

# The Effect of Agricultural Technologies on the Dynamics of the content of Mn, Zn, Cd, Co, Pb, and Cu in Leached Back Soil of Western Ciscaucasia and Maize Grains

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ABSTRACT: The problem of pollution of products grown on leached chernozem of the Western Ciscaucasia by heavy metals is rather acute for export grain producers. In order to identify factors affecting the accumulation of metals of hazard class 1 and 2 in maize grain, studies were conducted on the effect of agricultural technologies (fertilizer system, plant protection, and the method of tillage) on the balance of heavy metals in the soil and their absorption by the plants. The use of mineral fertilizers and manure does not affect the accumulation of acid-soluble forms of heavy metals in the topsoil and subsurface soil layers. The content of acid forms of heavy metals does not change with the introduction of fertilizers, and amounts to 500–550 mg/kg for manganese, 10–12 mg/kg for cobalt, 19–22 mg/kg for copper, 0.15–0.20 mg/kg for cadmium, 60–70 mg/kg for zinc, and 15–16 mg/kg for lead. In maize grains, the content of heavy metals does not exceed the maximum permissible concentrations (MPC) for human nutrition, except for cadmium, which is accumulated at the level of 1.4 MPC on the background of high dosages of the N120P120 fertilizers and manure of 600 kg per hectare in soil tillage with soil loosening to the depth of topsoil. Obtaining environmentally friendly grain is possible only with a reduction in the doses of fertilizers and manure, which negatively affects the productivity and profit of the producer.

Keywords: maize, monitoring, microelements, mineral fertilizers, manure, leached black soil, MPC.

# I. INTRODUCTION

The sown area of grain maize in Russia is about three million hectares, with about 22% located in the Krasnodar region. In terms of the grain yield, the Krasnodar Krai takes a position far from leading - 55.4 t/ha, compared to the Orel and Kursk regions - 80 kg/ha; therefore, the introduction of advanced technologies with scientifically substantiated nutrition conditions for the plants, including microelements, will allow optimizing the conditions for crops cultivation. The content of nutrients in maize plants and the harvest substantially depends not only on the type of the soil and the fertilizers used but also, according to the studies performed in Ohio, on the variety [1-4]. The yield of maize increases the most with the use of nitrogen additives, cattle manure, or bird droppings [5, 6]. The studies in Southern Wisconsin showed that good yield of up to 7.5 t/ha could be obtained using cow manure in the maize - soybeans - winter wheat - red clover crop rotation [7].

High dosages of fertilizers do not always have a positive effect on the yield and the quality of the product. For instance, researchers in Iran found that the dosages of urea of 500 kg/ha did not increase the maize yield and decreased the environmental index of the product [8, 9]. This was due to increasing the content of mobile forms of metals in the soil under the action of fertilizers, which resulted in increasing the absorption of not only essential elements but also toxic metals [10-12].

Maize belongs to the plants that actively absorb nutrition elements from the soil. According to the studies

performed between 2008 and 2013 in Central Iowa (the USA), the green mass for silage takes out 19 kg/ha of copper during harvesting, which amounts to up to 31 % of the content of the forms available to plants in the soil, about 26 kg/ha of manganese (9 % of the content in soil), and 141 kg/ha of zinc (up to 57 % of the accumulation in the soil) [13-15]. Given the buffer capacity of leached black soil in terms of microelements, depletion of essential elements from the topsoil is manifested quite significantly [16-18]. The lack of trace elements in the soil and, accordingly, in plants, can have an adverse effect on the quality of the grown products and the yield [19-23].

Studies on the balance of elements in the soil-plant system for growing maize carried out prior to 2019, did not cover the issue of soil and plant provision with micronutrient nutrition and pollution by heavy metals. However, the need to increase the export of maize grain of high environmental quality required from the producer for a new assessment and revision of existing agricultural technologies.

Therefore, at present, studying the balance of heavy metals in the fertilizer-soil-plant system is relevant for establishing the optimal conditions for grain maize cultivation in Western Ciscaucasia.

# **II. METHODS**

The studies were performed at the experimental station of the Kuban State Agrarian University on leashed black soil of Western Ciscaucasia in the conditions of the 11field grain-and-grass crop rotation. The effect of the tillage system, the dosages of the introduced mineral fertilizers and manure, and plant protection on the dynamics of trace elements in the soil and their accumulation in the grains of maize of the Krasnodar 358MB hybrid in 2015 – 2017 was studied.

