

STUDY OF THE LEVEL OF POLLUTION WITH TOXIC METALS ONION

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Abstract. The article studies the level of pollution by toxic metals with the method of inversion voltammetric analysis of onion varieties Sabir, cultivated in the Lankaran-Astara economic region of Azerbaijan. The effect of mineral fertilizers is also studied applied during cultivation on the productivity of onion plants and the quality of product storage. It is shown that the optimal dose of mineral fertilizers, introduced during the cultivation of the onion variety Sabir is the N130P180K150 variant. In this variant, the yield and product was the highest, and storage losses were the lowest. The concentration of toxic metals (Zn, Cd, Pb, Cu) in onion production at all studied doses mineral fertilizers was within the MPC (maximum permissible concentration) of the *Sanitary and epidemiological rules and norms of the Ministry of Health of the Republic of Azerbaijan Hygienic requirements for the safety and nutritional value of food products and WHO*. Only in the H190P210K180 variant, the concentration of cadmium was 0.033 mg / kg, which is slightly higher no allowable limit (0.03mg/kg).

Keywords: analysis, onion, toxic metals, MPC (maximum permissible concentration).

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1. Introduction

Vegetable growing is one of the profitable and labor-intensive branches of the agro-industrial complex and occupies an important place among food products. After all, vegetables contain vitamins, proteins, carbohydrates, minerals, organic acids, essential oils, etc., necessary for human nutrition and health. One of the most popular products among vegetable crops, due to its versatility, is onion, which contains sugar, organic acids, mineral salts and essential oils, is valued for its taste and healing properties. These substances give it a smell and a sharp taste, and most importantly, phytoncidal and bactericidal properties. Compared to other vegetables, onions have a large amount of dry matter (up to 22%), sugars from 5.1 to 13.0%, 0.8-2.0% protein, 1.9-17.0 mg / 100 g vitamin C, 0.17-0.34% organic acids, 6.3-35.0 mg/100 g of essential oils, etc. (Selivanova, 2019; Bebris *et al.*, 2018; Maharramov, 2015; Fataliev, 2017; Yaradua *et al.*, 2020).

Onions are the third most cultivated vegetable after tomatoes and watermelons in terms of area they cover in the world. According to FAO, in 2019 the total area of onion cultivation in the world was 4.4 million hectares, the yield was 19.3 t/ha, the gross product was 85.8 million tons. According to the report of the State Statistics Committee of the Republic of Azerbaijan, in 2021 by in the Republic of Azerbaijan, area of onion cultivation was 11.6 thousand hectares, the yield was 24.57 t/ha, and the gross output was 286.2 thousand tons. The Lankaran-Astara economic region is one of the regions with the most favorable conditions for growing onions. In the 2021 economic year, onions were planted on 1140.5 hectares in the region, the total yield was 15468.5 tons, and the yield per hectare was 13.6 tons (Agayev *et al.*, 2021; State Statistics Committee of the Republic

of Azerbaijan, 2020, 2022).

Relevance of the issue. The main task facing vegetable growers in agriculture is to ensure the safety and storage of the product with minimal losses, along with high productivity. Only 80-85% of manufactured products are delivered to consumers, which leads to a decrease in the profitability of the entire production. In addition to the genetic characteristics of the variety, the cultivation technology, storage conditions and rules for the use of mineral fertilizers have an important impact on the quality and safety of products. In this regard, in addition to improving plant cultivation technologies, important tasks are the creation and application of innovative science-intensive technologies that minimize crop losses during storage (Selivanova, 2019; Bebris *et al.*, 2018; Trots *et al.*, 2015; Kalmykov *et al.*, 2022; Borisov, 2016; Borisov *et al.*, 2021).

