Mycotoxins, pesticides and heavy metals content in the winter wheat grain at different cultivation technologies on leached Kuban chernozem

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Abstract. The influence of fertilizers and plant protection products for the mycotoxins, pesticides and heavy metals accumulation in the grain of winter wheat variety Antonina grown at the experimental station of the Kuban University was investigated. In the resulted grain there were no traces of the fungicide "Фалькон", insecticide "Эйфория" and herbicide "Секатор тупо" used in the cultivation. The content of T-2 toxin is almost at the level of MPC 0.1 mg / kg in all variants of the experiment that indicates the fungal infection invading from the soil. The content of Mn, Cu, Zn, Pb, Cd, Co, Ni, Cr in grain did not exceed MAC for adult nutrition.

1 Introduction

The rapid growth of the world's population, which will reach more than 9 billion by 2050, and the reduction of arable land is a major challenge to achieving global food security. Intensification of agriculture is carried out by increasing the amount of fertilizers and variation of plant protection products, which may be accompanied by contamination of products with heavy metals, herbicides and pesticides [3, 10-11]. The decrease in grain quality is associated not only with the accumulation of heavy metals and pesticide residues in it, but also with the formation of mycotoxins. Schöneberg T. (2016) notes a tendency to increase the percentage of colonized kernels by fungi in grain from systems using more fertilizers and pesticides. From another point of view, a pesticide such as tricyclazole contributes to the destruction of the external protective layer of melanin pigment in the fungus cells [7]. The renovated values of content the toxins, pesticides and heavy metals in grain products were introduced in the EU in 2013. The technical regulations of the Customs Union "On safety of grain" were introduced in the Russian Federation in 2011. In the period from 2002 to 2013, about 16 % of the oats samples in England contained more than 1000 $\mu\text{g kg}^{-1}$ toxin HT2 + T2, exceeded MPC regulated in the Russian Federation [2].

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Problems arising with the quality of winter wheat grain, both in Russia and abroad, require a new approach to agrobiotechnologies [4, 6]. Therefore, the purpose of our study was to develop a technology that allows obtaining quality winter wheat grain, suitable for the nutrition of adults and children.

2 Materials and methods

The research was conducted within the framework of long-term experience at the educational farm station "Kuban" in the territory of Krasnodar Region (Russia) in the period from 2015 to 2017. The cultivated crop is winter wheat (*Triticum aestivum* L.) cultivar Antonina, developed by scientists of Federal state budgetary scientific institution "NCG named after P. P. Lukyanenko" (Russia) and transferred to the state variety testing in 2013. The forecrop of winter wheat is sunflower. The crop rotation: corn for grain, winter wheat, sugar beet, winter wheat, spring barley with sowing of alfalfa, 2 and 3 years alfalfa; winter wheat, winter barley, sunflower, winter wheat. Soils are represented by leached Chernozem with the capacity of the humus layer 147 cm, the reaction of the aqueous medium 6.5-8.2, humus content 2.5 – 2.9 %, mobile forms of nitrogen – 8 %, phosphorus – 6.5 – 7.8 %, exchangeable potassium-50 t/ha [8-9]. The influence of three factors on the quality of winter wheat grain was studied: A – the amount of manure introduced in the beginning of rotation for corn on the grain, t/ha; B - mineral fertilizers and C - plant protection system (table 1).

Table 1. Scheme of experience.

Variants	Manure, t / ha (factor A)	Mineral fertilizers, kg / ha (factor B)	The system of plant protection (factor)*
000	–	–	–
002	–	–	Chemical
111	200	$N_{70}P_{45}K_{30} + N_{30}$	Biological
020	–	$N_{140}P_{90}K_{60} + N_{60}$	–
200	400	–	–
022	–	$N_{140}P_{90}K_{60} + N_{60}$	Chemical
202	400	–	Chemical
220	400	$N_{140}P_{90}K_{60} + N_{60}$	–
222	400	$N_{140}P_{90}K_{60} + N_{60}$	Chemical
333	600	$N_{280}P_{180}K_{120} + N_{120}$	Intensive

Note. * Protection systems: biological – "Геостим" treatment at a rate of 1-2 liters per ha and "Бикол" (*Bacillus thuringiensis* var. *thuringiensis*, wetting powder, titer not less than 45 billion spores / g, BA-2000 EA/ g) at a rate of 3-4 liters per ha ; chemical – weeding with the herbicide "Секатор тупбo" (amidosulfuron 100 g/l, iodosulfuron-methyl-sodium 25 g/l, mefenpyr-diethyl 25 g/l) at a dose of 0.075 kg/ha; intensive – chemical + fungicide "Фалькон", (tebuconazole 167 g/l + triadimenol 43 g/l + spiroxamine 250 g/l) at a rate of 0.6 litres per hectare) + insecticide "Эйфория", (thiamethoxam and lambda-cyhalothrin) at a rate of 0.2 liters per hectare.

The grown grain was analyzed in the Federal state institution agrochemical service center "KRASNODARSKII" for the residual content of pesticides and mycotoxins by the chromatographic methods and the heavy metals of the first and second classes of danger on the atomic absorption spectrometer.

3 Result and discussion

Analysis of winter wheat grain grown under intensive plant protection system showed that the content of insecticide residues, herbicides and fungicides does not exceed the MPC for adult nutrition table 2. Also, there are traces of organomercury pesticides and derivatives of 2,4-D acid in the grain, which were not used in wheat growing, due to their residual content in the soil. The content of T-2 toxin in the grain is almost at the level of MPC 0.1 mg / kg, both under control and with intensive technology, which indicates the presence of fungal infection in the soil.

