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SOMEREGULARITIESOFMERCURYACCUMULATIONINTHEMUSCLESOFFRESHWATERFISH

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Some Regularities of Mercury Accumulation in the Muscles of Freshwater Fish

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I. Introduction

The main anthropogenic sources of mercury are the chemical industry (production of chlorine, caustic, vinyl chloride, etc.), energy (the use of natural coal, oil, fuel oil), the electronics industry and metallurgy, the use of toxic chemicals and fungicides. One of the most significant sources of freshwater fish in the European part of Russia is the Volga River. It should be noted that for areas related to the entire flow of the river. The Volga is characterized by the presence of both natural and anthropogenic sources of mercury. The anthropogenic source of mercury can be considered the entire industrial agglomeration located on the banks of the Volga River. In these agglomerations, almost the entire line of industrial production is represented, including the sources of mercury listed above. Also, some mercury enters the natural environment when burning fossil fuels and its derivatives in boiler and heating systems.

The natural sources of mercury include the Astrakhan gas condensate field, located in the lower reaches of the. Volga river. It is confined to the intersections of the Karpinsky lineament and is characterized by deep, transverse faults. Here, the flow of mercury emanations is pulsating in nature and forms a similar character of atmochemical anomalies. A study of atmospheric air conducted in Astrakhan [1] revealed a fairly high concentration of mercury: 100–150ng/m^3 (MPL$_{avdaily}$ = 300 ng/m^3).

The concentration of total mercury in the water of the Volga reservoir chain varies from 0.02 to 0.42 μg/m3, the average concentration of mercury in surface water in the lower Volga reaches 0.05 μg/l (0.03–0.09 μg / l in depending on the time of year) [2,4]. In bottom sediments, which are the main storage of mercury in freshwater systems, the concentration of mercury ranges from 0.03 to 0.18 mg/kg (in the Rybinsk reservoir to 0.75 mg/kg) [3,4]. In the Astrakhan region, the mercury concentration in bottom sediments is 0.08-0.4 mg/kg. The above concentrations of mercury do not create a critical situation in the natural environment but can have a decisive influence on the accumulation of mercury in biota.

The accumulation of mercury in fish is directly dependent on its receipt in water. Mercury enters aquatic ecosystems, mainly with storm flows in the form of solutions and suspensions. After entering the reservoir, the conversion of mercury occurs in three main directions: it is restored to an elemental state and disappears into the atmosphere; forms strong, insoluble compounds (sulfides) and deposits in the bottom sediments; sorbed on the surface of bacterial membranes and goes into organic mercury compounds - methyl mercury and dimethyl mercury. Methyl mercury, methyl mercury hydroxide CH_3HgOH (MMHg), is the most stable form of methyl mercury in freshwater environments and is the most common organic compound of mercury in freshwater systems [5,6,7].

Methyl form of mercury is a potent neurotoxin, easily accumulated by aquatic biota, accumulates in plants, benthos, and animals, and ultimately concentrates in the upper links of the trophic food chain – fish. In the human body, methylmercury is well absorbed from the gastrointestinal tract, is spread by erythrocytes throughout the body.

The methylated form of mercury, due to its high solubility in fats, easily passes through biological membranes and penetrates the placenta as a result of which it can affect the developing embryo. The intake of mercury in the human body in the absence of intensive

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external sources is mainly determined by the level of fish consumption (up to 60% of the total intake) [8]. According to statistics [9, 10], in the Volga region regularly consume up to 32% of the respondents on average, and 58% consume fish at least 1–2 times a week. It should be noted that this is official data based on sales of fish and fish products through commercial networks.

Accounting for the volume of individual catch and fish consumption is completely absent. It should be noted that according to unofficial data, the consumption of fish obtained as a result of an individual catch in the Volga River accounts for between 18% and 80% of official statistics. In sum, this is a fairly large part of the fish and fish products consumed in the region. Therefore, it is very important to assess the level of accumulation of mercury in the tissues of fish that are most common in the Volga basin.

