THE EFFECT OF FERTILIZERS WITH NPK ON COPPER CONCENTRATION IN THE PRELUVOSOIL FROM ORADEA

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RESEARCH ARTICLE

Abstract
The research was carried out over a period of three years (2020 - 2022) in a long-term experience with chemical fertilizers, located on a preluvosol type soil in the North-West part of Romania. Following the application over a long period of different doses of chemical fertilizers with nitrogen, phosphorus and potassium, it was observed that the concentration of copper in the soil did not have high values compared to the alert poit (100 mg/kg). The concentration of copper in the soil increased with the increase in the doses of fertilizers, the differences being in some cases statistically significant. The values obtained were between 21.9% and 28.9% compared to it.

Keywords: copper, concentration, preluvosoil, chemical fertilizers
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INTRODUCTION

Naturally, the concentration of copper in soils around the globe is between 1 and 300 mg/kg, with an average concentration of 22.4 mg/kg. The soils in the Warsaw area had a copper concentration between 1-560 mg/kg (Lis J., 1992), and McGrath S.P. and Loveland P.J., (1992) determined in Great Britain concentrations between 1.2 and 1.508 mg Cu/kg. The average concentration of copper in European soils was 13 mg/kg (Salminen R. et al., 2005).

In the contaminated and polluted areas in Romania, especially in the soils adjacent to the non-ferrous ore processing units, the determined copper concentration was 2.000 – 3.000 mg/kg (Lăcătusu R., 2008).

The maximum allowed limit, in our country, for the concentration of copper in the soil is 20 mg/kg, the alert threshold 100 mg/kg, in the case of sensitive soils and 250 mg/kg in the case of the least sensitive ones, respectively the intervention threshold of was set at 200 mg/kg for sensitive soils and 500 mg/kg for less sensitive soils (Order no. 756/1997 of the Ministry of Water, of Forests and Environmental Protection).

The ability of different types of soil to retain and neutralize heavy metals, as well as their vulnerability to different types of polluting elements, is an important premise in their effective management.

Metals, and especially heavy metals, can be carried through precipitation into the lower layers of the soil, from where they reach plants - animals - humans through bioaccumulation. For these reasons, it was necessary to establish some critical loads of metals whose concentrations should not be exceeded, so that there is no risk of soil transformation into a potential supplier of environmental pollutants.

In Romania, five classes of vulnerability were established (very low, low, moderate, high, very high) and depending on the reaction state of the soil solution, in three subclasses: moderately and strongly acid, weakly acid and neutral, alkaline (Florea N. and Ianoș Gh., 2002).

MATERIAL AND METHOD

Wet mineralization was performed with concentrated strong acids and hydrogen peroxide (HNO_3, HCl and H_2O_2) using the MILESTONE digester.

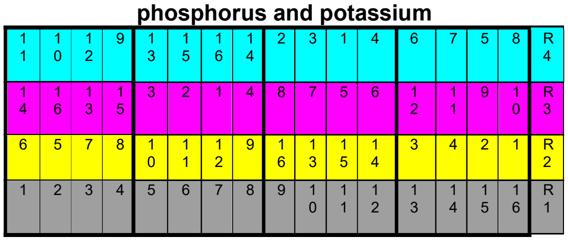
The dry sample is extracted with a mixture of hydrochloric acid/nitric acid and perhydrol by keeping it for 2 h in a microwave oven at a previously established mineralization program. The extract is then filtered and brought to volume with distilled water.

1.00±0.1 g of soil was weighed into MILESTONE microwave mineralization vials over which an oxidizing mixture was added: 6 ml of concentrated nitric acid, 3 ml of hydrochloric acid and 0.25 ml of perhydrol. The vials were sealed and the mineralization program was started (the digestion program also includes a ventilation of the samples to cool them down for 30 minutes). After completion of the program, the samples were kept overnight in the digestion vessels covered with a filter paper to avoid contamination. Then, the samples were filtered in 50 ml volumetric flasks and brought to the mark with water.

At each series of analyses, extractions were performed for the control, using the same procedure, but without the soil sample.

To determine the heavy metals under study, the soil samples, plant biological material, respectively animal biological material prepared according to the work methods presented previously were subjected to analysis by means of the SHIMADZU AA-6300 atomic absorption spectrophotometer.

