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EFFECT OF SOIL ACIDITY NEUTRALIZATION AND COPPER TOXICITY ON MAIZE PRODUCTIVITY, COPPER UPTAKE AND BIOMASS CATION CONTENT

Antoaneta Arsova

N. Poushkarov Institute of Soil Science and Agroecology, Shosse Bankya 5, Sofia 1080, Bulgaria

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Summary. In a pot experiment with maize grown on a copper contaminated acid soil was studied the combined effect of soil acidity neutralization and copper toxicity on yield, copper uptake by organs and cation content in biomass. It was confirmed that maximum production was obtained at a complete neutralization of the exchangeable soil acidity (pH ~ 6.0) for all levels of copper pollution. At pH > 6.0 copper uptake by organs diminished significantly to comparatively constant low values. Soil acidity neutralization decreased the acidity (H^+) and increased Ca^{2+} ions in maize tissues. This effect was not influenced by the pollution factor. Copper toxicity caused an increase of acidity and basic content (Ca^{2+} and K^+) in the liquid phase. Cation exchange capacity of the biomass was trace depending on copper pollution. Cation distribution in the biomass depended on neutralization, but not on copper toxicity. The effect of both factors on the acidic character of water soluble metabolic systems and bioadsorbents was studied.

Key words: cation content in biomass, copper toxicity, maize, soil acidity neutralization

Introduction

Important plant parameters (tissue capacity, cation content, acidic ionization of biopolymers etc.) depend on the complex influence of factors in the nutrient medium, including soil. Recently many reports take notice of heavy metals' behaviour as their agrochemical mobilization in soils and uptake by plants in toxic concentrations depends strongly on soil acidity (Merry et al., 1986; Alloway and Ayres, 1994; Ross, 1994). On the other hand, plant tolerance to heavy metals is a specific characteristic that should take into account in such investigations. Maize is a sensitive plant to soil acidity (Arsova, 1996), also to ion forms of amphoteric elements in soils and has a moderate accumulation of heavy metals (Ross, 1994).

Our aim was to study the combined effect of soil acidity neutralization and copper pollution on maize productivity, copper uptake by organs and cation content in biomass as criteria for plant metabolic reactions under these conditions.

Materials and Methods

A pot experiment with maize (P 3159) was carried out on a leached cinnamonic forest soil (Primorsko) with physico-chemical characteristics determined by author's method (Ganev and Arsova, 1980) as follows: pH(H_2O)=4.5; cation exchange capacity=23.2 mequ/100 g; exchangeable acidity (exch.Al)=3.1 mequ/100 g; exchangeable bases (Ca^{2+} + Mg^{2+})=13.6 mequ/100 g. Four levels of soil acidity neutralization with lime material were applied (g/100 g soil): Ca_0=0.0 g; Ca_1=0.067 g (partial neutralization, calculated as 1/2 exch.Al); Ca_2=0.283 g (complete neutralization, calculated according to the optimal liming rate for acid soils – Ganev, 1987); Ca_3=0.823 g (overliming). Copper applied to the soil simulated the pollution in Srednogorie region. CuO was used in four levels of Cu mg per kg soil: Cu_0=0 mg; Cu_1=100 mg; Cu_2=300 mg; Cu_3=900 mg. Mineral nutrition (0.2 g salts per 100 g soil) was applied: NH_4NO_3 – 0.040 g; $Ca(H_2PO_4)_2$ – 0.060 g; KH_2PO_4 – 0.0745 g; $MgSO_4$ – 0.032 g.

The 45-day-long experiment (7–8th leaf stage) was conducted in three replications at 2.5 kg soil per pot. Soil moisture was maintained about 60% field capacity. A month interaction between soil, copper and lime was carried out previously. Soil pH was measured in all variants and the dried biomass was weighed. Copper content in roots and leaf and stem biomass was determined by atomic-adsorption methods. H^+, Ca^{2+}, Mg^{2+} and K^+ ions in water soluble and exchange adsorbed state in the biomass were determined by author's method (Ganev and Arsova, 1982). A dispersion analysis was performed to evaluate the results of yield.