The purpose of the research was to determine the level of accumulation of mercury in the tissues of fish caught in the river Volga and the study of the features of this accumulation of certain species of fish.

II. Methods

The main commercial fish species in the Volga basin are roach, ruff, chub, crucian carp, rudd, bream, tench, roach, perch, sturgeon, carp, catfish, sturgeon, pike perch, pike and ide [11]. Fishing was carried out during the spring–summer–autumn seasons of 2016–2018. Basically, the capture was carried out directly by the participants of this project, partly the lack of fish was filled by buying from local fishermen. Fish catch areas are shown in Figure 1.

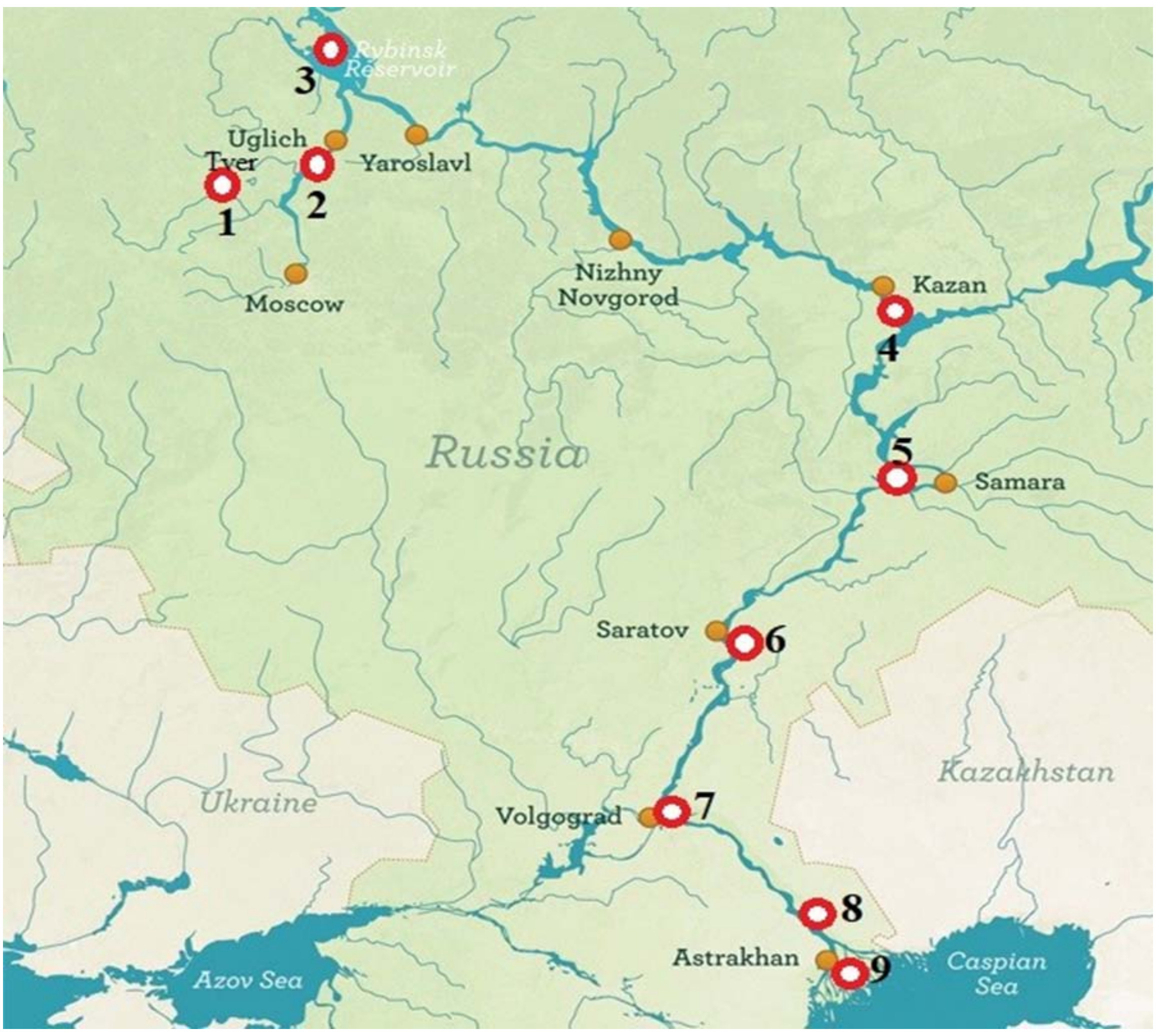

Figure 1: Sampling areas

1 –Upper Volga, the area of the city of Rzhev:Staritsa; 2 – Upper Volga, the region of the town of Kimry: the town of Bely Gorodok; 3 –Rybinsk Reservoir; 4 – District of Kazan; 5 –District of Samara; 6 – District of Saratov; 7 – District of Volgograd; 8 –Volga River delta, district of Tsagan:Aman; 9 –Volga River delta, district Ikryanoye:Beketovka

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A general list of selected samples with fish sizes is shown in Table 1. To assess the features of mercury accumulation by various species of fish, we experimented on catching fish in a semi-closed Bay of the Volga river in the area of point 2 (figure 1). The current In the Bay is only along the Central fairway, the water acidity was pH= 6.5-7.0. The most common types of fish were caught-perch, bream, and pike. In total, 42 samples of perch weighing from 12 to 589 grams, 27 samples of bream weighing from 21 to 560grams, 31 samples of pike weighing from 43 to 2700grams were selected.

Table 1: The general list of selected samples (n is the number of samples)

#	Objects, n is number of samples	Massag	
		Min-мax	**Mean**
1	Ruff. n = 9	15-35	25.4
2	Crucian carp (*Carassiuscarassius*), n = 19	100-220	171
3	Rutiluscaspicus, n = 21	82-141	100
