Peculiarities of mercury content in the muscle tissue of fish of the Vologda Region

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Abstract. Mercury is one of the most dangerous toxicants for all living organisms, having a high degree of biomagnification. The determination of mercury concentration in different species of fish is important for evaluation of the state of aquatic ecosystems. The aim of research is study of peculiarities of mercury content in fish of the Sheksna Reservoir, the Sukhona River, Kubenskoye, Borovskoye and Svyatoye lakes. Mercury concentration in fish muscles of the Vologda Region varies from 0.0397 mg/kg to 1.167 mg/kg of wet mass. The highest average of mercury content is established in the muscle tissue of river bass (0.477±0.202), and the lowest average is in the muscle tissue of eastern bream (0.133±0.082). Mercury level does not exceed maximum permissible concentration of heavy metal and weekly norm, harmless for a person weighing 70 kg in most of examined specimens. Comparison of mercury content in muscles of fish from surveyed water bodies showed a significant difference between river bass and most non-piscivorous species, as well as between individuals of river bass from Svyatoye and Borovskoye lakes. We also revealed a reliable correlation dependence of mercury content in the muscle tissue on mass and length of body for samples of river bass, northern pike and silver bream. Values of mercury concentration in the muscle tissue of river bass from Lake Kubenskoye and the Sheksna Reservoir vary in process of time.

1 Introduction

The Vologda Region is rich in water resources and important for human commercial species of fish, such as eastern bream, European pikehead, northern pike, European smelt, sheefish, European whitefish, etc. Fish in this region is easily accessible thanks to developed system of watercourses (over 20000 objects) and large (more than 5000) number of lakes [1].

On the one hand, fish is valuable source of digestible proteins, fats, vitamins and other useful substances. But on the other hand, heavy metals and their compounds that are capable of injuring both fish and piscivorous animals including human accumulate in organs and tissues of fish [2].

Mercury is one of the most dangerous toxicants. When compound with this metal enters the aquatic ecosystem from sewage, air and soil, there is a decrease of oxidation state of

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substance, it transforms to elementary mercury and then enters the atmosphere in case of evaporation with temperature rise. Unevaporated metal with binding to bivalent sulphur forms salts settling at the water bottom, but with absorption by bacteria a toxic organic compound, methylmercury, is formed. Thus, mercury starts transference through the food chain from bacteria and accumulates in tissues and organs of hydrobionts (especially fish) frequently used as organisms for determination of mercury pollution level of reservoir [2].

Water objects (especially large reservoirs and watercourses, like the Sheksna Reservoir, the Sukhona River or Kubenskoye Lake) of the Vologda Region are subject to strong anthropogenic load. Main anthropogenic sources of pollution of research water objects are Public company «Sokol pulp and paper plant», Limited liability company «Sukhona cardboard and paper plant», Joint-stock company «Severstal». From 950 to 1300 tons of mercury was released into the atmosphere during the time of operation (from 1956 to 2006) of «Severstal». Other mentioned enterprises can be potential sources of local environmental release of mercury, but reliable quantitative data about mercury pollution from these plants are absent. Main paths of mercury pollution from these sources are high-temperature processes of metal working, combustion of coal, oil and natural gas for transportation and getting heat, electricity and steam, processes of woodworking. In the time of these processes mercury releases into the atmosphere and enters the water with the help of precipitation and wind [3].

At present time there is an active research and evaluation of the state of fishery water bodies of the Vologda Region (specialty water objects of the Chagodoshcha area (2018), the Ustyuzhna area (2018), etc.) and another studied region of Russia, such as the Tomsk Region (2018), the Republic of Karelia (2004), the Murmansk Region (2004, 2018), etc., with the use of identification of mercury concentration in different species of fish [4-10]. However, mercury level in piscifauna of some lakes and watercourses of the Vologda Region (for example, in fish of minor water objects of the Kirillov area, such as Svyatoye and Borovskoye lakes) is staying unknown.

The aim of research is study of peculiarities of mercury content in fish of the Sheksna Reservoir, the Sukhona River, Kubenskoye, Borovskoye and Svyatoye lakes.