Results and Discussion

Data for maize production and copper content in top biomass and roots depending on soil acidity neutralization and copper pollution are presented in Table 1. It is confirmed that maximum yield is obtained at pH 6.0–6.2, e.g. at a complete neutralization of the exchangeable soil acidity (variant Ca_2) valid for all levels of soil copper (Fig.1). Copper toxicity does not influence the neutralization condition for maximum

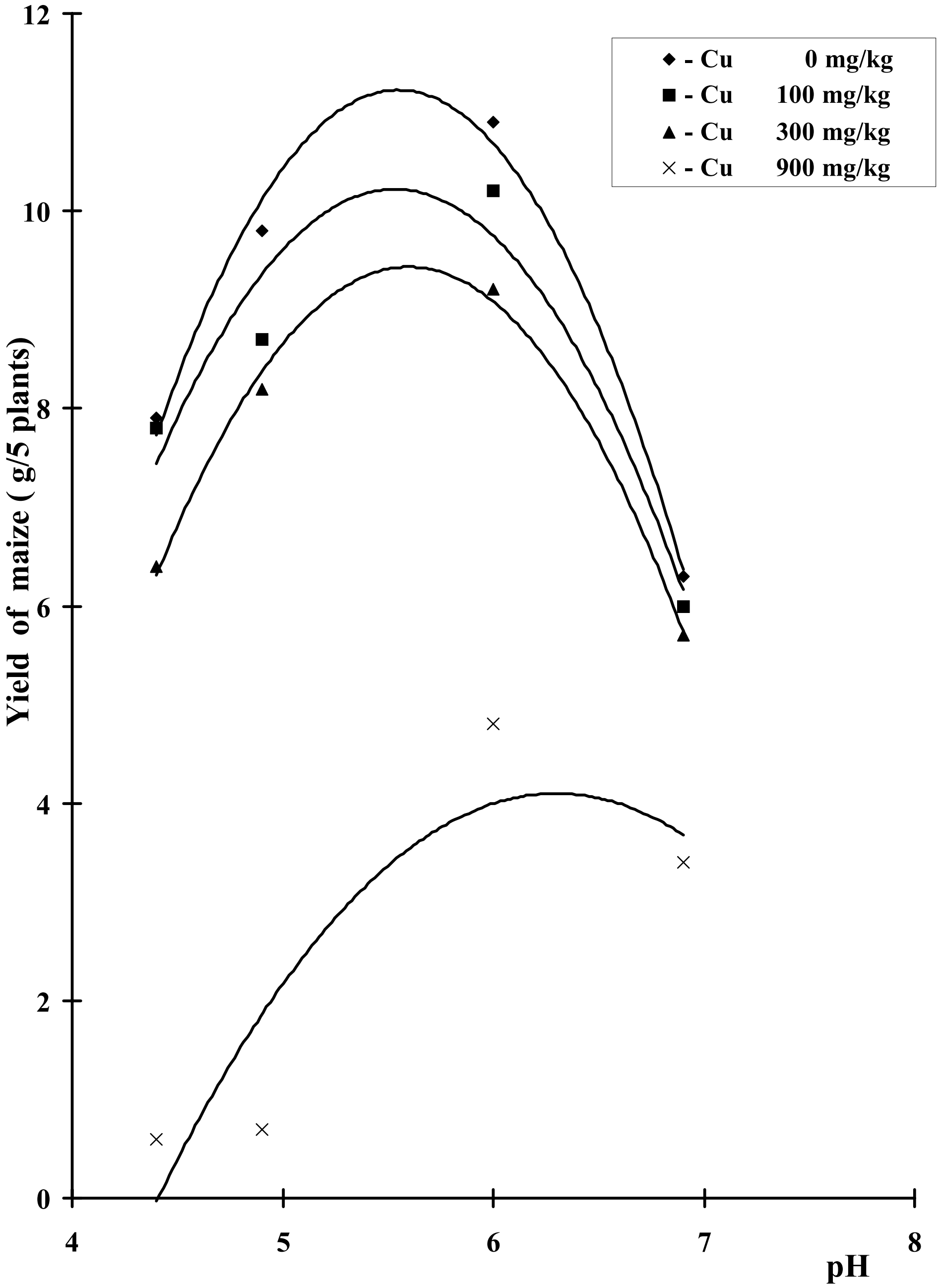

Fig. 1. Yield of maize in relation to soil acidity neutralization at different copper pollution levels