One of the main problems of the country's agro-industrial complex is the production of environmentally friendly food products in the face of increasing anthropogenic impact on the biosphere. Chemical and biological contaminants accumulate in food at all stages of the food chain, from primary production to consumption. Toxicants that pose a particular danger to agrobiocenoses include toxic metals that enter living organisms from the soil, air and plants, forming highly toxic carcinogenic compounds. Toxic metals have a high ability to accumulate in living organisms over a period of time, causing an increase in harmful effects over the years. In agriculture, the main sources of plant contamination with toxic metals are fertilizers, metal-based pesticides, polluted irrigation water, etc. It is believed that the quality of agricultural resources (soil and water) decreases annually due to pollution as a result of anthropogenic activities (Maharramov *et al.*, 2021; Monisha *et al.*, 2014; Jarup, 2013; Soudek *et al.*, 2009; Kirkillis *et al.*, 2012; Stasinov *et al.*, 2014). Considering the urgency of the problem, the influence of various doses of mineral fertilizers on the productivity of onion plants, product quality during storage and the concentration of toxic metals in products was analyzed.

Purpose of the study. The purpose of this work is to study the effect of various doses of fertilizers (nitrogen, phosphorus, potash, separately increasing and decreasing) doses applied during the cultivation of onions in the Lankaran-Astara economic region on plant yield, product quality during storage and the level of contamination of the product with toxic metals.

Research objects. As an object of research, a zoned onion variety "Sabir", grown at the Lankaran Experimental Station of the Research Institute of Vegetable Growing, was taken, and the field experiment was carried out according to the following scheme:

1. Control (no fertilizer)
2. N90P180K150
3. N130P180K150
4. N130P130K150
5. N130P180K70
6. N190P210K180

Research methods and sample preparation. Field experiments were carried out at the Lankaran Experimental Station of the Research Institute of Horticulture in 6 variants and 4 repetitions. The total area of the experiment is 540 m², 22.5 m² for each option.

Storage of products (09/01/2021-05/05/2022) was carried out in the laboratory "Food Technology" of the Department "Technology and Engineering Sciences" of the Lankaran State University (LSU) in refrigerators with a temperature of 3-5 ° C and air humidity of 68-78%. Chemical analyzes were carried out in the laboratory "Food safety

and ecology" of the indicated department of Leningrad State University. The concentrations of toxic metals (zinc, cadmium, lead and copper) in the studied onion product were determined according to the methods of MU 31-04/04. The mass concentration of toxic metals is measured according to the indicated methods, after evaporating the samples at a temperature of 1200-3500C and heating them to a temperature of 4500C in a muffle furnace in an inversion voltammetric analyzer of the TA type, based on the possibility of accumulating elements.

Chemical interferences that prevent accurate determination of toxic elements in samples are removed when the samples are mineralized. Mass concentrations of elements in a sample are determined by adding certified standards of these elements. The mass concentration of each element in the analyzed sample is calculated automatically using the following formula:

$$X_i = \frac{I_1 \cdot C_d \cdot V_d}{(I_2 - I_1) \cdot m} \cdot \frac{V_{min}}{V_{al}}, \text{ mg/kg} .$$

Here: X_i is the content of this element in the analyzed sample, mg/kg;

C_d is the concentration of the certified mixture of the element, from which the additive is made to the analyzed sample, mg/dm³;

V_d is the volume of the additive of the certified mixture of the element, cm³;

I_1 is the peak value of the element in the analyzed sample, μA ;

V_{min} is the volume of mineralizate obtained by dissolving ash in a known volume of solvent, cm³;

V_{al} is the volume of an aliquot taken for analysis from the mineralizate, cm³;

I_2 is the peak value of the element in the sample with the additive, μA ;

m is the mass of the sample taken for analysis, g.

2. Materials and discussions

The effect of doses of mineral fertilizers (NPK) applied during the cultivation of the zoned onion variety "Sabir", grown at the Lankaran Experimental Station of the Research Institute of Vegetable Growing in 2020-2022, on plant yield, product quality during storage and the presence of toxic metals (Zn, Cu, Pb, Cd). The results obtained are presented in tables 1-3 and figures 1-3.

Mineral fertilizers play an important role in increasing the yield of onions. Onions, unlike other vegetable crops, have a relatively low need for nutrients at the beginning of growth from sowing to mass shoots and in the phase of formation of 4-5 leaves. By this time, plants absorb 10–12% N, 6–7% P₂O₅, and 10% K₂O of the total need for the growing season (Selivanova, 2019; Borisov, 2016).