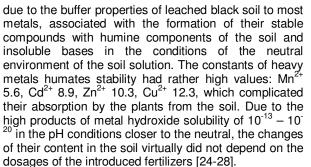
The variants of the experiment were presented as follows: the first digit was the amount of introduced manure for maize + total per rotation: 1 - (20 + 200), 2 - (40 + 400), 3 - (80 + 600) t/ha; the second digit was the dosage of mineral fertilizers for maze:  $1 - N_{30}P_{30}$ ,  $2 - N_{60}P_{60}$ ,  $3 - N_{120}P_{120}$ ; and the third digit was the system of plant protection: 1 - biological protection from diseases and pests, 2 - chemical protection from the weeds, 3 - integrated protection from pests, diseases, and weeds. The tillage systems were the following:  $D_1 -$  nonmoldboard,  $D_2 -$  moldboard to the depth of the topsoil, and  $D_3 -$  moldboard with deep loosening to the depth of the subsurface layer.

The content of acid-soluble, mobile forms of heavy metals in the soil, and their accumulation in maize grains were studied. The content of metals was determined in extracts by the method of atomic absorptive spectroscopy on the Quant 2AT device: acid-soluble — in nitric acid, mobile — in the acetate-ammonia buffer, the grains were ashed at 450 C, followed by ash dissolution in 5 % nitric acid.

### **III. RESULTS**

# A. The content of acid-soluble forms of heavy metals in the soil

The content of acid-soluble forms of heavy metals in the soil was practically independent on the agricultural technology used, varied within narrow limits, and did not exceed the permissible values: Mn — 500 to 530 (MPC 1,500) mg/kg, Cu — 18 to 23 (MPC 132) mg/kg, Zn — 60 to 70 (MPC 100) mg/kg, Co — 10 to 12 (MPC 40) mg/kg, Cd — 0.15 to 0.22 (MPC 2.0) mg/kg, and Pb — 14 to 17 (MPC 32) mg/kg (Fig. 1). This regularity was



The content of the acid-soluble forms of heavy metals in the topsoil and subsurface layers did not differ significantly (Fig. 1). The content of acid-soluble forms of metals in the soil depends on the tillage method: in case of deep loosening D<sub>3</sub>, Cu accumulation in the subsoil layer was the highest and exceeded 21 mg/kg. The highest content of zinc in the topsoil of more than 65 mg/kg was observed in the topsoil in the case of tillage method  $D_2$ , which was recommended for the region. The accumulation of lead in the subsoil layer was higher by 20 - 23 % than in the arable layer in the case of nonmoldboard D<sub>1</sub> and moldboard tillage with deep soil loosening D<sub>3</sub>. The content of cadmium in the topsoil was 12 - 17 % higher than in the subsurface layer in all variants of the experiment, including the reference.

Thus, the content of acid-soluble forms of heavy metals virtually did not change upon the introduction of fertilizers, which, in the opinion of A.Kh. Sheudzhen, was associated with restoring the balance due to the acid-insoluble forms contained in the leached black soil of the Kuban region [17]. The elevated levels of cadmium and lead in the topsoil were the result of their arrival to the soil surface with the dust blown by the wind, and with atmospheric precipitation [19].

14

12 10

8

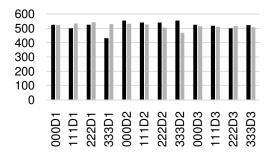
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4

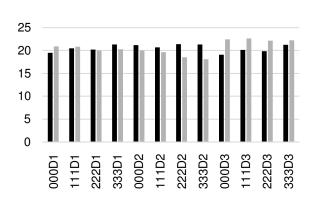
2

111D1 222D1 333D1

000T



Manganese

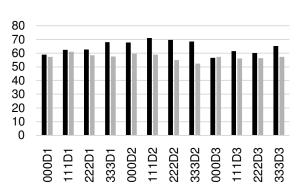




00002 11102 22202 33302 33302 00003 11103

222D3

33D3



Copper



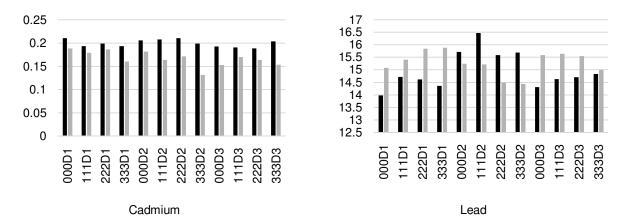


Fig. 1. content of heavy metals in the soil, depending on the tillage technology, mg/kg
 In the topsoil 0 − 30 cm deep; In the subsurface layer 30 − 60 cm deep.

