Study of the content of heavy metals in the berries of the Vaccinium genus in the background areas of the North-West of Russia

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Abstract. The study of heavy metal contamination of products of wild berries of the genus Vaccinium (blueberry, cowberry, cranberry), growing in intact forests in four regions of North-West Russia—Leningrad, Pskov, Novgorod and Vologda regions is carried out. It is established that the greatest accumulation in berries of all studied species is observed for zinc, chromium and manganese. At the same time, the excess of the maximum permissible concentrations was noted for other metals - lead and arsenic, the level of pollution was moderate. In relation to these pollutants, the most sensitive genus is cranberry. The most likely source is roads and logging activities. The obtained results indicate the need to control chemical contamination of food products of wild berries and to expand the range of controlled parameters, in particular, the establishment of maximum permissible concentrations for chromium and nickel due to their significant bioaccumulation in berries.

1. Introduction

The development of the consumer market of wild forest food products is one of the key opportunities to improve the efficiency of the use of forest resources of the boreal zone of Russia, which is currently not fully implemented. On the one hand, artificial cultivation of wild berry crops in Russia is poorly developed in comparison with foreign countries to lower nutritional qualities and contamination of products from plantations because of the inevitable use of pesticides and herbicides in compacted industrial plantings [1]. On the other hand, it is related to the abundance of wild berries in the North-West of Russia. The greatest industrial value is represented by berries of the genus Vaccinium – blueberries, cranberries, cranberries [2]. Wild berries are widely distributed in the boreal forests of Russia, have stable yields and are practically not susceptible to diseases, unlike those grown on plantations. Their products are superior to industrial ones in terms of accumulation of biologically active substances, in food and pharmacological value [3]. In addition to the use of berries in the food industry, the procurement of medicinal raw materials from various parts of
these plants is of great importance. Like all plants, Vaccinium species can also receive pollutants from the soil along with nutrients [4]. The usual soil pollutants in forests are heavy metals, which creates a risk of penetration into the production of berries and pharmacological raw materials. This type of pollution is widespread in forest areas due to the development of the road system and industrial enterprises. In the North-West of Russia, this problem is of great importance as in the course of economic development of territories, there is an increasing fragmentation of forests by linear objects. The increase in the area of contaminated forest land entails the need for environmental wild berry products control. Despite the urgency of the problem of contamination of forest food resources with heavy metals, the modern information about the contamination of berries and leaves of Vaccinium species is not sufficient for assessment of the forest berry products safety for the food and pharmaceutical use in the regions of the North-West of the Russian Federation

2. Methods and materials
The aim of this study was to assess the state of production of Vaccinium berries from different regions of the North-West of Russia, collected in the background areas – that is, in areas with minimal risk of contamination. For this purpose, intact forests located near specially protected natural areas (PNA) of the Leningrad, Novgorod, Pskov and Vologda regions were selected. The collection of material was carried out in 2017 – 2019 outside the protected areas, in places of traditional harvesting of forest berries.

The study of the content of heavy metals was performed using an X-ray fluorescence method [5] for the following heavy metals: strontium, lead, zinc, copper, vanadium, chromium, as well as iron, titanium and manganese oxides. Preparation of the material for the study involved the transportation of the material from the collection sites for 2 days, then - the selection of undiluted ripe berries without damage and drying them in a thermostat with strong ventilation at 20°C [6]. After no less than 40 hours of drying by weight control, the material was ready for further grinding using a disk eraser. The prepared samples were examined using X-ray fluorescence spectrometer «SPECTROSCAN-Max G».

As a result of the study it was established that the content of heavy metals in wild berries of shrubs of the genus Vaccinium (cranberries, blueberries and cranberries marsh) from the collection regions within the North-West of Russia had some differences, on average not more than 30-40% in different species (table 1).

There was a moderate excess of maximum permissible concentrations of heavy metals for arsenic and mercury. They are established by normative documents of the Russian Federation.

