Study of toxic elements in propolis

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Abstract. There is a threat of heavy metals and toxic elements entering the beekeeping products in relation to the deterioration of the ecological situation. In this regard, a study of one of the most popular beekeeping products, propolis, from the territory of two regions of Russia (Ryazan Oblast and Krasnodar Krai) for the level of Pb, Cd, Sr, and the toxic element As was undertaken. The studies were made from 2004 to 2019. The amount of elements was determined spectrophotometrically with an atomic absorption spectrophotometer Spectr AA 22OFS. Lead, cadmium, and strontium levels were determined using an air-acetylene flame on a gas atomizer. The level of arsenic was determined on a graphite oven of a spectrophotometer using a palladium modifier made by “Mersk”. The lead level in propolis was from 0 to 0.19 mg/kg that exceeds the threshold limit value by a factor of 1.2-12.3. The concentration of cadmium, strontium, arsenic in the studied propolis samples does not exceed the threshold limit value: 0-0.164 mg/kg, 2.1-21.01 mg/kg, 0-1.04 μg/kg, respectively. The accumulated experimental data indicate the need to adjust the threshold limit value (SanPiN 2.3.2. 1078-01) of lead level in propolis. The dynamics of propolis pollution with toxic elements was evaluated in the course of the research. The results of this evaluation confirmed the possibility of using propolis as a bioindicator of environmental pollution with heavy metals and toxic elements. It is necessary to monitor the propolis safety to determine its level of contamination with heavy metals and toxic elements, when using it as a source of biologically active compounds and as a raw material for Pharmacy (making extracts, tablets, ointments, syrups, suppositories, plasters).

1. Introduction

Humankind currently is faced with such dangerous phenomena as industrial pollution of the biosphere and the accumulation of xenobiotics and toxic substances (heavy metals, pesticides, radionuclides, etc.) in soil, atmosphere and hydrosphere.

Environmental pollution and active chemicalization of agriculture contribute to the ingress of foreign substances into beekeeping products that pose dangers to human health and life.

In recent years, work has been actively carried out to study the nature of the migration of toxic elements from soil and plants into beekeeping products. Fatkullin and co-authors did a study on the territory of the forest steppe zone of the Southern Urals to evaluate the contamination of the trophic chain “soil-plant-bee body-beekeeping products” [1]. The influence of contamination of the forage area with heavy metals on bees and beekeeping products is also presented in the studies of Eskov E.K. [2].

Pastukhova M. A. studied the features of the accumulation of heavy metals in beekeeping products in areas with different levels of pollution [3]. The content of heavy metals in propolis, pollen, honey, wax and bodies of bees was investigated. The most informative indicators of pollution, according to
the author, are propolis and pollen. We can talk about the possibility of using beekeeping products, and in particular propolis, in apimonitoring the ecological situation of the region. In the studies of Murashova E.A. it was also found that the most contaminated product of the bee family with heavy metals is propolis, pollen, bee bread, and the cleanest product is honey. The studies were carried out using the method of atomic absorption spectroscopy [4].

Foreign colleagues, researchers from Serbia, Brazil, Turkey, are actively involved in determining the concentration of toxic elements in propolis using the method of atomic emission spectroscopy with inductively coupled plasma (ICP-AES), and say that the determination of the amount of toxic elements in this particular beekeeping product is an effective method of environmental monitoring [5], [6].

Similar data were obtained at the Federal State Budgetary Scientific Institution "Federal Scientific Center of Beekeeping" that showed that environmental pollution with toxic elements leads to their increased concentration in all beekeeping products, but to a greater extent in propolis and pollen [7].

However, it should be noted that in addition to technogenic sources of propolis pollution, toxic elements can accumulate in it when using contaminated equipment and veterinary medicines [8].

Thus, propolis is one of the beekeeping products that contain the greatest amount of toxic elements [9], and some of propolis raw materials do not meet the safety requirements for the production of medicines and cosmetics [10].

A number of authors explain the increased content of heavy metals (Pb, Cd) in propolis by the high content of fat-like substances and waxes in it [11].

The work of R D O Orsi shows that a small amount of heavy metals passes into ethanol extract of propolis [12]. The authors investigated native propolis, the degree of its contamination with heavy metals, as well as the amount of metals that got into propolis extracts during the preparation of this dosage form.

Despite such optimistic conclusions, the active use of propolis as a raw material for the production of medicines, cosmetic preparations and dietary supplements for food leads to the need to evaluate the ecological purity and safety of this beekeeping product.

In addition, systematic monitoring of the level of toxic elements in propolis collected in the same territories can serve as a basis for an objective evaluation of the ecological situation in this region [13].

Thus, the work on studying the concentration of toxic elements in propolis and evaluating the dynamics of the level of its pollution is relevant.

2. Material and methods
The purpose is to evaluate the degree of contamination of propolis with toxic elements and the dynamics of the level of its contamination in Ryazan Oblast and Krasnodar Krai in the period of 2004-2019.

The material for the study was propolis samples taken in the regions of Ryazan Oblast and Krasnodar Krai.

The content of elements was determined at the Federal State Budgetary Scientific Institution "Federal Scientific Center of Beekeeping" by the spectroscopy method using a Spectr AA 220FS atomic absorption spectrophotometer made by the company "Varian".