B. The content of mobile forms of heavy metals in the soil

The content of mobile forms of manganese, cobalt, and zinc in the topsoil increased with increasing the dosages of the introduced mineral fertilizers and manure; for cadmium, lead, and copper, no such regularities were found (Table 1 (i) The introduction of fertilizers increased the level of accumulation of macroelements — total nitrogen (N), phosphorus (P), and potassium (K) — in the soil.

Table 1: The content of mobile forms of heavy metals in the topsoil and subsurface layer under maize for
grain, depending on the tillage method, mg/kg of soil.

Variant	Layer	Mn	Cu	Zn	Pb	Cd	Co
000D1	0-30	72	0.27	1.03	0.51	0.07	0.31
	30 - 60	52	0.12	0.78	0.42	0.03	0.26
	Δ, %	-27	-55	-24	-18	-57	-16
	0-30	83	0.34	1.87	0.82	0.061	0.34
111D1	30 - 60	53	0.14	0.97	0.55	0.028	0.24
	Δ, %	-24	-59	-48	-33	-54	-29
	0-30	93	0.30	2.26	0.50	0.063	0.46
222D1	30 - 60	46	0.12	0.71	0.42	0.037	0.23
	Δ, %	-50	-60	-68	-16	-41	-50
	0-30	98	0.39	3.96	0.86	0.066	0.58
333D1	30 - 60	58	0.14	1.06	0.45	0.037	0.23
	Δ, %	-41	-64	-73	-47	-44	-60
	0-30	69	0.30	0.81	0.67	0.058	0.40
000D2	30 - 60	85	0.15	0.69	0.95	0.050	0.25
	Δ, %	+23	-50	-15	+42	-14	-38
111D2	0-30	83	0.27	0.87	0.61	0.062	0.45
	30 - 60	87	0.19	1.03	0.88	0.042	0.27
	Δ, %	+4	-29	+18	+30	-32	-40
	0 - 30	89	0.29	1.14	0.74	0.058	0.48
222D2	30 - 60	90	0.15	1.01	0.89	0.042	0.32
	Δ, %	+1	-48	-11	+20	-28	-33
	0-30	92	0.28	0.87	0.77	0.08	0.41
333D2	30 - 60	99	0.21	0.99	0.50	0.03	0.27
	Δ, %	+8	-25	+13	-35	-62	-34
	0-30	67	0.23	2.45	0.58	0.084	0.32
000D3	30 - 60	79	0.18	0.60	0.37	0.032	0.22
	Δ, %	+18	-22	-76	-36	-62	-32
	0-30	88	0.29	1.79	0.83	0.062	0.35
111D3	30 - 60	89	0.16	0.58	0.48	0.026	0.29
	Δ, %	+1	-45	-68	-35	-58	-17
	0-30	67	0.24	1.73	0.71	0.054	0.33
222D3	30 - 60	80	0.17	0.65	0.51	0.026	0.26
	Δ, %	+19	-29	-62	-28	-51	-21
333D3	0-30	87	0.29	2.06	0.68	0.066	0.39
	30 - 60	90	0.20	1.05	0.47	0.039	0.30
	Δ, %	+3	-31	-49	-31	-41	-23
LSD <sub>05</sub>		5.3	0.11	0.21	0.10	0.009	0.05
MP		140	3	23	6	0,1	5

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The dependence of the content of mobile forms of manganese, cobalt, and zinc in the topsoil on NPK accumulation is expressed by the following regression equations (Statistica 6.1):

 $\begin{array}{l} C_{MF}(Mn) = 41.9 + 0.72 \cdot C(N) - 0.04 \cdot C(P) + 0.05 \cdot C(K); \\ C_{MF}(Co) = 0.21 + 0.05 \cdot C(N) - 0.005 \cdot C(P) + 0.002 \cdot C(K); \\ C_{MF}(Zn) = -3.78 + 0.02 \cdot C(N) - 0.02 \cdot C(P) + 0.001 \cdot C(K); \\ The obtained coefficients were significant for nitrogen, and to a lesser extent — for potassium, manganese, cobalt, and zinc. For cadmium, lead, and copper, no linear dependence existed, which was due to the effect of anthropogenic factors and the arrival of these metals to the soil with atmospheric precipitation [20]. \\ \end{array}$ 