Table 1. Yield of maize and copper in biomass and roots depending on soil acidity neutralization and copper contamination

Lime (g/100g soil)	Cu (mg/100g soil)	Soil pH (H_2O)	Yield (g/5 plants dry matter)	Cu (mg/kg dry matter)	
				in biomass	in roots
0.00	0.0	4.8	7.99	4.0	16.0
0.07	0.0	4.9	9.86	8.0	9.0
0.28	0.0	6.2	10.89	8.0	12.0
0.82	0.0	6.9	6.34	3.0	6.0
0.00	100	4.4	7.81	10.0	55.0
0.07	100	4.7	8.70	5.0	48.0
0.28	100	6.1	10.13	7.0	23.0
0.82	100	6.8	6.05	7.0	12.0
0.00	300	4.4	6.48	9.0	162.0
0.07	300	4.7	8.22	7.0	82.0
0.28	300	6.1	9.19	6.0	40.0
0.82	300	6.7	5.75	7.0	25.0
0.00	900	4.5	0.62	231.0	427.0
0.07	900	4.7	0.67	118.0	200.0
0.28	900	6.0	4.80	17.0	80.0
0.82	900	6.8	4.56	10.0	60.0

GD 1% = 0.246 ***
0.1% = 0.326 ***

biomass production. However, maize productivity decreases with increasing pollution because of the depressing effect of heavy metals. The reduction in biomass amount corresponds to an increase of copper uptake by plant organs (Fig. 2). At pH ~6.0 copper in roots decreases at all pollution levels because of immobilization of Cu^{2+} ions to insoluble hydroxides (Chuldjian, 1978; Ganev et al., 1993). The effect of neutralization to pH 6.0 is expressed clearly at level 900 mg Cu per kg soil, where the uptaken copper decreases strongly. At 300 and 900 mg Cu per kg copper in biomass shows a tendency to keep a low level because of its high accumulation in roots. At pH above 6.0 small amount of copper in biomass is observed because slightly available forms are present in soil under these conditions (Chuldjian, 1978).

From the data in Table 2 some metabolic effects of neutralization and copper pollution could be discussed. In the variants without copper (Cu_0) the increasing neutralization from variants Ca_0 to Ca_3 decreases the tissue's acidity (H^+ ions in water soluble and exchange adsorbed state). Among the basic cations in the liquid phase calcium increases and potassium decreases. Similar results have been reported in previous author's works (Arsova, 1994, 1996). Important in this study is that the cations' changes are not influenced by soil copper concentrations, e.g., the neutraliza-