4	Ballerusballerus, n = 5	105-540	215
5	Pelecuscultratus, n = 27	300-690	410
6	Bream, n = 30	100-560	340
7	Aspiusaspius, n = 16	520-3100	890
8	Goby, n = 15	155-420	215
9	Whitefish, n = 7	273-725	405
10	Roach, n = 28	49-96	75
11	Carp, n = 11	450-1100	743
12	Perch, n = 36	12-145	66.5
13	Common carp (*Cyprinuscarpio*) , n = 16	510-2320	1330
14	Zander, n = 25	156-533	331
15	Sturgeon, n = 4	5100-8300	6200
16	Pike, n = 21	90-2700	909
17	Silurusglanis, n = 5	1000-2600	1750

Samples were taken in zip-lock plastic bags, cleaned of external contaminants, and washed with distilled water. For long-term transportation, samples were frozen at -20 °C. In total, about 300 samples were taken. In preparation for the analysis, the fish were thawed and placed in enameled cuvettes, then cut from the left side, starting from the dorsal fin to the beginning of the ribs along the body, 2–4 g of skeletal muscles. The entire instrument and glassware were washed with 5–10 percent nitric acid and rinsed with distilled water. Samples were taken for analysis with natural moisture content.

III. Results

The main criterion for the quality of fish and fish products is the value of the maximum permissible concentration (MPC) of mercury in fish meat. The value of the maximum permissible concentrations (MPC) accepted in the Russian Federation of mercury for various types of fish and fish products are given in Table 2.

Table 2: MPL of mercury in fish and fish products [12]

Products		MPL, mg/kg
Live, chilled, frozen fish, minced meat, fillet	Freshwaternon-predatory	0.3
	Freshwaterpredatory	0.6
Caviar and milk of fish and products from them		0.2
Liver fish and products from it		0.5
Shell fish crustaceans		0.2

Table 2 provides general data on the concentration of mercury in the muscles of fish caught in the Volga River basin. These data are arranged as the average arithmetic concentration increases and shows that the maximum permissible concentration of mercury for all fish species is not exceeded.