2 Material and methods

The identification of mass concentration of mercury in the muscle tissue of fish collected from prime to fall 2022 in 5 water objects (Svyatoye, Borovskoye and Kubenskoye lakes, the Sukhona River and the Sheksna Reservoir (Fig. 1)) was realized in a Regional center of collective use ChSU (Cherepovets city) from November to December 2022 using a mercury analyzer PA-915+ with a PIRO attachment (Lumex). The checking accuracy of measurement methods was conducted with the use of certified biological material DORM-4 (the National Research Council of Canada). The nonparametric Kruskal-Wallis test and Spearman coefficient ($p < 0.05$) were used for statistical analysis of obtained data. 162 specimens of 10 species of fish were studied, such as river bass, northern pike, ide, eastern bream, ablet, European roach, European cisco, ruff, silver bream and European pikehead. Obtained results were compared with maximum permissible concentration of mercury for non-piscivorous (0.3 mg/kg of wet mass) and predatory fish (0,6 mg/kg of wet mass) accepted in Russia (according to literature source, «Sanitary Regulations and Standards. «Food raw materials and provision. Hygienic Requirements for quality and safety of food raw materials and provision». SanPiN 2.3.2. 560-96. M.: Russian Federation Oversight Committee for Sanitation and Epidemiology, 1997, 269 pp.») and with weekly norm of mercury consumption for a person weighing 70 kg (0.049 mg of metal; save for human daily dose of mercury per kilogram of a person weight is 0.0001 mg) accepted in USA (according to literature source, «U.S. EPA. 1997. Mercury study report to Congress. V. IV:

an assessment of exposure to mercury in the United States. U.S. EPA, Office of Air Quality Planning and Standards and Office of Research and Development. EPA/452/R-97-006»).

Fig. 1. Research reservoirs: 1 – Svyatoye Lake, 2 – Borovskoye Lake, 3 – Kubenskoye Lake, 4 – the Sukhona River, 5 – the Sheksna Reservoir

Total characteristic of large research water objects (Table 1) is presented according to literature data [11-13].

Table 1. Total characteristic of large research water objects

	Lake Kubenskoye	The Sukhona River	The Sheksna Reservoir
Water catchment area, km^2	14440	35600	19445
Length, km	54	558	262
Extreme width, km	10	0.29	33
Water surface area, km^2 (for reservoirs)	~400	-	1665
Water volume, km^3 (for reservoirs)	1.2	-	6.52
Sinuosity coefficient (for watercourses)	-	1.3	-

3 Results and discussion

Mercury is capable of atmospheric transport and is found even in water objects located at a great distance from industrial enterprises, especially in low-mineralized and acidified lakes. High degree of upsilting and bogginess of catchment basin, increased activity of microorganisms, low value of hydrogen ion exponent of aquatic environment and low growth rate of fish are main factors determining high level of mercury accumulation in muscles of fish from water objects that do not have local anthropogenic sources of mercury pollution [7].

The comparison of mercury concentration in muscles of different species of fish from all reservoirs under consideration showed reliable difference between river bass and all non-piscivorous species, with the exception of European cisco, and also between eastern bream and silver bream.

The comparison of mercury content in the muscle tissue of river bass from studied water objects (Svyatoye, Borovskoye and Kubenskoye lakes, the Sukhona River and the Sheksna Reservoir) is shown in the table 2.

Table 2. Mercury content in muscles of river bass

	Lake Svyatoye	Lake Borovskoye	Lake Kubenskoye	The Sukhona River	The Sheksna Reservoir
N, sp.	33	4	10	6	7
AM, mg/kg	0.542	0.278	0.499	0.321	0.388
Min, mg/kg	0.275	0.194	0.188	0.168	0.264
Max, mg/kg	1.167	0.335	1.109	0.497	0.470
Q25, mg/kg	0.420	0.228	0.278	0.171	0.357
Q75, mg/kg	0.616	0.328	0.571	0.493	0.429
SD, mg/kg	0.184	0.064	0.271	0.147	0.066
K-W	b	a	ab	ab	ab

Note: N – number (or quantity) of specimens, AM – average (or mean) value, Min – minimum value, Max – maximum value, Q25 – lower quartile, Q75 – upper quartile, SD – standard deviation, K-W – Kruskal-Wallis test with $p < 0.05$ (a, b – values with letter superscript reliably differential between reservoirs; values marked with two letters (ab) are insignificantly different both among themselves and with respect to one-letter values).

Maximum value of mercury concentration in the muscle tissue of river bass is 1.167 mg/kg of wet mass, minimum value is 0.168 mg/kg of wet mass. Statistically significant difference between specimens of river bass from Svyatoye and Borovskoye lakes was determined. It is indicative of different levels of mercury accumulation in studied water objects. Average of mercury concentration in studied specimens of this fish ranges from 0.278 mg/kg (Lake Borovskoye) to 0.542 mg/kg (Lake Svyatoye) of wet mass. It shows that Lake Svyatoye has the highest level of mercury accumulation. It may be due to upsilting and bogginess of reservoir, and, as a consequence, increased activity of microorganisms and high pH-value of water and benthal deposits.

