Fig. 3. Correlations between Mn concentrations from plant leaves and grains with sludge & chemical doses used

Changes in concentrations of manganese was thus between about 130 mg from check variant to about 126 mg from the highest biomass. In the maturity stage of wheat, the grains production were correlated less obvious with Mn contents of grains. Regression enrolled as between about 100 mg in check variant and decreased to about 86-87 mg at the biggest grain productions. As with the other two chemicals, grain needed less increasing rates of Mn- as concentrations increase plant biomass due to organo- mineral fertilization. Thus, both in flower and in the final stage of maturity, the element Mn was not necessary. Supply of wheat in this trace element took place in young stages, starting from the beginning of intense growth and of flowering. In the maturity stage so that the Mn was not so necessary, and thus stored and exported through this valuable crop plant, winter wheat.

### CONCLUSIONS

By using processed sludge (anaerobic digested, treated and dried) was improved eco-environment of luvosoil: increased content of organic matter (OM) and specific ions of  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Mn^{2+}$ .

Of chemically, cross- environment has improved significantly agro-background- soil. Zinc has oscillated between 50 and 120  $mg.kg^{-1}$  d.w. total forms, copper ranged between 19 and 25  $mg.kg^{-1}$  d.w. total forms, and manganese ranged between 704 and 861  $mg.kg^{-1}$  d.w. by the same overall shape. Mobile forms ranged from about 2-11  $mg.kg^{-1}$  d.w. Zn, between 3-4  $mg.kg^{-1}$  d.w. Cu and between 370 and 465  $mg.kg^{-1}$  d.w. Mn.

Requirements of wheat plants in ions of  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Mn^{2+}$  takes specific issues, in close relationship both with environmental factors, but according to sources of food provided. Thus, winter wheat has absorbed during the flowering period following quantities: zinc between 26 and 39  $mg.kg^{-1}$  d.w., copper at about 6  $mg.kg^{-1}$  d.w. and manganese around 130  $mg.kg^{-1}$  d.w. The winter wheat stored in grains: 70  $mg.kg^{-1}$  d.w. zinc, 6-7  $mg.kg^{-1}$  d.w. copper and 93-100  $mg.kg^{-1}$  d.w. manganese.

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