The schema of the long term trial with nitrogen, phosphorus and potassium



1.$N_0P_0K_0$	**5.$N_{80}P_{40}K_0$**	**9.$N_{80}P_{80}K_0$**	**13.$N_{160}P_{80}K_0$**
2.$N_0P_0K_{40}$	**6. $N_{80}P_{40}K_{40}$**	**10.$N_{80}P_{80}K_{40}$**	**14.$N_{160}P_{80}K_{40}$**
3.$N_0P_0K_{80}$	**7. $N_{80}P_{40}K_{80}$**	**11.$N_{80}P_{80}K_{80}$**	**15.$N_{160}P_{80}K_{80}$**
4.$N_0P_0K_{120}$	**8. $N_{80}P_{40}K_{120}$**	**12.$N_{80}P_{80}K_{120}$**	**16.$N_{160}P_{80}K_{120}$**

RESULTS AND DISCUSSIONS

In the three years studied (2020-2022), the lowest copper concentration was recorded in the control version ($N_0P_0K_0$), 21.938 mg/kg in 2020, 22.262 mg/kg in 2021, respectively 22.792 mg/kg in 2022. The concentration of copper increased by 3.3% in 2020, 3.4% in 2021, respectively by 3.7% in 2022, the differences not being statistically ensured, within the $N_{80}P_{40}K_{40}$ variant. In the $N_{80}P_{80}K_{80}$ variant, the differences recorded were greater than those in the control variant by 9.4% (23.998 mg/kg) in 2020, 10.9% (24.679 mg/kg) in 2021 and 11.2% (25.339 mg /kg) in 2022. The difference recorded in 2020 was statistically insignificant, and the differences from the years 2021 and 2022 were statistically significant. In the version fertilized with $N_{160}P_{80}K_{120}$, the biggest differences were recorded compared to the unfertilized version, these registering values of 27.474 mg/kg in 2020, 27.943 mg/kg, respectively 28.882 mg/kg, higher by 25.2%, 25 .5%, respectively 26.7%, being distinctly significant. (Table 1.)

In the experiment with nitrogen, phosphorus and potassium fertilizers, the concentration of copper in the soil did not exceed the alert threshold (100 mg/kg), established by the Order of the Ministry of Water, Forests and Environmental Protection no. 756/1997. The concentration of copper in the $N_0P_0K_0$ variant (control) represents 21.9% in 2020, 22.3% in 2021, respectively 28.9% in 2022, of the alert threshold value. In the version fertilized with $N_{80}P_{40}K_{40}$, copper recorded concentrations of 22.6% in 2020, 23% in 2021 and 23.6% in 2022 relative to the alert threshold value. In the $N_{80}P_{80}K_{80}$ variant, the copper concentration recorded 24% in 2020, 24.7% in 2021, respectively 25.3% in 2022 of the alert threshold value. In the $N_{160}P_{80}K_{120}$ variant, compared to the alert threshold, the copper concentration had values of 27.5% in 2020, 27.9% in 2021, respectively 28.9% in 2022. (Figure 1.)

On average over the three years studied. in the $N_0P_0K_0$ variant the concentration of copper in the preluvosol from Oradea was 22.330 mg/kg. and in the other variants the concentrations were higher by 3.5% in the $N_{80}P_{40}K_{40}$ variant. 10.5% in variant $N_{80}P_{80}K_{80}$. respectively 25.8 mg/kg in the variant $N_{160}P_{80}K_{120}$. Reaching values of 23.105 mg/kg. 24.672 mg/kg. respectively 28.099 mg/kg. In the $N_{80}P_{40}K_{40}$ variant. the recorded difference was not statistically ensured. In the $N_{80}P_{40}K_{40}$ variant it was statistically significant. respectively in the $N_{160}P_{80}K_{120}$ variant it was distinctly significant. (Table 2.)

Among the 5 types of functions tested (exponential, linear, logarithmic, polynomial, power), the polynomial function best quantifies the relationship between the doses of chemical fertilizers and the concentration of copper in the soil, R^2 = 0.9612. (Figure 2.)

Table 1

The influence of doses and combinations of NPK fertilizers on copper concentration in preluvosoil from long term trial

Variant	Cu concentration		Difference		Statistical significance
	mg/kg	%	mg/kg	%	
2020					
$N_0P_0K_0$	21.938	100	-	-	*Control*
$N_{80}P_{40}K_{40}$	22.659	103.3	0.721	3.3	-
$N_{80}P_{80}K_{80}$	23.998	109.4	2.071	9.4	-
$N_{160}P_{80}K_{120}$	27.474	125.2	5.536	25.2	**
		LSD 5%	2.202		
		LSD 1%	3.900		
		LSD 0.1%	6.410		
2021					
$N_0P_0K_0$	22.262	100	-	-	*Control*
$N_{80}P_{40}K_{40}$	23.021	103.4	0.759	3.4	-
$N_{80}P_{80}K_{80}$	24.679	110.9	2.417	10.9	*
$N_{160}P_{80}K_{120}$	27.943	125.5	5.681	25.5	**
		LSD 5%	2.310		
		LSD 1%	4.122		
		LSD 0.1%	7.233		
2022					
$N_0P_0K_0$	22.792	100	-	-	*Control*
$N_{80}P_{40}K_{40}$	23.635	103.7	0.843	3.7	-
$N_{80}P_{80}K_{80}$	25.339	111.2	2.547	11.2	*
$N_{160}P_{80}K_{120}$	28.882	126.7	6.090	26.7	**
		LSD 5%	1.970		
		LSD 1%	3.122		
		LSD 0.1%	6.321		