In addition to environmental factors, mercury content in muscles of fish depends on the trophic level of the animal. The greater the value of mercury concentration, the higher the trophic level of species it corresponds to [14].

The comparison of mass concentration of mercury in muscles of different species of fish from Lake Svyatoye is shown in the table 3.

Table 3. Mercury in muscles of fish from Lake Svyatoye

	River bass	Ablet	European roach	Eastern bream	European cisco	Silver bream	Ruff
N, sp.	33	9	10	12	2	13	15
AM, mg/kg	0.542	0.175	0.224	0.152	0.364	0.230	0.242
Min, mg/kg	0.275	0.114	0.100	0.064	0.332	0.149	0.112
Max, mg/kg	1.167	0.239	0.358	0.330	0.396	0.326	0.440
Q25, mg/kg	0.420	0.151	0.178	0.075	0.332	0.201	0.173
Q75, mg/kg	0.616	0.189	0.274	0.221	0.396	0.233	0.298
SD, mg/kg	0.184	0.036	0.076	0.090	0.046	0.054	0.092
K-W	b	a	a	a	ab	a	a

Note: N – number (or quantity) of specimens, AM – average (or mean) value, Min – minimum value, Max – maximum value, Q25 – lower quartile, Q75 – upper quartile, SD – standard deviation, K-W – Kruskal-Wallis test with $p < 0.05$ (a, b – values with letter superscript reliably differential between species; values marked with two letters (ab) are insignificantly different both among themselves and with respect to one-letter values).

Statistically significant difference between river bass and most non-piscivorous species (ablet, European roach, eastern bream, ruff and silver bream) was determined. Obtained results reflect different trophic level of studied species. Average of mercury concentration in studied fish varies from 0.152 mg/kg (eastern bream) to 0.542 mg/kg (river bass) of wet mass. It shows that river bass occupies a high level of food chains in the ecosystem of Lake Svyatoye.

The comparison of mass concentration of mercury in muscles of different species of fish from the Sheksna Reservoir is shown in the table 4.

Table 4. Mercury in muscles of fish from the Sheksna Reservoir

	Eastern bream	Ide	Northern pike	River bass
N, sp.	7	6	9	7
AM, mg/kg	0.100	0.181	0.287	0.388
Min, mg/kg	0.040	0.080	0.144	0.264
Max, mg/kg	0.200	0.313	0.727	0.470
Q25, mg/kg	0.054	0.104	0.158	0.357
Q75, mg/kg	0.153	0.312	0.314	0.429
SD, mg/kg	0.058	0.106	0.181	0.066
K-W	a	a	ab	b

Note: N – number (or quantity) of specimens, AM – average (or mean) value, Min – minimum value, Max – maximum value, Q25 – lower quartile, Q75 – upper quartile, SD – standard deviation, K-W – Kruskal-Wallis test with $p < 0.05$ (a, b – values with letter superscript reliably differential between species; values marked with two letters (ab) are insignificantly different both among themselves and with respect to one-letter values).

Statistically significant difference between river bass and non-piscivorous species (eastern bream, ide) was determined. Obtained results reflect different trophic level of studied species. Average of mercury concentration in fish ranges from 0.100 mg/kg (eastern bream) to 0.388 mg/kg (river bass) of wet mass. Also realization of research revealed that average of mercury concentration in the muscle tissue of river bass (0.388 mg/kg of wet mass) is higher than in muscles of northern pike (0.287 mg/kg of wet mass). It shows that river bass occupies a high level of food chains in the ecosystem of the Sheksna Reservoir.

Correlation dependence of mercury concentration in the muscle tissue of fish from studied water objects (Svyatoye, Borovskoye and Kubenskoye lakes, the Sukhona River, the Sheksna Reservoir) on mass and length of body is shown in the table 5.