The content of humus (H) in the soil varied from 3.2 to 3.9%; the regression analysis showed that the dependence of the content of mobile forms of manganese and cobalt on the humus content was close to the linear one:

$$\begin{split} &C_{MF}(Mn) = 23 \bullet C(H)^{1.03}, \\ &C_{MF}(Cu) = 0.11 \bullet C(H)^{1.11}. \end{split}$$

The highest content of mobile forms of manganese, copper, zinc, and cobalt was observed in the topsoil with non mold board tillage D1; therefore, the absence of deep loosening prevented the migration of mobile forms to lower layers. The content of heavy metals in the topsoil was higher than in the subsurface layer, which could be due to their arrival with atmospheric precipitation, or with the transition from inaccessible forms into mobile ones due to the intensification of oxidation processes in the presence of atmospheric oxygen (Table 1). This regularity was confirmed by manganese, since its content in the form of mobile forms in the soil was quite high primarily due to its ability to exhibit several degrees of oxidation from +2 to +7, and compounds Mn (V) and Mn (VII) were readily soluble in the soil solution in a neutral medium, which was characteristic of black soils.

The greatest influence on the content of mobile forms of heavy metals in the soil according to the values of the regression coefficients was exerted by humus (H) and nitrogen (N) compounds (Fig. 2):

 $C_{MF}(Mn) = 460.7555 - 1.8115 \cdot C(N) - 192.0892 \cdot C(H) - 0.0518 \cdot C(N)^2 + 2.7697 \cdot C(H) \cdot C(N) + 0.3988 \cdot C(H)^2;$ 

 $C_{\text{MF}}(Cu) = -2.3831 - 0.0711 \cdot C(\text{N}) + 2.9242 \cdot C(\text{H}) - 0.0001 \cdot C(\text{N})^2 +$ 

+  $0.0284 \cdot C(H) \cdot C(N) - 0.7181 \cdot C(H)^{2};$ 

 $C_{MF}(Pb) = 6.7939 - 0.1171 \cdot C(N) - 1.0289 \cdot C(H) - 0.0015 \cdot C(N)^2 +$ 

+  $0.0953 \cdot C(H) \cdot C(N) - 0.8434 \cdot C(H)^{2};$ 

 $C_{MF}(Zn) = -100.0821 - 1.7764 \cdot C(N) + 93.7187 \cdot C(H) - 0.0034 \cdot C(N)^2 +$ 

+  $0.6951 \cdot C(H) \cdot C(N) - 20.727 \cdot C(H)^{2};$ 

 $C_{MF}(Cd) = 0.5168 + 0.0036 \cdot C(N) - 0.3632 \cdot C(H) + 4.3518E-5 \cdot C(N)^2 -$ 

 $-0.0029 \cdot C(H) \cdot C(N) + 0.0863 \cdot C(H)^{2}$ .

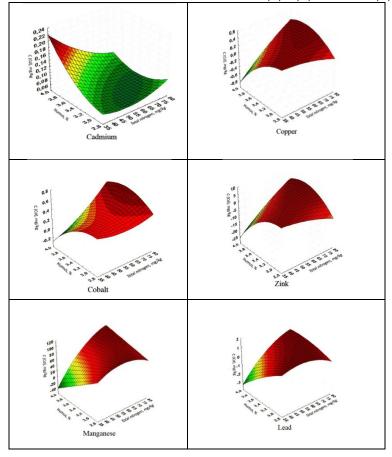


Fig. 2. The humus content and total nitrogen dependence on the accumulation of mobile forms of heavy metals in the soil.

The dependence of the content of humus, total nitrogen, and mobile forms of Mn, Cu, Zn, Co, and Pb had a similar regularity: with increasing the total net content of nitrogen to 40 mg/kg and that of humus to 3.0 - 3.4 %, the accumulation of mobile forms of metals increased, with further increase in the level of fertility, the share of the forms of metals available for the plants decreased. The accumulation of mobile forms of cadmium, on the contrary, decreased with increasing the content of nitrogen and decreasing the content of humus in the soil.

In general, upon the introduction of high dosages of fertilizers, no tendency to accumulating heavy metals in the soil was found, but the amount of mobile forms increased. The degrees of heavy metals mobility decreased in the row: Cd (29 %) > Mn (14 %) > Pb (4.5 %) > Co (4.1 %) > Zn (2.5 %) > Cu (1.5 %).

