Environmental safety of wild plants in the republic of Tatarstan by heavy metals content

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Abstract. Based on the results of biogeochemical studies in the territory of Western Predkamye (Pestrechinsky, Mamadyshsky, Zelenodolsky districts), Eastern Zakamye (Almetyevsky, Bugulminsky districts), Predvolzhye regions (Verkhneuslonsky district) of the Republic of Tatarstan and the Kazan city, the range of heavy metals natural concentrations in the herbaceous vegetation was determined. It has been established that the heavy metals content in herbaceous plants of the Republic of Tatarstan does not exceed the world average clarke. Separate local biogeochemical specializations of plants determined by the natural geochemical background of the region have been established. Wild plants species in the Zelenodolsky district were identified with Pb and Cd content exceeds the established standards.

1 Introduction

Increasing environmental pollution every year and the negative consequences caused by it put forward the need to study the processes of migration of chemical elements in natural ecosystems. Particularly dangerous are heavy metals, which, unlike a number of other man-made pollutants (surfactants, pesticides, petroleum products, etc.), are not subject to degradation processes, but only change their forms of presence in environmental components. As promising cumulative indicators of heavy metals pollution, we should note higher terrestrial plants that lead a lifestyle attached to a certain area of the terrain and, therefore, are not capable of purposefully avoiding geochemical stress. Thus, studying the content of heavy metals in the components of natural ecosystems, along with classical methods of bioindication, will make it possible to control the degree of transformation of biogeochemical cycles under the influence of intense technogenic impact on the biosphere.

Natural meadow and forest phytocenoses of the suburban area have recently been increasingly used by population for the procurement of medicinal plant raw materials. However, in the context of the increasing impact of technogenesis on the environment, it is possible that the permissible levels of toxic elements in wild vegetation may be exceeded. This may pose a threat to human health. It is known that in the process of preparing decoctions, in some cases, from 50 to 90% of the heavy metals present in the original plant material can pass into the aqueous solution [1]. In this regard the goal of the work was to

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assess the environmental safety of wild plants in the Republic of Tatarstan by heavy metals content.

2 Materials and methods

The Republic of Tatarstan is located in the centre of the Russian Federation on the East European Plain, at the confluence of two largest rivers – the Volga and the Kama. Tatarstan is part of Middle Volga region.

The material for the study was 90 species of wild herbaceous plants and soils of natural meadow and forest phytocenoses and urban phytocenoses of Kazan city, selected in 2006-2007. The research covered the areas of Western Predkamye (Pestrechinsky, Mamadyshsky, Zelenodolsky districts), Eastern Zakamye (Almetyevsky, Bugulminsky districts), Predvolzhye regions (Verkhneuslonsky district) of the Republic of Tatarstan and the Kazan city. A total of 160 plant samples were taken. Biological replication in one sample is 3-20 copies. The plants were dried to an air-dry state, crushed in a laboratory mill, and weighed portions of the dry material were ashed in a muffle furnace at a temperature of 500^0C by GOST 30692-2000. In soils we determined the pH of the water extract, the content of acid-soluble and mobile forms of heavy meetals extracted with 5 M nitric acid and an ammonium acetate buffer solution with pH 4.8, respectively by RD 52.18.191-89 and RD 52.18.289- 90. The concentrations of Fe, Zn, Cu, Cd, Pb were determined by the atomic absorption method on an AAS-30 spectrophotometer. Statistical data processing was carried out using the Statistica 8.0 package. As criteria for comparing means between two groups of compared indicators, the Mann-Whitney test was used, and between three or more groups, the Kruskal-Wallis test was used. To describe the distribution of variables, the median and interquartile range were used in the work. The nomenclature of Latin plant species is given according to S.K. Cherepanov [2].