The highest concentration of mercury is characteristic of carp, carp, pike, perch, sturgeon,and catfish; the lowest concentration of mercury is for ruff and crayfish. From literary sources, it is known that up to 80-90% of mercury accumulated in fish falls into methylated forms [7, 13,14]. As noted above, methylmercury is highly soluble in fats and easily penetrates cell barriers. Given the fact that each egg is a drop of fat, it was possible to assume that the concentration of mercury in the eggs and muscles of the fish will be the same or at least close in magnitude between these biomaterials.

However, the data presented in Table 3 show that in the eggs of the ruff, roach, pike, and perch, the concentration of mercury is minimal. This concentration averages 8.6 μg/kg, and the concentration of mercury in roach roe is eight times less than the concentration in the muscles, and the concentration of mercury in the eggs of pike, and perch is 20 times lower than the same concentration in the muscles of these fish.

These data show that with an increase in mercury concentration in the muscles of fish, no increase in the concentration in the eggs is observed, a correlation between the concentration of mercury in the eggs and muscles is not found.

Table 3: Hg content in the muscles of the fish Volga basin
(n is the number of samples)

#	Object	C Hg, mkg/kg (ppb)	
		Min-Max	C_{av}
1	Ruff, n = 9	6-16	11
2	Crucian carp (*Carassiuscarassius*), n = 19	18-42	31
3	Vobla*(Rutiluscaspicus)*, n = 21	16-46	31
4	Cyanets(*Ballerusballerus)*, n = 5	13-51	32
5	Chehon*(Pelecuscultratus)*, n = 27	21-60	42
6	Bream, n = 30	29-93	45
7	Zhereh*(Aspiusaspius)*, n = 16	29-71	51
8	Goby, n = 15	22-92	57
9	Whitefish, n = 7	31-125	73
10	Roach, n = 28	38-105	83
11	Carp, n = 11	35-151	98
12	Perch, n = 36	35-241	126
13	Common carp (*Cyprinuscarpio*), n = 16	43-260	150
14	Zander, n = 25	98-380	152
15	Sturgeon, n = 4	102-276	189
16	Pike, n = 21	65-301	213
17	Som, n = 5	173-342	260
18	*Crayfish, n = 9*	3.5-16.5	11
19	*Calfruff, n = 3*	5.0-9.3	7.1
20	*Roeroach, n = 4*	8.7-13.5	11
21	*Caviarpike, n = 4*	7.5-14	11
22	*Redfishroe, n = 9*	4.4-8.5	5.2

Figure 2 shows the change in the concentration of mercury in the muscles of bream, roach, perch, pike, and pike-perch caught in the areas of Rzhev–Staritsa, Rybinsk Reservoir, Samara and the Volga River delta. Volga. The lowest concentration of mercury is typical for the Upper Volga region – the region of the city of Rzhev–Staritsa, the maximum concentration is characteristic of the Rybinsk reservoir, which is consistent with the data from literary sources [3, 4]. Most mercury accumulates in the muscles of pikeperch and pike, then perch, roach and bream follow in the direction of reduction. In general, the ratio in the accumulation of mercury represented by fish species persists throughout the Volga River.