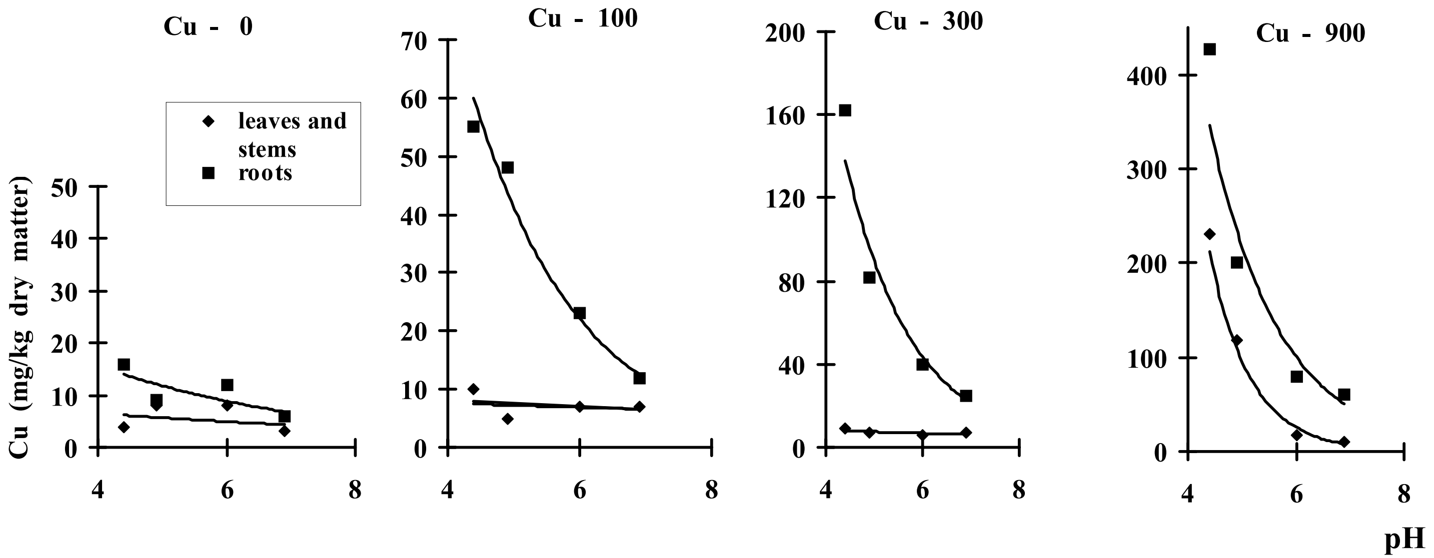

Fig. 2 Copper uptake in maize in relation to soil acidity neutralization and copper pollution (mg/kg soil)

Table 2. Cations in water soluble and exchange adsorbed state (in mequ/100g dry matter) in maize biomass depending on soil acidity neutralization and copper pollution

Treatment	H^+	Ca^{2+}	Mg^{2+}	K^+	Σ	H^+	Ca^{2+}	Mg^{2+}	K^+	Σ
	in water soluble state					in exchange adsorbed state				
Ca_0Cu_0	39.6	40.5	3.8	49.3	133.2	15.0	27.1	1.3	2.8	46.2
Ca_0Cu_1	39.6	42.5	3.8	52.5	138.4	14.8	27.5	1.2	2.8	46.3
Ca_0Cu_2	40.8	45.0	4.0	52.5	142.3	14.5	27.8	1.3	2.9	46.5
Ca_0Cu_3	42.0	49.0	4.1	54.6	149.7	14.4	28.4	1.4	2.9	47.1
Ca_1Cu_0	34.0	45.5	4.0	48.6	132.1	11.2	28.2	1.4	1.9	42.7
Ca_1Cu_1	35.6	47.5	4.0	51.0	138.0	11.2	29.1	1.3	1.9	43.5
Ca_1Cu_2	36.4	49.0	4.1	51.7	141.2	11.6	29.5	1.4	2.0	44.5
Ca_1Cu_3	37.6	50.0	4.1	53.2	144.9	10.8	30.4	1.3	2.1	44.6
Ca_2Cu_0	31.6	50.0	4.0	35.8	121.4	9.2	29.5	1.3	1.5	41.5
Ca_2Cu_1	32.8	51.0	4.1	38.1	126.0	9.2	29.8	1.4	1.5	41.9
Ca_2Cu_2	34.4	52.0	4.1	38.2	128.7	9.6	30.5	1.4	1.6	43.1
Ca_2Cu_3	36.0	53.0	4.2	40.1	133.3	9.8	31.5	1.5	1.7	44.5
Ca_3Cu_0	30.0	55.0	4.1	32.0	121.1	7.0	32.0	1.4	1.1	41.5
Ca_3Cu_1	30.0	55.0	4.2	34.2	123.4	7.0	32.5	1.4	1.2	42.1
Ca_3Cu_2	32.4	57.5	4.2	35.1	129.2	6.8	33.0	1.5	1.3	42.6
Ca_3Cu_3	34.8	58.5	4.2	38.2	135.7	6.6	34.1	1.5	1.4	43.6

tion effect does not depend on the pollution factor. The increase of Ca^{2+} ions in the liquid phase indicates that soil acidity neutralization facilitates the neutralization of organic acids formed in the metabolic processes. It should be noticed that Ca^{2+} ions increase in a higher degree compared to the degree of protons' decrease. For example, the decrease of H^+ from variants Ca_0 to Ca_3 is 15.5 mequ. It means that the neutralization effect is more strongly expressed in a neutralization of new synthesized organic acids than in the neutralization of the available ones.