3 Results and analysis

The choice of sites for research is determined by the presence in the Republic of Tatarstan the districts and cities with different levels of technogenic load, in the suburban areas of which studies to assess the condition of wild plants would be of interest. According to the map of the ecological situation of the Republic of Tatarstan, the soils of Kazan city and the Almetyevsky district are characterized by «medium» pollution by heavy metals, the Bugulminsky district – «high», Zelenodolsky, Verkhneuslonsky, Pestrechinsky and Mamadyshsky – «low». The ecological situation in the Zelenodolsk, Almetyevsky, Bugulminsky districts is characterized as «severe», in Kazan – «alarming», in the Pestrechinsky district – «tense», in Mamadyshsky and Verkhneuslonsky – as «moderately tense». According to the Map of the Predisposition of the Territory of the Republic of Tajikistan to the manifestation of unfavorable situations, the Zelenodolsk and Bugulminsky districts belong to the territories «predisposed to a significant extent» to the manifestation of adverse environmental situations, the Almetyevsky district – to the «predisposed», Pestrechinsky district – to the «relating to the «norm»», Kazan city, Mamadyshsky and Verkhneuslonsky districts – to «sustainable».

According to the results of the study, it was established that the Cu content in plants of various studied districts varies from 2.0 mg/kg in the Pestrechinsky district in the forest to 6.7 mg/kg in the Bugulminsky district, the Fe content – from 46.1 in the Zelenodolsky district in the meadow phytocenosis to 202.9 mg/kg in Bugulminsky district. The minimum content of Zn (6.4 mg/kg) was found in the plants of the Pestrechinsky district in the meadow, the maximum (45.3 mg/kg) was found in the plants of the coniferous forest edge

in the Zelenodolsky district. The Pb content in plants varies from 0.1 mg/kg in the Pestrechinsky district in the meadow phytocenosis to 8.3 mg/kg in meadow plants in the Zelenodolsky district, the Cd content ranges from 0 to 1.5 mg/kg dry weight in meadow plants in the Zelenodolsky district.

Thus, plants in the Bugulminsky district have the highest content of Cu and Fe, plants in the Zelenodolsky district have the highest content of Zn, Pb and Cd. Calculation of the Kruskal-Wallis test indicates the significance of differences in the heavy metals content between plants in different districts ($p<0.05$).

The average heavy metals content in plants was as follows (mg/kg dry weight): Fe (63.5) > Zn (10.8) > Cu (3.0) > Pb (0.7) > Cd (0.1).

The heavy metals content in wild plants, as a source of medicinal plant raw materials, is the most important indicator of the biological and hygienic quality of plants. To assess the safety of medicinal plants based on their Pb and Cd content for human health, the obtained values of metal concentrations in plants were compared with the values of the maximum permissible concentrations of Pb (6 mg/kg) and Cd (1 mg/kg) in plant-based dietary supplements (dry teas) by SanPin 2.3.2.1078-01. At the same time, an excess of the maximum permissible concentrations of Pb and Cd was found in some plants of the Zelenodolsky district.

A significant excess of the maximum permissible concentration (MPC) of Pb was detected in plants of *Convolvulvus arvensis* L. – in 5.5 times. In plants of *Leucanthemum ircutianum* Turcz. ex DC. Tzvelev, *Hypericum perforatum* L. and *Potentilla argentea* L., the maximum permissible concentration of Pb was exceeded by 2 times, in plants of *Calamagrostis epigeios* (L.) Roth – in 3.1 times, in *Fragaria vesca* L. in 1.9 times. In forest plants of the Zelenodolsky district, no significant excess of MPC was detected. An excess of Pb in 1.2 times was found in *Linnaea borealis* L. Plant samples whose Pb concentration exceeds the MPC account for 8.8% of those studied.

The Cd content in some plants in the Zelenodolsky district also exceeds the MPC. In plants of *Tussilago farfara* L. and *Senecio jacobaea* L. the excess is 1.3 times, in plants of *Pimpinella saxifraga* L., *Linaria vulgaris* Mill., *Galium mollugo* L. in 1.2, 1.5 and 1.6 times, respectively. In *Agrostis tenuis* Sibth. the Cd concentration exceeds the MPC in 2.3 times, in *Fragaria vesca* L. and *Convolvulvus arvensis* L. in 4.1 and 4.4 times, respectively. In the plants of the coniferous forest edge, an excess of Cd concentration was detected in the plants of *Achillea millefolium* L. and *Convallaria majalis* L. in 1.3 and 2.0 times. Exceeding the MPC of Cd was observed in 8.1% of the studied plant samples.