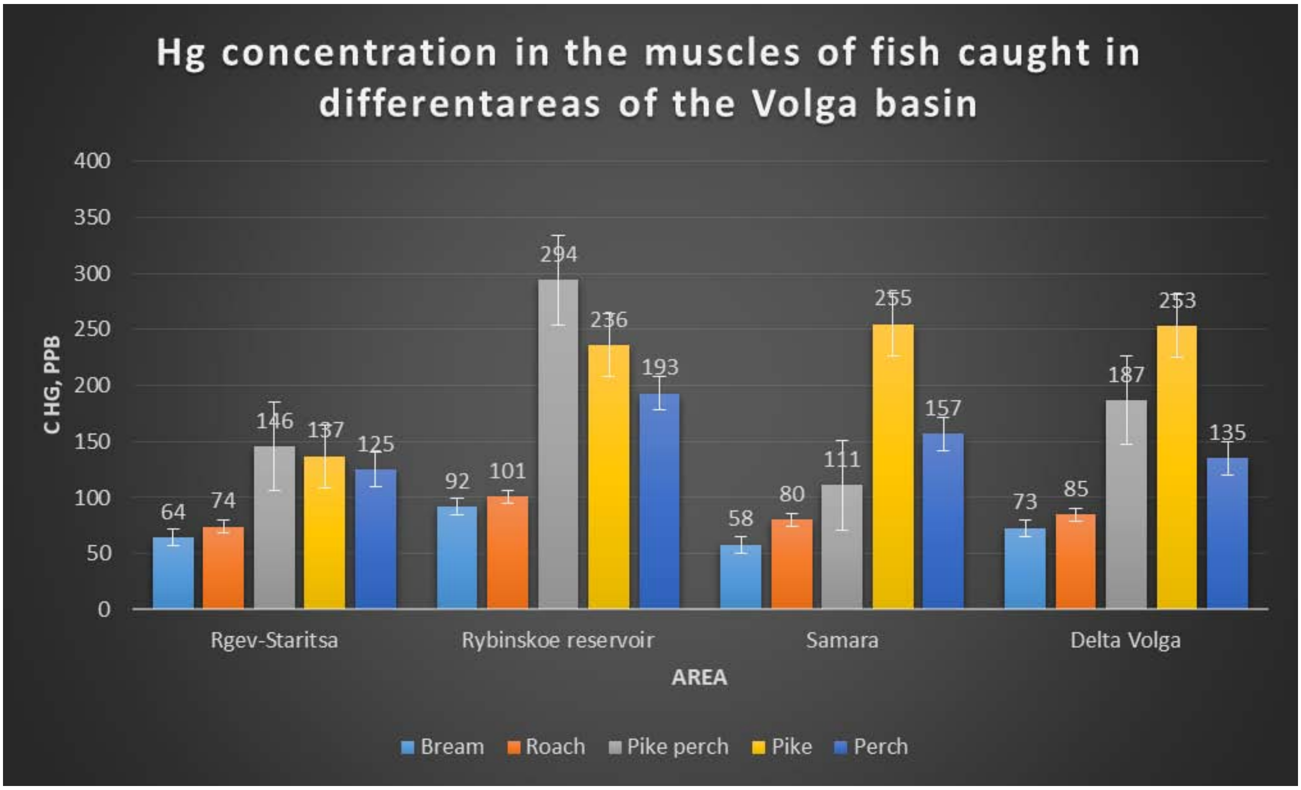

Figure 2: The concentration of mercury in fish caught in the upper (Rzhev – Starica, Rybinskoe Reservoir), middle (Samara) and lower (Delta Volga) areas of the Volga river

IV. Discussion

From literature sources, it is known that under certain conditions, the accumulation of mercury in the muscles of the fish is natural. In particular, cases have been described where the concentration of mercury in the muscles of the lake perch was directly proportional to the weight of the fish [15, 6, 7]. In the same works, it was reported that no such dependence for pike was observed. To assess the characteristics of mercury accumulation in the muscles of perch, pike, and bream, we conducted an experiment to catch these species of fish in the bay Chechera at the confluence of the Volga River.

The characteristic features of these fish are listed below:

Perch: This is one of the most common predator fish in the Russian freshwater. Zooplankton, insect larvae, worms, mollusks, the caviar of other fish, small fish,and juveniles are included in the perch diet. In general, it is one of the most voracious and omnivorous carnivorous fish. It feeds on everything in the pond. Perch grows very slowly. For the first year, its size is about 5 cm. A two years, the average perch is 11 cm long and weighs 23 g; by nine years old it is 29cm and 580 g, respectively.