Bulb onion varieties "Sabir" was planted in the third decade of February for the purpose of purchasing onions and the total yield was determined, including marketable, non-commercial, yield per hectare, weight of one bulb. The results obtained are shown in table 1.

Table 1. Onion yield of the Sabir variety (average for 2020-2021)

№	Experiment options	Productivity c/ha	Commodity		Gain to Control		The whole of one bulb, g
			c/ha	%	s/ha	%	
1	control	186	158	84,9	-	-	75
2	N ₉₀ P ₁₈₀ K ₁₅₀	204	179	87,7	18	9,6	81
3	N ₁₃₀ P ₁₈₀ K ₁₅₀	223	203	91,1	37	19,8	86
4	N ₁₃₀ P ₁₃₀ K ₁₅₀	207	188	90,9	21	11,3	82
5	N ₁₃₀ P ₁₈₀ K ₇₀	218	194	88,8	32	17,2	84
6	N ₁₉₀ P ₂₁₀ K ₁₈₀	232	208	89,9	46	24,7	92

As can be seen from Table. 1, the yield in individual doses of mineral fertilizers varied. So, if the control variant "Without fertilizers" gave 186 c/ha, then compared with the variant "Without fertilizers", the lowest yield was 204 c/ha with a reduced dose of nitrogen fertilizers (N₉₀P₁₈₀K₁₅₀), and the maximum yield was 232 c/ha. c/ha with an increased dose of NPK (N₁₉₀P₂₁₀K₁₈₀)/ha. This testifies to the high role of mineral fertilizers, mainly nitrogen fertilizers, in the mineral nutrition of bulbous plants. Compared to the control "Without fertilizers", the yield increase is the largest in the N₁₉₀P₂₁₀K₁₈₀ variant, 46 c/ha, 24.7%, but the most optimal variant is the dose of N₁₃₀P₁₈₀K₁₅₀. Because in this variant, the output of marketable products was at the highest level of 91.1%. With reduced doses of phosphorus and potassium, the yield was lower than with other variants of mineral fertilizer.

The influence of doses of mineral fertilizers on the shelf life of onion products and the amount of storage losses was determined, the results are shown in table 2.

Table 2. Onion loss during storage

№	Experiment options	onion weight loss, in %			Total loss, in %
		Natural losses	Germination	Rot	
1	Control	3,8	1,9	7,7	13,4
2	N ₉₀ P ₁₈₀ K ₁₅₀	3,5	2,2	5,9	11,6
3	N ₁₃₀ P ₁₈₀ K ₁₅₀	3,1	1,2	2,5	6,8
4	N ₁₃₀ P ₁₃₀ K ₁₅₀	3,5	2,6	3,3	9,4
5	N ₁₃₀ P ₁₈₀ K ₇₀	3,3	1,6	6,9	11,8
6	N ₁₉₀ P ₂₁₀ K ₁₈₀	4,1	3,9	8,3	16,3

As can be seen from Table 2, different doses of mineral fertilizers (NPK) ensured longer onion storage. In the control variant "Without fertilizers", the total losses amounted to 13.4%, and in the other variants, 6.8-16.3% were observed. The smallest losses were observed in the N₁₃₀P₁₈₀K₁₅₀ variant, in which the total losses were two times less than the control variant, only 6.8%. With an increased dose of mineral fertilizers (N₁₉₀P₂₁₀K₁₈₀), there were 2 times more sprouted bulbs than in the control "Without fertilizers", and the total loss was 1.5 times more.

There is sufficient evidence that mineral fertilizers are one of the sources of potential contamination of vegetable crops with toxic metals in agriculture. This requires monitoring the problem in vegetable products and developing adequate technological

methods that minimize the impact of toxic metals (Trots *et al.*, 2015; Borisov, 2016; Borisov *et al.*, 2021). Doses on the concentration of toxic metals (Zn, Cd, Pb, Cu) during storage of products have been studied and the results are shown in Table 3.