Table 2. Content of mycotoxins and pesticides in winter wheat grain varieties Antonina.

Indicator	Content, mg / kg		MPC*, mg/kg
	000	333	
Mycotoxins:			
aflatoxin B1 .	0.003	0.003	0.005
deoxynivalenol	0.23	0.27	0.70
T-2 toxin.	0.09	0.10	0.10
zearalenone	0.15	0.18	1.00
ochratoxin A	0.004	0.004	0.005
Pesticides :			
DDT and its metabolites	0.01	0.01	0.02
organomercury pesticides	0.01	0.01	absent
2,4-d acid, its salts, esters	0.04	0.04	absent
spiroxamine	trace quantities	0.011	0.2
propiconazole	trace quantities	0.09	0.1
tebuconazole	trace quantities	0.05	0.2
thiabendazole	trace quantities	0.1	0.2
triadimenol	0.005	0.015	0.2
Insecticides :			
lambda-cyhalothrin	trace quantities	0.05	0.01
thiamethoxam	trace quantities	0.02	0.05
Herbicides :			
amidosulfuron	trace quantities	следы	0.1
sodium iodosulfuron-methyl	trace quantities	следы	0.1
mefenpyr-diethv	trace quantities	следы	0.5

Notes. * Technical regulations of the Customs Union "On grain safety" TR CU 015/2011 dated 9.12.2011.

Heavy metals have dual nature, on the one hand - microelements (Mn, Cu, Zn, Co), on the other - especially dangerous substances of 1-3 class (Zn, Cu, Pb, Cd, Cr, Ni) [1, 5, 12]. The heavy metals content in winter wheat grain of Antonina variety does not exceed MPC for food of the adult population (table 3).

Table 3. Content of heavy metals in winter wheat grain varieties Antonina, mg / kg.

Variants	Mn	Co	Cr	Ni	Zn	Cu	Pb	Cd
000	20.6	0.054	0.031	0.43	18.3	3.9	0.14	0.071
111	21.2	0.048	0.016	0.53	17.6	3.8	0.15	0.058
002	23.5	0.051	0.038	0.62	22.3	4.3	0.19	0.067
020	23.6	0.045	0.016	0.59	16.8	2.8	0.12	0.061
200	23.4	0.066	0.020	0.43	21.8	3.5	0.16	0.062
022	22.6	0.063	0.014	0.50	17.1	2.9	0.15	0.066
202	22.8	0.072	0.015	0.44	12.9	2.4	0.14	0.057

220	24.0	0.070	0.016	0.38	14.2	2.9	0.14	0.071
222	22.7	0.043	0.020	0.38	18.9	2.9	0.10	0.064
333	22.4	0.046	0.017	0.28	19.2	2.5	0.17	0.078
LSD ₀₅	1.9	0.01	0.01	0.05	0.5	0.2	0.05	0.01
MPC [3]	140	1.0	0.5	1.0	50	10	0.50	0.1

The high doses introduction of fertilizers and manure does not contribute to the accumulation of cobalt, chromium, nickel and copper in the grain; the content of manganese, zinc, lead and cadmium does not change significantly with different technologies.

The dependence of manganese, copper and zinc content in the grain is expressed by regression equations (Statistica 6.1), for lead, nickel and cadmium the regularity is not revealed:

$$C(\text{Zn}) = 45.9 - 0.5 \times A - 0.7 \times B + 0.8 \times C,$$

$$C(\text{Cu}) = 47.7 - 0.3 \times A - 0.3 \times B + 0.2 \times C,$$

$$C(\text{Mn}) = 33.4 + 0.23 \times B - 0.34 \times C,$$

$$C(\text{Cr}) = 0.32 - 0.1 \times B,$$

$$C(\text{Co}) = 0.72 + 0.1 \times B,$$

where A - is manure,

B - fertilizers,

C - plant protection system.

The obtained coefficients are significant for manganese, copper and zinc in terms of the mineral fertilizers influence (20–35 %) and plant protection systems (about 35 %). For cadmium, lead and nickel there is no linear dependence, due to the influence of anthropogenic factors and the arrival of these metals in the soil with atmospheric rainfall.

The decrease in grain content in the variant with intensive technology compared to the control reaches – cobalt 20 %, chromium 45 %, nickel and copper 35 %, mainly due to the increase in yield and vegetative mass of plants.

4 Conclusion

The use of plant protection products, including herbicide application "Секатор турбо" (amidosulfuron, iodosulfuron-methyl-sodium, mefenpyr-diethyl), fungicide "Фалькон", (tebuconazole, triadimenol, spiroxamin), insecticide "Эйфория" (thiamethoxam and lambda-cyhalothrin) did not contribute to the accumulation of drugs residual quantities in the grain of winter wheat varieties Antonina.

T-2 toxin accumulation was observed at the level of MPC of 0.1 mg/kg in the control variant and with the use different doses of fertilizers and plant protection agents, that indicates the presence of fungal infection in the soil.

The content of Mn, Cu, Zn, Co, Cr, Ni, Cd, Pb in grown grain did not exceed MPC in all variants of the experiment. There was a decrease in the content of cobalt, chromium, nickel and copper in the grain by 20-35% compared with the control, when applying high doses of fertilizers.

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