Such excesses are more common in the Leningrad region than in other regions studied. Contamination of berry products with lead and arsenic is more pronounced in cranberries. Cases of exceeding the content of heavy metals were observed in all studied species of shrubs, despite the difference in the areas of growth. The data obtained indicate the presence of local sources of pollution, given the absence of industrial enterprises near the studied forests, the most likely source of pollution can be considered roads and timber harvesting.

The greatest accumulation in the berries of the studied species have such metals as strontium, zinc and chromium (total) (Figure 1), while cobalt, vanadium and titanium oxide are virtually absent.

3. Results and discussion
High content compared to other metals is observed for manganese oxide (Figure 2), it is 10 – 100 times higher than strontium, lead, arsenic, zinc, nickel and chromium (table 1). Strontium, zinc and chromium have the highest accumulation in berries of all studied species in all regions (Figure 1).
Table 1. The content of TM in berries of the genus blueberries, cranberries and cranberries marsh different regions of the North-West of Russia (bold text indicates values that exceed the maximum permissible concentrations [7], [8]).

| Genus   | Gathering place   | Heavy metal content, mg / kg | Sr  | Pb  | As  | Zn  | Ni  | MnO | Cr  |
|---------|-------------------|-----------------------------|-----|-----|-----|-----|-----|-----|-----|
| Cowberry | Novgorod region   | 29±3                        | 7±2 | 5±1 | 2±0 | 46±2 | 2±0 | 554±36| 37±4|
|         | Vologda region    | 40±3                        | 4±1 | 6±1 | 2±0 | 35±1 | 2±0 | 577±210| 35±3|
|         | Pskov region      | 36±4                        | 2±0 | 5±1 | 1±0 | 38±2 | 1±0 | 657±40| 36±4|
|         | Leningrad region  | 25±5,3                      | 3±2 | 4±1 | 2±0 | 36±2 | 2±0 | 418±32| 36±4|
| Blueberry | Novgorod region   | 31±4,8                      | 3±1 | 3±1 | 2±0 | 53±6,8| 2±0 | 759±612| 40±2|
|         | Vologda region    | 43±2,2                      | 6±1 | 4±1 | 3±1 | 31±4,5| 3±1 | 699±23| 38±3|
|         | Pskov region      | 39±3                        | 5±1 | 4±1 | 1±0 | 39±4,2| 1±0 | 577±35| 36±5|
|         | Leningrad region  | 31±4,6                      | 8±2 | 3±1 | 1±0 | 34±1,5| 1±0 | 697±61| 35±4|
| Cranberry | Novgorod region   | 34±5,2                      | 3±1 | 3±1 | 1±0 | 39±5,4| 1±0 | 501±253| 30±5|
|         | Vologda region    | 20±2,4                      | 4±1 | 2±0 | 1±0 | 41±6 | 1±0 | 501±253| 30±5|
|         | Pskov region      | 31±6,1                      | 3±1 | 3±1 | 1±0 | 40±5,2| 1±0 | 612±544| 34±6|
|         | Leningrad region  | 27±8                        | 5±1 | 4±1 | 2±0 | 43±3,5| 2±0 | 605±27| 40±5|

Figure 1. Average accumulation of heavy metals in berries of wild shrubs of the genus Vaccinium
Figure 2. Average accumulation of manganese oxide in berries of wild shrubs of the genus Vaccinium

4. Conclusion
The studied species of wild berry bushes are confined to different forest biotopes; their habitats practically do not intersect. However, the accumulation of heavy metals in the studied species has a similar character: manganese oxide, strontium, zinc and chromium are preferably accumulated. High values of zinc content are typical for plant material in the norm, as it is required in large quantities for the biochemical processes of the plant. Strontium, zinc and chromium are present in low concentrations and reflect the geochemical characteristics of the soils of the collection sites of plant material. The accumulation of zinc is increased in comparison with other metals due to the high physiological need of plants for it. Moderate excess established in Russia maximum permissible concentrations was noted only for lead and arsenic However, other heavy metals can be considered as potentially dangerous for raw berries due to local contamination of biotopes and should be subject to control, for the effectiveness of which it is necessary to introduce standards of content, especially for nickel and chromium, intensively accumulating in berries.

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