Table 3. Mass concentration of toxic metals (Zn, Cd, Pb, Cu) in onions

No	Experiment options	Mass concentration (mg/kg)							
		Zn		Cd		Pb		Cu	
		Before storage	After storage	Before storage	After storage	Before storage	After storage	Before storage	After storage
1	Control	0,013	0,34	0,0022	0,0050	0,013	0,025	1,20	0,30
2	N ₉₀ P ₁₈₀ K ₁₅₀	0,054	0,075	0,0072	0,0072	0,037	0,037	0,86	0,86
3	N ₁₃₀ P ₁₈₀ K ₁₅₀	0,077	0,15	0,0062	0,0066	0,037	0,020	0,86	0,71

As can be seen from Table 3, in all studied dosages of fertilizers in the control variant, there were certain changes in the concentration of toxic metals before and after storage. So, if the concentration of zinc (Zn) in fresh onion products was 0.013 mg/kg in the control variant, then it was observed in all variants where mineral fertilizers were applied, more - in the range of 0.054-1.40 mg/kg.

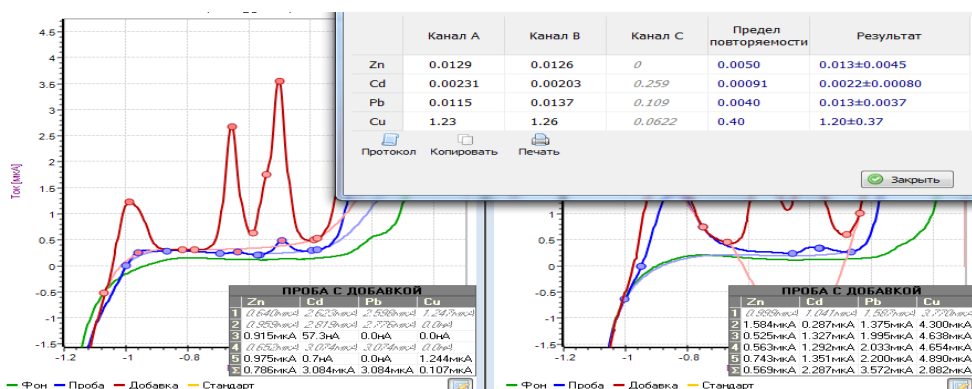


Figure 1. Voltamperogram of mass concentrations of toxic metals in onions before storage

As can be seen from Figure 1, despite the fact that the amount of cadmium (Cd) in fresh products in the control variant was 0.0022 mg/kg, a sharp increase was observed at all studied doses of fertilizers. Compared to the control ("non-fertilizing") variant, the concentration of cadmium was 0.0055 mg/kg, which is 2.5 times higher in decreasing doses of phosphorus and potassium (N₁₃₀P₁₃₀K₁₅₀; N₁₃₀P₁₈₀K₇₀), at a dose of N₁₉₀P₂₁₀K₁₈₀ 0.033 mg/kg, that is, 15 times more.

During storage, an increase in the concentration of cadmium by 2.2 times was observed in the control variant compared to the fresh product, while no significant increase was observed at higher doses of fertilizers. There was an increase of 6.4%; 30.1%.

Although the zinc concentration increased with all increasing doses of nitrogen after storage, the concentration of zinc with decreasing dose of potassium (N₁₃₀P₁₈₀K₇₀)

decreased from 0.28 mg/kg in fresh products to 0.067 mg/kg after storage (Fig. 2).

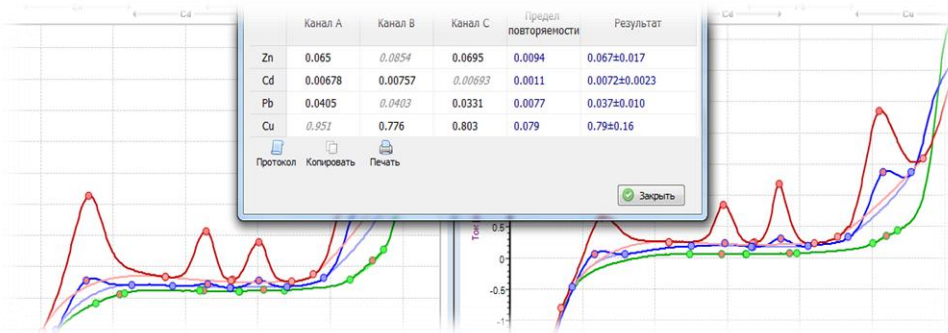


Figure 2. Voltamperogram of mass concentrations of toxic metals in onions after storage with the N130P180K70 variant