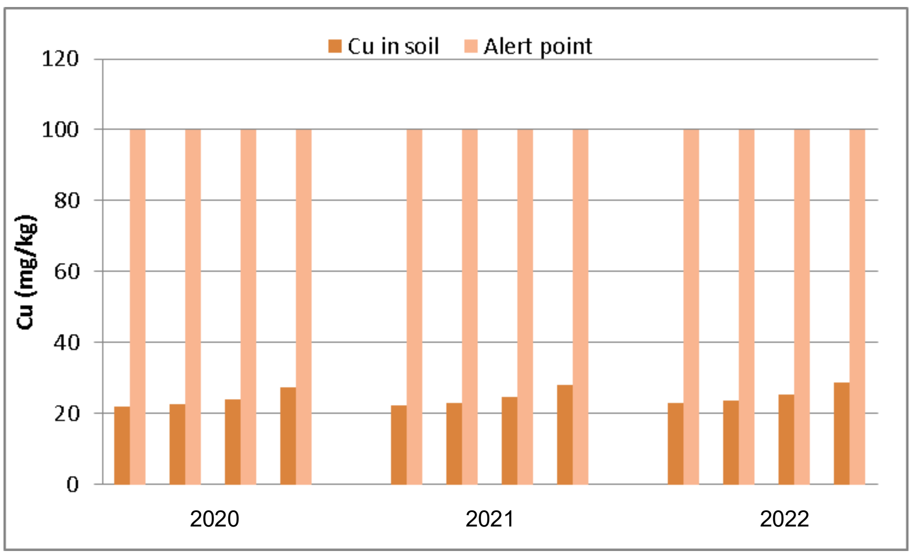


Figure 1 **Graphical representation of cooper values in soil based on doses and combinations of NPK fertilizer compared to the alert point**

Table 2

The influence of doses and combinations of NPK fertilizers on copper concentration in preluvosoil from long term trial, average data, (2020-2022)

Variant	Cu concentration		Difference		Statistical significance
	mg/kg	%	mg/kg	%	
$N_0P_0K_0$	22.330	100	-	-	*Control*
$N_{80}P_{40}K_{40}$	23.105	103.5	0.775	3.5	-
$N_{80}P_{80}K_{80}$	24.672	110.5	2.342	10.5	*
$N_{160}P_{80}K_{120}$	28.099	125.8	5.769	25.8	**
		LSD 5%	2.161		
		LSD 1%	3.714		
		LSD 0.1%	6.655		

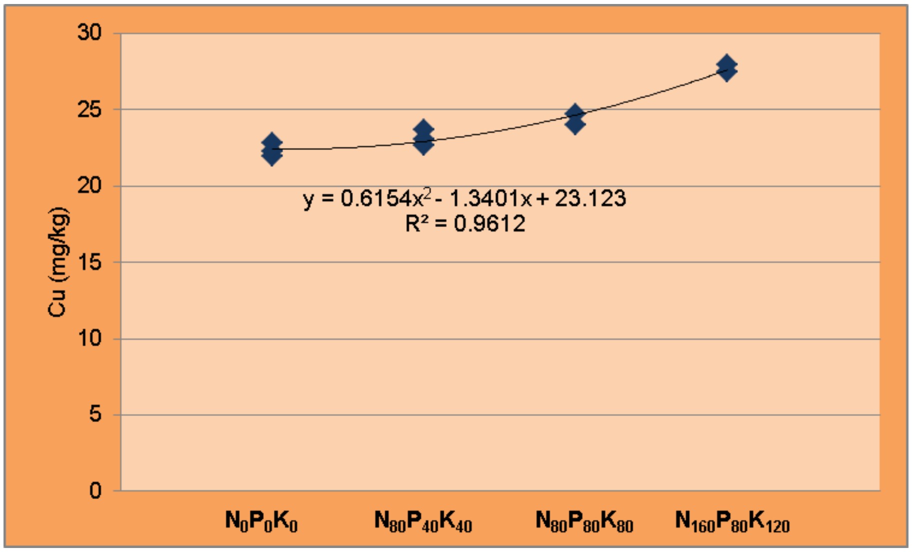


Figure 2 **Correlation between doses of NPK fertilizers and copper concentration in soil**

CONCLUSIONS

On average over the three years studied, compared to the non-fertilized control, the copper concentration of the soil in the studied variants is increased. In the control variants, the copper concentration had an average value of 22.330 mg/kg. The highest increase in the average concentration of copper in the soil, 5,769 mg/kg, was determined following fertilization with 160 kg of nitrogen, 80 kg of phosphorus and 120 kg of potassium. In the case of the other variants analyzed, the increases were not significant.

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