The Pb and Cd concentration in the plants of the remaining studied areas, including of urban phytocenoses plants, turned out to be significantly lower than the maximum permissible concentration in food products. High levels of Pb and Cd content in plants of the Zelenodolsky district may be due to both an increased regional background of Pb and Cd in the soils of Predkamye [3,4], and aerotechnogenic input of these metals.

The share of metals in emissions from industrial enterprises reaches 80-90% of the total mass [5]. Pb particles from the air settle on plant leaves. Lead dust is almost not washed off by rainwater. According to observations, under conditions of severe pollution, up to half of the lead contained in them can enter plants in this way. As a result of experiments with plants growing in containers under the open sky in an area where Pb fell to the surface from 74 to 127 g/ha/year, it was found that about 90% of the Pb contained in ryegrass and wheat was of aerogenic origin. In spinach, this Pb accounted for 73% [6]. It is also known that Cd is rapidly absorbed by plants from contaminated soils, but aerial absorption is also possible [7].

Metals such as Pb, Cr, Ni, Cd, Fe, mainly in the form of inorganic compounds, are the largest by mass of emissions and by the degree of prevalence in the emissions of industrial enterprises of the Kazan city [8]. The dominant wind directions in the republic are southern

and southwestern; in the summer, the frequency of western and northwestern winds increases [9]. The location of the test sites in the Zelenodolsky district is influenced by emissions from large enterprises of the Zelenodolsk city (JSC POZiS, JSC Zelenodolsk Plant named after A.M. Gorky, etc.), but may be influenced by emissions from large enterprises of the Kazan city when the wind direction changes. The main sources of air and soil pollution in the Kazan city are enterprises of the chemical and petrochemical industries, aircraft and instrument-making enterprises, enterprises of the fuel and energy complex (Kazan CHP-1, CHP-2, CHP-3 plants), motor vehicles [9, 10]. It is known that with the emissions of PJSC Kazanorgsintez 0.14 t/year of Pb, 0.04 t/year of Fe and 0.04 t/year of Cd are released into the atmosphere in terms of metal [8]. The A.R. Valetdinov and co-authors works [11, 12] showed increased contamination of snow cover with heavy metals in the territories of Kazan city and the Zelenodolsky district compared to other areas studied in this work. This can also explain the increased Pb content in plants of forest biotopes in the Zelenodolsky district compared to plants of forest phytocenoses in other areas (Pestrechinsky and Mamadyshsky districts). At the same time, soil contamination with heavy metals on average in the Kazan city is assessed as «acceptable» (Z_f less than 16) [10].

The absence of Cd in plants of forest biotopes in the Zelenodolsky district and the low content of Pb compared to meadow plants indicates the external barrier function of the tree layer. It should also be noted that the rhizosphere of woody plants plays a key role in controlling the pollution of ecosystems with heavy metals. The rhizosphere is characterized by higher actual, hydrolytic and metabolic acidity when compared with the zone outside the rhizosphere [13]. It effectively detoxifies free metal ions through their complexation with organic matter [14]. Organic acids synthesized and sold into the rhizosphere, such as low molecular weight (oxalic, citric, tartaric, lactic, malic) and high molecular weight (fulvic acids, etc.) can act as chelating agents, thereby reducing the activity and toxicity of such ions like Pb, Cd, Cu, Fe, Al [14].