Pike: The main food of the pike is all kinds of fish that live in a particular body of water, and preference is given to narrow-bodied breeds. Along with the narrow-bodied fish, which she prefers, large frogs, tadpoles, mice, etc. were repeatedly encountered in the stomachs of pikes. Pike grows very fast. During the first year of life, it reaches a length of 25–30 cm with a weight of up to 300 grams, in the second year 25–45 cm weighing up to 1.5 kg. For the third year, it grows to 60 cm and can reach a weight of just over 2 kg. A ten-year-old pike can weigh 10 kg with a length of 1 meter.

Bream: The physiological characteristics of the bream imply a purely bottom way of life. Bream feeds mainly on larvae, small crustaceans, mollusks, earthworms, land larvae and insects, and all sorts of vegetable food (young shoots of aquatic plants, etc.). Bream grows somewhat faster than perch but significantly slower than pike: by the end of the second year of life, it has an average length of about 15–17cm and a weight of about 150–170g.

As shown above, these fish are fundamentally different in growth rate and food base. Therefore, a large contrast of the experimental results was expected. Figure 3 shows graphs of mercury accumulation in the muscles of perch, pike, and bream. As can be seen from these graphs, there is a directly proportional relationship between the concentration of mercury in perch muscles and the mass of fish ($r = 0.881$, $p = 0.018$).