Table 5. Correlation dependence of mercury concentration in the muscle tissue of fish of the Vologda Region on mass and length of body

Species	N, sp.	r_s		p	
		Hg (mg\kg)/m (kg)	Hg (mg\kg)/l (cm)	Hg (mg\kg)/m (kg)	Hg (mg\kg)/l (cm)
River bass	60	**0.563**	**0.585**	**< 0.001**	**< 0.001**
Ablet	9	0.169	0.316	0.664	0.407

European roach	12	-0.175	-0.167	0.586	0.604
Silver bream	29	**0.703**	**0.754**	**< 0.001**	**< 0.001**
Ruff	15	-0.146	-0.116	0.604	0.681
Eastern bream	19	0.329	0.314	0.169	0.190
Northern pike	9	**0.850**	**0.812**	**0.004**	**0.008**

Note: N – number (or quantity) of specimens, r_s – Spearman coefficient, p – significance level, Hg/m – dependence of mercury concentration on mass of fish body, Hg/l – dependence of mercury concentration on length of fish body; correlation dependence is reliable with $p < 0.05$.

Reliable correlation dependence of mercury content in the muscle tissue on mass and length of body is revealed for samples of river bass ($rs = 0.563$, $p < 0.001$; $rs = 0.585$, $p < 0.001$), northern pike ($rs = 0.850$, $p = 0.004$; $rs = 0.812$, $p = 0.008$) and silver bream ($rs = 0.703$, $p < 0.001$; $rs = 0.754$, $p < 0.001$). Data obtained for these species of fish correspond to general pattern of mercury accumulation in organs and tissues of fish: the greater the age of the fish, the greater the mass and the length of fish body, and, as a consequence, the higher the level of mercury in tissues and organs of fish [15].

No reliable correlation dependence was found for the other species of fish.

Mercury accumulation occurs constantly in all species of both non-piscivorous and predatory fish. Mercury concentration in the same species from different water objects is different because of physico-chemical characteristic of reservoir or water course [15].

The comparison of obtained data with results of earlier research on the Sheksna Reservoir and Lake Kubenskoye [2] was conducted for evaluation of dynamics of mercury concentration in muscles of river bass and shown in the table 6.

Table 6. Dynamics of mercury concentration in muscles of river bass from Kubenskoye Lake and the Sheksna Reservoir

Reservoir	Year	Number of specimens	Hg, mg/kg (AM)	Reference
Lake Kubenskoye	2002	26	0.480	2
Lake Kubenskoye	2022	10	0.499	-
The Sheksna Reservoir	2002	21	0.230	2
The Sheksna Reservoir	2022	7	0.388	-

Note: AM – average (or mean) value.

It follows from the table that values of mercury concentration in the muscle tissue of river bass change in process of time. It is noted that mercury content in muscles of fish from Lake Kubenskoye increases insignificantly from 2002 (average of mercury concentration is 0,480 mg/kg of wet mass) to 2022 (average of mercury concentration is 0,499 mg/kg of wet mass), while mercury content in the muscle tissue of river bass from the Sheksna Reservoir for 2022 (0,388 mg/kg of wet mass) exceeds obtained result for 2002 (0,230 mg/kg of wet mass) more than 1,5 times. It is possible that it is due to an increase of degree of anthropogenic load.

The comparison of data obtained in the time of measurement of mercury content in muscles of fish from Lake Svyatoye and the Sheksna Reservoir with results of research of mercury concentration on the Mologa River, the Chagodoscha River, Lake Vanya (water objects of the Vologda Region) and the mouth of the Tom River (water object of the Tomsk Region) [6, 10] was conducted for evaluation of spatial variability of mercury content in

muscles of ruff, eastern bream, river bass, European roach, northern pike and European pikehead and shown in the table 7.

Results obtained in the time of research of mercury content in muscles of fish from studied water objects (Lake Svyatoye and the Sheksna Reservoir) are generally comparable with data of previous studies. It follows from the table that species living in different water objects occupy different trophic levels. So, the highest trophic level is typical for river bass from Lake Svyatoye (average of mercury concentration is 0,542 mg/kg of wet mass) and the Sheksna Reservoir (average of mercury concentration is 0,388 mg/kg of wet mass), for northern pike from the Mologa River (average of mercury concentration is 0,665 mg/kg of wet mass), the Chagodoscha River (average of mercury concentration is 0,601 mg/kg of wet mass) and Lake Vanya (average of mercury concentration is 0,709 mg/kg of wet mass), and for European pikehead from the Tom River (average of mercury concentration is 0,930 mg/kg of wet mass).