Despite the increased content of both acid-soluble and mobile forms of Cu, Zn and Pb in the soil of urban phytocenoses, the heavy metals content in plants did not exceed both background and average planetary values. It is possible that plants growing in an urban environment in a ravine were protected from the effects of vehicle emissions by residential areas. In addition, a common effect of human activity on urban soil is an increase in soil pH due to construction debris, which may include cement, concrete, brick, and other construction waste [15, 16]. Under conditions of neutral pH soil solution, the solubility of most metal ions is limited due to their sedimentation or as a result of binding to oxides, hydroxides, carbonates or phosphates, clay minerals or organic matter [17]. Thus, the absence of exceeding the MPC of metals in plants of urbophytocenoses may be due to the slightly alkaline reaction of their soils (soil pH are 7.15 and 7.83), the presence of carbonates, and, consequently, the low mobility of heavy metals. Increased values of Cu, Pb and Zn mobile forms in the soil of urban phytocenoses may be due to the ingress of construction waste particles into the soil sample.

Taking into account also the fact that wild plants are an important feed resource, the obtained concentrations of standardized elements were compared with the values of the maximum permissible levels (Temporary maximum permissible level (TMPL) of chemical elements in the feed of farm animals No. 123-41281-87 dated July 15, 1987) in feed (SanPin 2.1.7.573-96). At the same time, it was found that the average species Cu and Zn content in plants is significantly lower than the MPL (MPL for Cu and Zn – 30 and 50 mg/kg, respectively). The average Fe content in plants in the Zelenodolsky district, in Kazan city, in the Almetyevsky district corresponds to the MPL (100 mg/kg). In plants of the Bugulminsky district the average species Fe content corresponds to 2 MPL. For example, in *Vicia cracca* L. the Fe concentration is 1.8 MPL, in *Fragaria viridis* L. – 2.9

MPL. The MPL for Pb in green feed is 5 mg/kg, and for Cd is 0.3 mg/kg. Thus, in the same plants in which an excess of the MPC of Pb in food products is observed, its MPL in feed is also exceeded. Since the MPL of Cd, intended for assessing the safety of feed, in plants is significantly lower than the values of the MPC of Cd, intended for assessing the safety of food products, namely plant-based dietary supplements (dry teas), then in the same species where excesses of the MPC Cd are observed, also observed significant excesses of the MPL of Cd in feed. In plants of *Tussilago farfara* L. and *Senecio jacobaea* L. the excess of MPL Cd is 4.3 times, in plants of *Pimpinella saxifraga* L., *Linaria vulgaris* Mill., *Galium mollugo* L. in 4, 4.9 and 5.5 times, respectively. In *Agrostis tenuis* Cd concentration exceeds the MPC in 7.6 times, in *Fragaria vesca* and *Convolvulus arvensis* in 13.6 and 14.7 times, respectively. It should be noted that the average sample value of Cd content in plants in the Zelenodolsky district exceeds the MPL from 1.7 to 5 times.

4 Conclusion

In general, the regional background content of standardized elements in wild plants does not exceed the MPC in food products and MPL in feed. According to the results of our research, the studied wild plants in the Verkhneuslonsky, Pestrechinsky, Mamadyshsky, Bugulminsky and Almetyevsky districts are environmentally safe in terms of the Pb and Cd content.

Thus, in large cities and beyond, not only the distance of pollution sources from potential places of collection of medicinal plant materials, but also the wind rose, as well as the presence of a «barrier» to the movement of anthropogenic emissions is important. The absence of increased concentrations of metals in plants of urban phytocenoses does not allow us to recommend them for use as medicinal plant raw materials, since in addition to inorganic pollutants in large cities, plants are capable of accumulating organic pollutants – pesticides, petroleum products, dioxins, surfactants, etc. In wild medicinal plants of local area in the Zelenodolsky district of the Republic of Tatarstan increased the content of standardized elements. Intensively accumulating of Pb (2.0-5.5 MPC) species are *Leucanthemum ircutianum*, *Hypericum perforatum*, *Potentilla argentea*, *Calamagrostis epigeios*, *Convolvulvus arvensis*. Accumulators of Cd (1.3-4.4 MPC) are *Tussilago farfara*, *Linaria vulgaris*, *Galium mollugo*, *Agrostis tenuis*, *Fragaria vesca*, *Convolvulvus arvensis*.

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