Determination of the level of Pb, Cd and Sr was carried out on a gas atomizer of a spectrophotometer using an air-acetylene flame. The As level was determined using a graphite oven of a spectrophotometer; a palladium modifier made by the company "Mersk" was used.

The measurement was carried out in two repetitions; the arithmetic average of parallel measurements was taken as the final result. The resulting values are measured in mg/kg.

Statistical processing of the results was carried out in the programme Microsoft Excel 2010.

3. Results and discussion
Research of propolis in Ryazan Oblast.

Samples of propolis were collected in apiaries of Rybnovsky, Sasovsky, Ryazhsky, Kasimovsky, Kadomsky, Pronsky, Shatsky and Chuchkovsky districts of Ryazan Oblast.
As a result of the research, the following was revealed.

In propolis samples collected in apiaries of Ryazan Oblast, the lead content on average exceeds the threshold limit value (no more than 1.0 mg/kg [14], [15]) and averages (5.62 ± 0.69 mg/kg) (Fig. 1). Differences in lead concentration between propolis samples of different years of collection are from 1.2 to 7.14 times. The maximum amount of lead in propolis in Ryazan Oblast was determined in 2011 - 10.15 mg/kg; 2014 - 8.39 mg/kg; 2016 - 7.13 mg/kg and 2018 - 8.09 mg/kg.

![Figure 1. Lead content in propolis collected in Ryazan Oblast, 2006-2019](image)

The cadmium content varies from 0 to 0.19 mg/kg. The level of cadmium content in propolis for the entire observation period did not exceed the TLV - no more than 1.0 mg/kg [14], [15] (Fig. 2).

The maximum level of cadmium in propolis was determined in 2009, 2017. 0.19 mg/kg and 0.164 mg/kg, respectively. Cadmium was not detected in propolis samples collected in 2008, 2011, 2016, 2018, 2019.

![Figure 2. Content of cadmium in propolis in Ryazan Oblast, 2006-2019](image)
The content of arsenic in propolis collected in Ryazan Oblast varies from 0 to 1.04 mg/kg. (Fig. 3), at a rate of 1.5 mg/kg [14], [15]. The maximum content of arsenic in propolis was determined in 2009; it was 1.04 mg/kg.

![Figure 3. Arsenic content in propolis in Ryazan Oblast, 2006-2013](image)

The strontium content in propolis collected in Ryazan Oblast varies from 2.1 to 21.01 mg/kg (Fig. 4). The strontium content is not regulated [14], [15].

The maximum strontium content in propolis was determined in 2016 and 2013, 21.01 mg/kg and 12.78 mg/kg, respectively.

![Figure 4. Strontium content in propolis in Ryazan Oblast](image)

Research of propolis of Krasnodar Krai.

Propolis samples collected in apiaries of Krasnodar Krai were analyzed for Pb and Cd content. The content of lead in propolis, collected in 2004-2011, exceeds the threshold limit value (no more than 1.0 mg/kg) [14], [15] (Fig. 5).

Differences in lead concentration between propolis samples of different collection periods range from 0.69 to 12.33 mg/kg. The maximum amount of lead in propolis in Krasnodar Krai was determined in 2008 - 5.2 mg/kg, 2010 - 12.33 mg/kg, 2011 - 6.43 mg/kg.
Figure 5. Lead content in propolis in Krasnodar Krai

The cadmium content varies from 0 to 0.063 mg/kg (Fig. 6). The normative cadmium content in propolis is no more than 1.0 mg/kg [14], [15].

The maximum cadmium content in propolis was determined in 2005 and 2010, 0.063 mg/kg and 0.046 mg/kg, respectively. The level of cadmium content in propolis on the territory of Krasnodar Krai, during the observation period, did not exceed the TLV.

Figure 6. Content of cadmium in propolis in Krasnodar Krai

4. Conclusions

The evaluation of propolis toxicity using an atomic adsorption spectrophotometer showed the level of toxic elements in propolis samples from Ryazan Oblast and Krasnodar Krai.

The content of arsenic in propolis of Ryazan Oblast for the entire period of the study did not exceed the TLV (no more than 1.5 mg/kg); in fact it was in the range of 0-1.04 mg/kg.

The strontium content in propolis of Ryazan Oblast ranged from 2.1 to 21.01 mg/kg.

The content of cadmium in propolis of Ryazan Oblast varies from 0 to 0.19 mg/kg; in propolis of Krasnodar Krai - from 0 to 0.063 mg/kg. The threshold limit value of cadmium is not more than 1.0 mg/kg [14], [15].
The average lead content in propolis in Ryazan Oblast was 5.62 ± 0.69 mg/kg. The content of lead in propolis in different years of collection exceeds the threshold limit value of lead by a factor of 1.2 to 7.14.

The amount of lead in propolis of Krasnodar Krai exceeded the regulatory requirements by a factor of 3.8-12.33.

The increased content of lead in propolis found in the study of propolis is consistent with the data of M.N. Kharitonova [16], Eskov E.K. [2], Kodes L.G. and Bychkova N.V. [17]. There is a need to revise the lead amount in propolis, which is 1.0 mg/kg, and in bee pollen and bee bread - not more than 6.0 mg/kg.

The results of the studies that were carried out suggest that samples of native propolis can be used as bioindicators of environmental pollution with heavy metals and toxic elements.

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