Table 7. Mercury content (mg/kg of wet mass) in muscles of fish from the Vologda Region and the Tomsk Region

Species	Lake Svyatoye	The Sheksna Reservoir	The Mologa river	The Chagodoscha River	Lake Vanya	The Tom River
Ruff	0.242 (0.112-0.440)	-	0.064 (0.011-0.133)	-	0.087 (0.076-0.099)	-
Eastern bream	0.152 (0.064-0.330)	0.100 (0.040-0.200)	0.358 (0.294-0.480)	0.163 (0.101-0.239)	0.365 (0.046-0.487)	0.580
River bass	0.542 (0.275-1.167)	0.388 (0.264-0.470)	0.226 (0.060-0.499)	0.372 (0.101-0.239)	0.399 (0.191-0.727)	-
European roach	0.224 (0.100-0.358)	-	0.115 (0.035-0.151)	0.121 (0.024-0.345)	-	-
Northern pike	-	0.287 (0.144-0.727)	0.665 (0.141-1.711)	0.601 (0.205-1.052)	0.709 (0.679-0.739)	0.380
European pikehead	0.174	-	-	-	-	0.930

Note: the average of mercury concentration in the muscle tissue of fish is shown before parentheses; the range of values from minimum to maximum is in parentheses.

Difference of mercury concentration in the muscle tissue of fish from different water objects is due to both the food supply of fish and the physico-chemical characteristics of reservoirs and water courses.

Fish is the main source of mercury for human because of mercury accumulation in food chains of aquatic ecosystems.

Data comparison with maximum permissible concentration of mercury for non-piscivorous and predatory fish showed that mercury does not exceed maximum permissible concentration of toxicant for European pikehead and ablet (Lake Svyatoye), for eastern bream (the Sheksna Reservoir) and river bass (the Sukhona River, the Sheksna Reservoir and Lake Borovskoye) in 100 percent of cases. Simultaneously, more than 70 percent of animals of the total number of specimens of both non-piscivorous and predatory species have a concentration of metal within the limits of maximum permissible concentration.

In the time of comparison of calculated mass of mercury in muscles of fish with weekly metal norm harmless for a person weighing 70 kg was noted that mercury mass exceeds norm in 40.12 percent of examined specimens.

The mercury content in muscles of fish from studied water objects varies widely. Minimum value (0.0397 mg/kg of wet mass) within the range is noted in eastern bream from the Sheksna Reservoir, and maximum value (1.167 mg/kg of wet mass) is noted in river bass from Lake Svyatoye.

Such range of mercury concentration in the muscle tissue of fish shows different levels of mercury accumulation in fish from each of considered water objects (Svyatoye, Borovskoye and Kubenskoye lakes, the Sukhona River and the Sheksna Reservoir).

Mercury accumulation by fish in concentrations exceeding content of this heavy metal in water can be used in the study of mercury contamination of reservoirs and water courses.

4 Conclusions

Mercury concentration in fish muscles of the Vologda Region varies from 0.0397 mg/kg to 1.167 mg/kg of wet mass. The highest average of mercury content is established in the muscle tissue of river bass (0.477±0.202), and the lowest average is in the muscle tissue of eastern bream (0.133±0.082).

Considerable difference between river bass and all non-piscivorous species, with the exception of European cisco, and also between eastern bream and silver bream is shown after comparison of mercury content in muscles of fish from all studied water objects.

Statistically significant difference between specimens of river bass from Svyatoye and Borovskoye lakes was determined. Statistically significant difference between river bass and all non-piscivorous species, with the exception of European cisco is shown in the time of comparison of mercury level in muscles of different species of fish from Lake Svyatoye. Statistically significant difference between river bass and non-piscivorous species from the Sheksna Reservoir was established after comparison of heavy metal content in fish from this water object.

Reliable correlation dependence of mercury content in the muscle tissue on mass and length of body is revealed for samples of river bass, northern pike and silver bream.

Values of mercury concentration in the muscle tissue of river bass from Lake Kubenskoye and the Sheksna Reservoir vary in process of time. It is shown that ruff, river bass and European roach from Lake Svyatoye, northern pike from Lake Vanya, eastern bream and European pikehead from the Tom River are leading in the level of mercury in muscles in the time of comparison of mercury content of these species of reservoirs and watercourses from different water objects of the Vologda Region and the Tomsk Region.

Mercury does not exceed maximum permissible concentration of toxicant for European pikehead and ablet (Lake Svyatoye), for eastern bream (the Sheksna Reservoir) and river bass (the Sukhona River, the Sheksna Reservoir and Lake Borovskoye) in 100 percent of cases. Mercury mass does not exceed weekly norm, harmless for a person weighing 70 kg, in 59,88 percent of examined specimens.

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