The concentration of lead (*Pb*) in fresh onion products increased by 2.1-7.5 times depending on the doses of fertilizers in all studied options compared to the control option. After storage, the concentration of lead in onions increased by 2 times compared with fresh products in the control variant, while in other doses of fertilizers, a decrease was mainly observed.

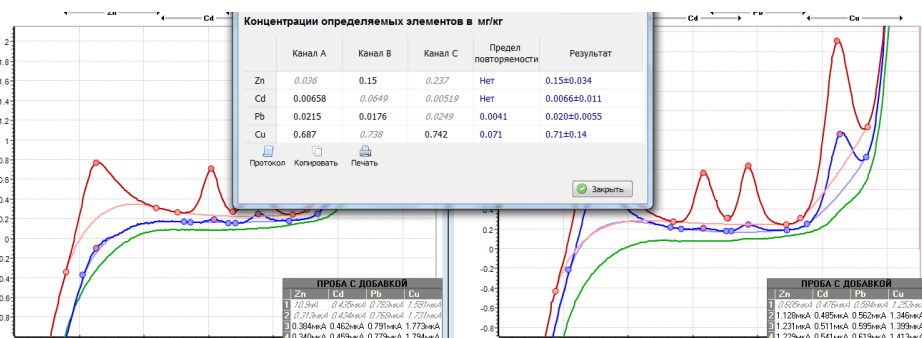


Figure 3. Voltamperogram of mass concentrations of toxic metals in onions after storage in the N130P180K150 variant

The concentration of copper (*Cu*) in fresh onion products was 1.20 mg/kg in the control variant "Without fertilizers", while in the studied doses of mineral fertilizers it was relatively low - 0.86-1.0 mg/kg. After storage, compared with fresh products, only variants N130P130K150 and N190P210K180 showed an increase in copper density by 10%, and in all other variants, on the contrary, a decrease in copper density was observed.

3. Conclusion

From our studies, we can conclude that the N130P180K150 variant is considered the most optimal dose of mineral fertilizers applied when cultivating onion varieties "Sabir" in the Lankaran economic region. In this variant, the yield is high - 223 centners per hectare, compared with the control variant, the yield increase is 37 centners per hectare, 19.8%, the yield of marketable products is 91.1%, the highest among all the

studied options. At the same time, the smallest losses during storage of onion products were noted in the N130P180K150 variant, in which the total losses were two times less than the control variant, only 6.8%.

As a result of the use of mineral fertilizers, there were certain changes in the concentration of toxic metals in fresh onion products and after storage. With an increase in the doses of NPK introduced in all the studied variants, compared with the control variant, i.e. “without fertilizers”, in fresh onion production, a sharp increase in the concentration of toxic metals zinc, cadmium and lead was observed, while a decrease in the concentration of copper was observed. The concentration of toxic metals (Zn, Cd, Pb, Cu) in onion products in all studied options with increasing doses of mineral fertilizers complies with the sanitary and epidemiological standards and rules of the Ministry of Health of the Republic of Azerbaijan (Hygienic requirements for the safety and nutritional value of food products) and MPCs adopted by WHO (maximum permissible concentration), the concentration of cadmium in the N190P210K180 variant was slightly higher than the permissible limit (0.03 mg/kg) by 0.033 mg/kg.

Novelty and practical significance of the study. The influence of dosages of mineral fertilizers applied during the cultivation of onion products grown in the Lankaran-Astara economic region on the quality of products and changes in the concentration of toxic metals in products during storage has been studied, and the optimal dosages of fertilizers have been determined, which will make it possible to obtain high-quality and environmentally friendly products.

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