The effect of freezing currant berries on their chemical composition and the content of heavy metals

O A Novikova, O V Smolenkova and M G Asadova
Kursk State Agricultural Academy named after I. I. Ivanov, Kursk, Russia
E-mail: oksana.no2011@yandex.ru

Abstract. Black currant is the most attractive source of ascorbic acid compared to other berries and fruits. The seasonality of berry production makes think about ways to preserve them. One of the most environmentally friendly ways is to freeze berries. However, in terms of biochemical value, frozen berries differ from fresh ones. After defrosting, a decrease in the content of ascorbic acid, soluble solids and titratable acids is observed in the berries. Analysis of currant berries during the harvest period for the content of heavy metals makes it possible to evaluate the quality of the finished product, used fresh and as raw material for further processing. Preservation of currant berries by freezing led to a change in the content of heavy metals: an increase in manganese, copper, iron and a decrease in nickel, zinc, cadmium, cobalt.

1. Introduction
According to the concept of state policy in the field of healthy nutrition of the population of the Russian Federation, it is necessary to pay special attention to food products with high nutritional and biological value. At the same time, an important task for agricultural and food industry specialists is not only to produce the required amount of high-quality food products, but also to preserve them using various techniques and methods, without deteriorating the initial quality indicators.

Black currant is one of the most promising berry crops, which contains in its berries a large amount of biologically active substances and vitamins, primarily ascorbic acid, thiamine, citrine, folic acid, essential oils, macro and microelements [1, 2].

Along with the useful components of berries, they can accumulate substances toxic to human health during the growing season. Heavy metals are one of the most significant groups of food contaminants.

In accordance with international requirements developed by the joint FAO / WHO commission, it is necessary to control the content of heavy metals in food. In Russia, the MPCs of the most toxic heavy metals in different groups of agricultural raw materials and processed products are indicated [3, 4].

However, many heavy metals (zinc, copper, cobalt, manganese and others) in small concentrations are vital for humans, because they are part of the molecules of enzymes, vitamins, hormones and are essential trace metals [1, 5, 6].

Certain heavy metals perform important functions in plant metabolism - they are part of enzymes, DNA, ribosomes, and increase crop yields [7].

Doses of microelements, harmless and even necessary for the functioning of the human body, animal and plant, accumulate, poison the body and can lead to serious disturbances in the digestive, excretory, and reproductive systems of humans [5, 8, 9, 10].
Heavy metals enter the human body mainly with food, partly with water and, to a lesser extent, through the respiratory system [11].

The intensive growth of industry, a significant increase in all types of transport, the intensification and chemicalization of agricultural production leads to the pollution of the biosphere (soil, air, water). The migration of heavy metals leads to environmental pollution and the production of food of low quality, and sometimes toxic [1, 11].

The industrial cities of Russia are characterized by pollution not by individual heavy metals, but by their group, which can have a stronger effect on the human body. It has been proven that most of the heavy metals come from food, both plant and animal origin. Migration of heavy metals goes along the biological chain: soil (water) - plant - animal - product - man [11, 12].

The presence of heavy metals in berries, as in other products of plant origin, is influenced not only by the concentration of heavy metals in soil, air, water, but also by their mobility (shape). It is known that only mobile forms of heavy metals are absorbed by plants and are able to migrate along trophic chains, entering the human body [5].

The migration of heavy metals from the soil into the root system of the plant, then into the vegetative mass and, ultimately, getting into the fruits and seeds, in most cases decreases during the process [5, 11].

Scientists have revealed the selective ability of the species composition to accumulate heavy metals [7, 11].

In their works of A.N. Sennovskaya (2003), Klimova E.V. (2007) note the varietal characteristics of plants for the accumulation of copper, zinc, lead and cadmium [13, 14].

It was found that such a technological operation as washing fruits and vegetables helps to reduce the content of heavy metals [15, 16].

The dynamics of heavy metals in plant raw materials during storage and processing has not been sufficiently studied. The extension of the terms of sale of products, undoubtedly, affects their chemical composition and the final quality of the product.

The available literature data on the accumulation of heavy metals in black currant berries show that the intensity of the intake of toxic substances depends not only on the conditions of pollution with heavy metals of the environment, but also on the variety, weather conditions during the growing season, soil characteristics and agricultural practices [14, 17].

There is information that heavy metals accumulate in black currant berries under the same growing conditions more than in other berries [1, 7].

At present, freezing is widely used to extend the implementation period and preserve berries, both in industrial conditions and in domestic conditions for personal use. For consumers, freezing berries at home has recently become dominant over other methods of preserving products.

According to the literature data, the chemical composition of berries changes during freezing [18]. Despite the fact that these changes are much smaller than with other types of processing and fresh storage, they also affect the final quality of the product.

The purpose of the study was to study the chemical composition and dynamics of the content of heavy metals in black currant berries grown within the boundaries of an industrial city and subjected to further freezing and storage in frozen form.

2. Materials and methods
The research was carried out in the laboratory of the Kursk State Agricultural Academy named after I.I. Ivanov and the laboratories of FSBI GSAS "Kurskaya". The object of research was black currant berries grown within the city of Kursk in 2019.