Electrolytic content (sum of cations in water soluble state) and cation exchange capacity (sum of exchange adsorbed cations) decreases with the increase of soil copper. Regarding the liquid phase this fact could be explained by the different degree of changes in Ca^{2+} and K^+ content, that is the potassium decrease is higher than the calcium increase. As a result the electrolytic content diminishes. For example, the differences in K^+ concentration between variants Ca_0 and Ca_3 are 17.3 and 16.4 mequ at levels Cu_0 and Cu_3, while the same differences for Ca^{2+} are smaller, respectively 14.5 and 9.5 mequ. As regards the cation exchange capacity of biomass the higher values of the variants without neutralization (46.2 mequ at Ca_0Cu_0 and 47.1 mequ at Ca_0Cu_3) are due to the enhanced adsorption of protons in acid medium, which creates new adsorption sites for cation exchange (Ganev and Arsova, 1982). For this reason maize grown on the strongly acid leached cinnamonic soil has higher biomass capacity compared to the capacity determined under slightly acid soil conditions (Arsova, 1996).

In the liquid phase H^+ ions (organic acids) and Ca^{2+} ions (Ca-salts of organic acids) increase with the increase of copper toxicity, resp. with copper uptake. For example, H^+ ions enhance with 2.4 mequ and Ca^{2+} ions with 8.5 mequ from variant Ca_0Cu_0 to Ca_0Cu_3. From variant Ca_3Cu_0 to Ca_3Cu_3 the increase of H^+ is 4.8 mequ and the increase of Ca^{2+} is 3.5 mequ. Besides the increase of acidity, copper toxicity causes an increase of K^+ ions in the liquid phase in contrast to the neutralization effect. At the variants mentioned above, for example, K^+ ions enhance respectively with 5.3 and 6.2 mequ. The sum of Ca^{2+} and K^+ ions rises too. It means that the increased tissues' acidity is compensated by an intensive neutralization of organic acids with basic cations. A similar tendency of high accumulation of calcium and potassium in some medical plants grown in contaminated regions has been reported (Ivancheva et al., 1996). Such base accumulation caused by the enhanced tissues' acidity could manifest plant adaptability to toxic factors in nutrient medium.

Electrolytic content in the liquid phase rises with the increase of soil copper but in dependence of the neutralization degree. Maximum increase is observed in variant Ca_0 – the difference in the electrolytic content between copper levels Cu_0 and Cu_3 is 16.5 mequ and in variant Ca_2 (optimal neutralization) the increase is minimal – 11.9 mequ. As electrolytic and basic content rise with the increase of copper toxicity it follows that the pollution causes changes in both organic acids and their salts at all neutralization levels.

In the adsorption phase of tissues the effect of copper toxicity on cation content and, respectively, on cation exchange capacity is not as significant as the neutralization effect. Obviously, the capacity of maize biomass is a comparatively stable value in relation to copper pollution factor.

In Table 3 is presented the content of cations in water soluble and exchange adsorbed state in percentage of their sums. The soil acidity neutralization influences the relative share of cations in the liquid phase under conditions of copper pollution. The cation distribution at variants Ca_0 and Ca_1 follows the row: $K^+ > Ca^{2+} > H^+ \gg Mg^{2+}$. At variant Ca_2 and Ca_3 calcium has a priority in the row: $Ca^{2+} > K^+ > H^+ \gg Mg^{2+}$. Copper toxicity has no influence on the cation distribution in the liquid phase.