### C. The content of heavy metals in maize plants

An increased degree of cadmium mobility in the soil contributed to increasing its availability to maize plants. It was found that the content of Cd for children's food exceeded the MPC 1.5 times in grain of maize in all variants of the experiment, including the reference. A

significant excess of 1.4 MPC for the adult population was only observed in the case of using intensive technologies (333), which was consistent with the data about increasing the absorption of mobile forms of cadmium from the soil with increasing the level of fertility. Thus, the accumulation of cadmium in maize grain occurred on the background of the safe level of this element's mobile forms content in the topsoil and subsurface layer of leached black soil (0.5 MPC); therefore, atmospheric precipitation was likely to play a significant role in these conditions [29, 30].

With increasing the mineral nutrition, the content of cadmium in maize grain with the recommended  $(D_2)$  and moldboard  $(D_3)$  tillage increased by 20 - 30 %, compared to the reference (Tables 2 and 3).

The content of zinc and manganese in maize grain with increasing the dosages of the introduced fertilizers increased insignificantly — from 4 to 10 %. In the conditions of intensive technology (333), the accumulation decreased: Cu (6 – 20 %); Co (20 – 40 %), and Pb (20 – 52 %). The introduction of manure and mineral fertilizers contributed to a significant (by 50 – 70 %) decrease in the content of lead in maize grains.

Table 2: The effect of various agricultural technologies on the content of manganese, copper, and cobalt in maize grains in the case of moldboard tillage and soil loosening to the depth of topsoil (D<sub>2</sub>).

	Mn			Cu		Со	
Variant	mg/kg	Δ (from 000), %	mg/kg	Δ (from 000), %	mg/kg	Δ (from 000), %	
000	14.56	—	2.52	_	0.69	_	
111	14.03	-3.6	2.28	-9	0.15	-78	
222	11.78	-19	2.27	-10	0.16	-23	
333	11.75	-19	1.75	-31	0.34	-51	
002	12.63	-13	2.58	+0.06	0.12	-173	
020	13.33	-8.4	2.12	-16	0.36	-48	
022	10.59	-27	2.00	-21	0.42	-39	
200	13.72	-5.7	2.36	-6.4	0.31	-79	
202	14.71	+1.0	2.33	-7.6	0.34	-49	
220	13.98	-4.0	2.03	-20	0.14	-20	
113	13.71	-5.8	2.49	-1.2	0.21	-69	
131	13.71	-5.8	1.94	-23	0.33	-52	
133	13.02	-11	1.87	-26	0.24	-65	
Δ (from the average), mg/kg	± 1.1	_	±0.09	_	±0.05	_	
MPC	120		10		1,0		

The effect of reducing the content of microelements needed by the plants (copper and manganese by 20 - 30%) at increased dosages of the fertilizers (variants 222 and 333) is negative. Cobalt deficiency is observed in all studied agricultural technologies, especially where herbicides are used on the background of initial fertility (002) – it reaches 173%, compared to the reference.

The content of zinc in maize grains in all variants of the experiment was at the level of < 0.5 MPC, which met the requirements for environmentally friendly products. The maximum accumulation of zinc (up to 9.3 %), compared to the reference, was found on the background of initial fertility upon the introduction of double dosages of mineral fertilizers (variant 020).

The content of lead in maize grains of < 0.5 MPC was noted in the variants on the background of increased and high fertility (200, 202, 220, 222, and 333). In the conditions of initial and medium fertility (000, 002, 022, 111, and 113), lead accumulation was 0.5 - 0.7 MPC, which indicated a negative trend, and exceeded the MPC for baby food.

The quality of the grown maize grains corresponded to DSTU 4526:2006 and EU 742/2010 in terms of the content of protein of 11 – 12 % (not less than 9 %), fat content of 3.8 - 4.2 %, nitrogen content of 1.7 - 2.1 %, starch content of 64 - 67 %, and phosphorus content of 0.3 - 0.6 % (not rated).