During harvesting and at the end of the research, the content of soluble dry substances in the berries (using a refractometer), their acidity (by titration with alkali) and the content of ascorbic acid (using the iodometric method) were determined.

After harvesting, the berries were analyzed for the content of copper, lead, zinc, cadmium, manganese, nickel, cobalt and iron.
The berries were frozen at a temperature of minus 23° C, and then stored at a temperature in a chamber of minus 16° C (an ordinary household refrigerator chamber). After nine months of storage, the heavy metal content was re-analyzed.

The determination of heavy metals was carried out by the atomic absorption method, in accordance with GOST 30692 and guidelines for the determination of heavy metals in agricultural soils and crop production.

3. Results and discussion

Studies on black currant berries grown within the city of Kursk showed that the content of ascorbic acid during the harvesting period was quite high. It reached 237.4 mg per 100 grams (table 1), which is very important for the consumer.

Table 1. Chemical composition of black currant berries in the process of research.

| Indicator name, unit of measurement | Test results during harvest | after defrosting |
|------------------------------------|----------------------------|-----------------|
| Soluble solids, %                  | 11.13                      | 9.5             |
| Titratable acidity, %              | 2.47                       | 1.48            |
| Ascorbic acid content, mg/100g     | 237.4                      | 103.7           |

During freezing and during further storage of berries, changes in their chemical composition were observed. There was a 56.3% decrease in ascorbic acid in berries after nine months of frozen storage, but the level was quite high and 100 grams of berries provided the daily intake of vitamin C for any category of citizens.

During storage of frozen products, there was a decrease in titratable acids by 40.1% compared to the initial value.

The smallest decrease was noted in the content of soluble solids - only 14.7% from the initial value.

The increased anthropogenic load on the environment influenced the accumulation of heavy metals in berries (Table 2).

During the research, the excess of the maximum permissible concentration (MPC) of heavy metals (HM) in berry products was recorded. During the harvesting period, the content of copper was 38% higher than the MPC, zinc by 8%. The highest indices of the HM content in black currant berries, in comparison with the MPC, were noted for lead, cadmium and nickel. Their indicators exceeded the MPC standards by more than two times, and nickel by more than three times.

Table 2. Content of heavy metals in fresh black currant berries and after defrosting.

| Indicator name, unit of measurement | Test results during harvest | after defrosting | LSD₀.₀₅ MAC₀.₀₅ |
|------------------------------------|----------------------------|-----------------|-----------------|
| Cu (copper), mg/kg                 | 6.90                       | 11.09           | 2.1 5.0         |
| Pb (lead), mg/kg                   | 1.02                       | 0.87            | 0.3 0.5         |
| Zn (zinc), mg/kg                  | 10.8                       | 7.49            | 1.81 10.0       |
| Cd (cadmium), mg/kg               | 0.07                       | 0.045           | 0.017 0.03      |
| Mn (manganese), mg/kg             | 5.97                       | 7.45            | 0.57 -          |
| Ni (nickel), mg/kg                | 1.71                       | 1.35            | 0.16 0.5        |
| Co (cobalt), mg/kg                | 0.45                       | 0.07            | 0.02 -          |
| Fe (iron), mg/kg                  | 26.94                      | 50.84           | 4.19 -          |

According to [5] the release of lead into the atmosphere and soil is closely related to the exhaust gases of internal combustion engines. Lead and zinc come from the abrasion of car tires. At present, the car park has more than doubled, plus public transport and transport of industrial enterprises, and this cannot but affect the environment.
Zinc also enters the soil and atmosphere with precipitation, which sometimes carries industrial and transport emissions. The increased content of nickel and lead is associated with the application of fertilizers [7].

The high values of HM can be partially explained by dry June (precipitation was less than 70% of the norm), which could contribute to an increase in the intensity of transpiration during the ripening of berries, and as a consequence, an increase in the supply of HMs to plants, which is consistent with the data of T.A. Roevoy, S.M. Motyleva (2013). It should be noted that black currant demands much moisture because of the superficial location of its root system.

The iron content in the studied currant berries was the highest of all the determined heavy metals. This is probably due to its high content in soils. According to the literature data, even on soils poor in iron, there is no deficiency of its available forms for plants.

After freezing and further storage of berries in frozen form, there were changes in the content of heavy metals, these changes were significant, which was shown by analysis of variance (except for the content of lead).

By the end of storage, the dynamics of heavy metals in berries was different. The content of manganese, copper and iron increased by 24.8; 60.7 and 88.7%, respectively, compared with the initial value, which aggravated the situation in the presence of toxic substances. During storage, the content of such heavy metals as nickel, zinc and cadmium in berries decreased by 21.1; 30.7 and 35.7%, respectively. The largest decrease (6.4 times) was noted for cobalt.

4. Conclusion
The main advantage of fresh and frozen black currant berries is the high content of the main antioxidant - ascorbic acid at all stages of the study.

Long-term storage (nine months) in the frozen state led to an increase in heavy metals such as manganese, copper, iron and a decrease in nickel, zinc, cadmium, cobalt.

The results obtained indicate the need to monitor the content of heavy metals not only in the berries during the harvesting period, but also during their freezing, which will provide the population with food that is harmless to health.

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