Table 3. Cations in water soluble and exchange adsorbed state (in % of Σ) in maize biomass depending on soil acidity neutralization and copper pollution

Treatment	H^+	Ca^{2+}	Mg^{2+}	K^+	H^+	Ca^{2+}	Mg^{2+}	K^+
	in water soluble state				in exchange adsorbed state			
Ca_0Cu_0	29.7	30.4	2.9	37.0	32.5	58.7	2.8	6.1
Ca_0Cu_1	28.6	30.7	2.7	37.9	32.0	59.4	2.6	6.0
Ca_0Cu_2	28.7	31.6	2.8	36.9	31.2	59.8	2.8	6.2
Ca_0Cu_3	28.1	32.7	2.7	36.5	30.6	60.3	3.0	6.2
Ca_1Cu_0	25.7	34.4	3.0	36.8	26.2	66.0	3.3	4.4
Ca_1Cu_1	25.8	34.4	2.9	37.0	25.7	66.9	3.0	4.4
Ca_1Cu_2	25.8	34.7	2.9	36.6	26.1	66.3	3.1	4.5
Ca_1Cu_3	25.9	34.5	2.8	36.7	24.2	68.2	2.9	4.7
Ca_2Cu_0	26.0	41.2	3.3	29.5	22.2	71.1	3.1	3.6
Ca_2Cu_1	26.0	40.5	3.3	30.2	22.0	71.1	3.3	3.6
Ca_2Cu_2	26.7	40.4	3.2	29.7	22.3	70.8	3.2	3.7
Ca_2Cu_3	27.0	39.8	3.2	30.1	22.0	70.8	3.4	3.8
Ca_3Cu_0	24.8	45.4	3.4	26.4	16.9	77.1	3.4	2.7
Ca_3Cu_1	24.3	44.6	3.4	27.7	16.6	77.2	3.3	2.9
Ca_3Cu_2	25.1	44.5	3.3	27.2	16.0	77.5	3.5	3.1
Ca_3Cu_3	25.6	43.1	3.1	28.1	15.1	78.2	3.4	3.2

In the adsorption phase cations form the followed row according to their share in the cation exchange capacity: $Ca^{2+} > H^+ > K^+ >= Mg^{2+}$. The preferential adsorption of calcium on the biopolymers is confirmed. The distribution of exchange adsorbed cations is trace depending on the variation of both neutralization and pollution factors. Obviously, changes in the cation content caused by external factors are better expressed in the liquid phase than on the bioadsorbents.

The acidic strength of water soluble metabolic systems and bioadsorbents could be evaluated according to the relative share of H^+ ions in liquid and adsorption phases taking into account that the equilibrium between the phases realizes a transport of more protons from a highly acid system to a slightly acid one. In Table 3 it could be seen that the soil acidity neutralization has a significant effect on the acidic character of the systems in the liquid and adsorption phases. At the acid control (Ca_0) the organic acids are stronger acids than the bioadsorbents: H^+ water soluble (28.1–29.7%) < H^+ exch. adsorbed (30.6–32.5%). With the increase of neutralization degree at variant Ca_1 the acidic strength of both systems becomes equalized. At variant Ca_2 (optimal neutralization) and especially at variant Ca_3 (overliming) the acidic strength of bioadsorbents rises. For example, at variant Ca_3 the proton relation is: H^+ water soluble (24.8–25.6%) > H^+ exch.adsorbed (15.1–16.9%). It means that the decrease of tissue acidity in the neutralization process is due both to the neutralization of the available organic acids and to a synthesis of weak organic acids. This effect of soil acidity neutralization is determinative for the acidic character of water soluble metabolic systems and bioadsorbents and does not depend on the pollution level.

Conclusions

1. It is confirmed that optimal soil acidity neutralization under copper toxicity conditions results in maximum productivity of maize and strong decrease of biomass copper uptake.

2. Soil acidity neutralization increases Ca^{2+} ions in maize tissues, decreases H^+ ions and electrolytic content and determines the acidic strength of water soluble metabolic systems and bioadsorbents. The neutralization effect is trace depending on copper pollution levels.

3. Copper toxicity raises the acidity (H^+ ions), bases (Ca^{2+} and K^+ ions) and electrolytic content in the liquid phase of maize biomass. The increase of the electrolytic content depends on the degree of neutralization.

4. Cation exchange capacity of biomass is a comparatively stable value in relation to the increasing copper pollution and diminishes weakly as affected by soil acidity neutralization.

5. Cation distribution in the liquid phase of maize tissues depends on soil acidity neutralization but not on copper pollution levels. The variation of both factors has no influence on the cations' share in the adsorption phase of tissues.

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