	Zn			Pb		Cd	
Variant	mg/kg	Δ (from 000), %	mg/kg	Δ (from 000), %	mg/kg	Δ (from 000), %	
000	22.52	_	0.34	-	0.077	-	
111	22.99	+2.1	0.27	-20.5	0.060	-28	
222	20.68	-8.0	0.12	-64.7	0.110	+43	
333	19.15	-14.9	0.11	-67.7	0.140	+82	
002	22.81	+1.3	0.25	-26.5	0.104	+35	
020	24.62	+9.3	0.15	-55.9	0.104	+35	
022	23.06	+2.4	0.30	-11.8	0.064	-17	
200	21.21	-5.8	0.10	-70.6	0.087	+13	
202	23.20	+3.0	0.17	-50.0	0.074	-4	
220	20.26	-10.0	0.17	-50.0	0.076	-1	
113	22.16	-1.6	0.36	+5.89	0.105	+36	
131	19.71	-12.5	0.21	-38.2	0.073	-52	
133	19.94	-11.5	0.15	-55.9	0.044	-43	
Δ from the average), mg/kg	±1.05	_	±0.051	_	±0.031	_	
MPC	50		0.5/ 0.3*		0.1/ 0.06*		

Table 3: The effect of various agricultural technologies on the content of zinc, lead, and cadmium in maize grains in the case of moldboard tillage and soil loosening to the depth of topsoil (D<sub>2</sub>).

Heavy metals have mixed effect on the quality of maize grain. A calculation of the linear regression coefficients between the content of heavy metals in the grain and the quality indicators showed that the accumulation of cadmium had the greatest effect on the content of protein and starch:

 $C(\text{phosphorus}) = 0.92 + 0.33 \cdot C(\text{Mn}) - 0.37 \cdot C(\text{Cu}) - 0.08 \cdot C(\text{Zn}) - 0.54 \cdot C(\text{Pb}) - 6.81 \cdot C(\text{Cd}) - 3.76 \cdot C(\text{Co}).$ 

No correlation of zinc and manganese content was observed with the grain quality. The value of the copper, lead, and cobalt regression coefficient with a negative sign indicates a decrease in the effect of the metal content in the grain on improving the quality of protein accumulation. Starch content is significantly determined by the presence of cadmium, copper, and cobalt in the grains.

The maize grain yield (Y) increased from 32 kg/ha in the reference variant to 52 kg/ha in the variant with the intensive technology (333). Increasing productivity according to the linear regression was accompanied by increasing the effect of manganese and cadmium accumulation in the grains:

The accumulation of essential microelements — cobalt, zinc, and copper — had an inverse relationship with the increase in the maize grain yield, which is evidence of an insufficient amount of these elements for plant nutrition.

### **IV. CONCLUSION**

(a) The content of manganese, copper, zinc, cobalt, lead, and cadmium in the topsoil and subsurface layer does not significantly depend on the tillage technology.

(b) The content of mobile forms of essential elements in the soil increases with increasing the dosages of used mineral fertilizers and manure, which is associated with the formation of water-soluble humates and slight acidification of the soil solution due to the hydrolysis of nitrogen fertilizers. The higher accumulation of heavy metals in the topsoil than in the subsurface is associated with atmospheric precipitation and weather factors and is observed in all tillage technologies.

(c) The degree of heavy metals mobility in the soil increases in the row: Cd, Mn, Pb, Co, Zn, and Cu. The highest degree of mobility of up to 30 % is characteristic of cadmium, about 13 % — of manganese; for other metals, the content of the forms available for plants does not exceed 5 % in the variant with a high dosage (600 kg/ha) of the N<sub>120</sub>P<sub>120</sub> fertilizer and manure.

(d) The content of heavy metals in the green mass of maize does not exceed the MPC for fodder crops in all variants of the experiment and varies for manganese within 50 to 70 mg/kg, for cobalt — 0.5 to 1.0 mg/kg, for zinc — 20 to 30 mg/kg, and for copper — 10 to 12 mg/kg. With increasing the dosages of fertilizers, the accumulation of Mn, Cu, Zn, and Cu in the green mass reduces; for cadmium and lead, no clear regularity is found.

(e) The use of fertilizers contributes to the accumulation of cadmium in maize grains, the highest content of 140 mg/kg (1.4 MPC) is observed in the variant with the increased dosage (600 t/ha) of the  $N_{120}P_{120}$  fertilizer and manure. The content of lead in maize grains decreases with increasing the dosages of fertilizers, a 10 % excess of the MPC for baby food is observed in the reference variant. The content of manganese and zinc in the grains does not depend on the tillage technologies used and does not exceed the permissible concentrations. The content of copper and cobalt in maize grains decreases with increasing the dosages of fertilizers, which indicates insufficient supply of these elements to the plants from the soil

(e) In order to restore the microelement nutrition of maize plants grown on leached chernozem, the application of foliar fertilizers with copper, zinc, and cobalt in the initial phases of growth is promising. This

will allow avoiding buffering of soil in relation to most trace elements and increasing their access to plants, which will further lead to increase in productivity and product quality.

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