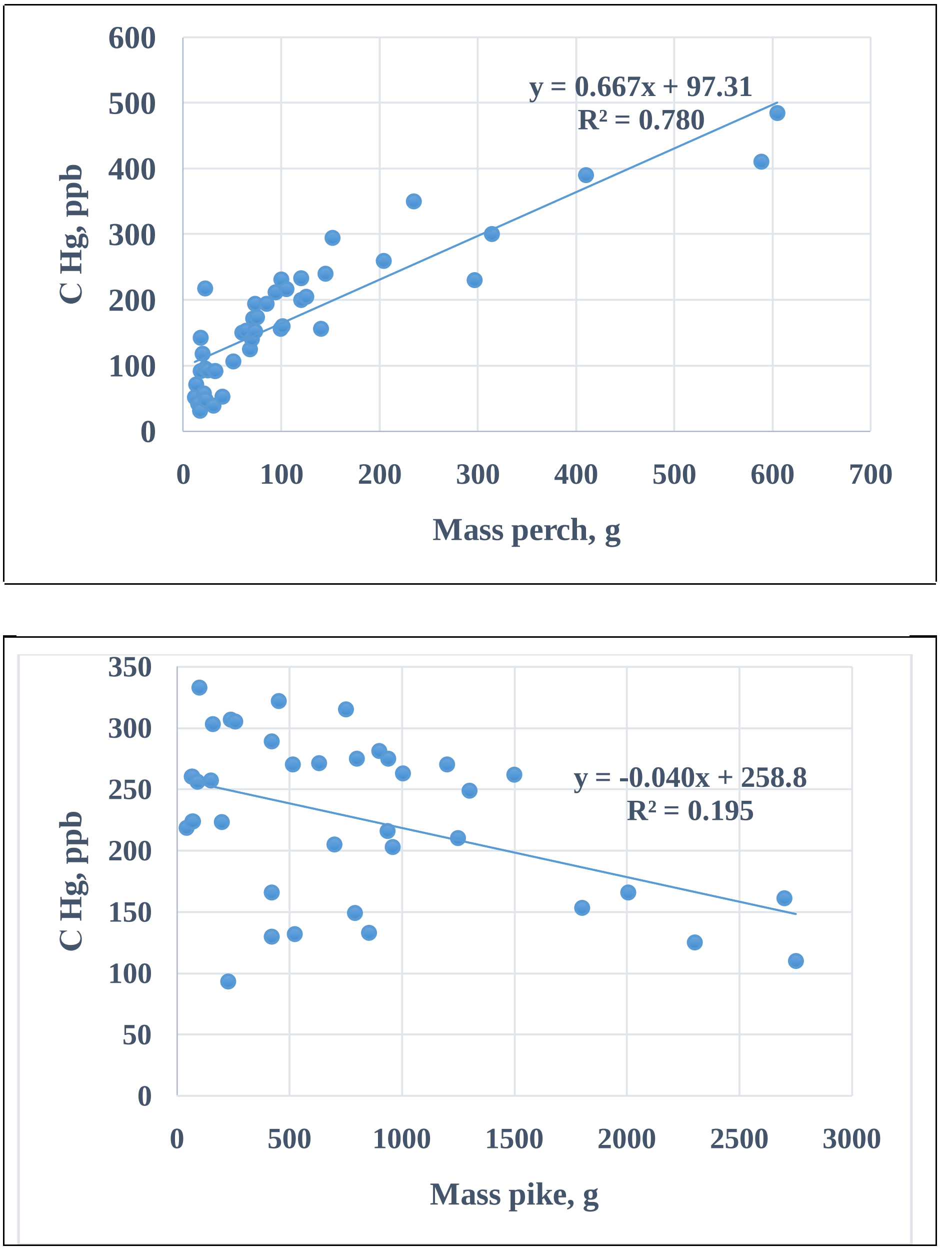

Figure 3: Character of mercury accumulation in perch and pike muscles

For a pike, on the contrary, the maximum mercury concentration is typical for fish weighing up to 1 kg, then a decrease in mercury concentration is observed (one should emphasize that we are talking about concentration and not abut total mercury in fish), the correlation coefficient was r = - 0.653, p = 0.029 (the calculation was carried out using the Minitab 17 program).

In the first case, we can state a high degree of dependence, in the second - a moderate degree of dependence of mercury concentration on the mass of fish. In the first case, it is a dependency with a sign (+), in the second case - with a sign (-). These facts raise some questions: in our case, the habitat of both pike and perch is the same. The habitat conditions of both types of fish are the same; the food base and the catch time are also the same. The concentration of mercury in the water did not change during capture and was 0.025-0.033 mcg/l (ppb). Nevertheless, a fundamental difference was found in the regularity of mercury accumulation in the muscles of perch and pike. The explanation of this phenomenon must be sought in fundamentally different growth rates of perch and pike. As mentioned above, the perch grows very slowly, it gains a mass of 500g and more by 8-9 years of life, while pike can gain a mass of 9-10kg over the same period. Consequently, the distribution of mercury coming from food occurs in a significantly larger mass, which leads to a peculiar decrease in the value of mercury concentration in the pike muscles. For bream, the dependence of mercury concentration in muscles on body mass was not found.

V. Conclusions

1. The concentration of mercury in the muscles of all fish species represented in work does not exceed the accepted standards (MPL). The highest concentration of mercury is characteristic of carp, carp, pike perch, pike, perch, sturgeon, and catfish;the lowest concentration of mercury is for ruff and crayfish. It has been found that mercury concentration in eggs is minimal and does not depend on the concentration of mercury in the muscles of the fish;
2. In the study of the spatial distribution of mercury in fish throughout the Volga river, it was found that in general the maximum concentration of mercury in the muscles of fish is characteristic of the Rybinsk reservoir, the minimum is for the Upper Volga;
3. The features of mercury distribution in the muscles of perch, pike, and bream were evaluated. It was found that the accumulation of mercury in the muscles of perch in the absence of human-made impact and the level of acidity of water 6.5-7.0 is directly proportional, in the muscles of pike-inversely proportional. For bream, the dependence of the concentration of mercury in the muscles on body weight was not found.

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