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#### Article

## Assessing the consumptive safety of fish with different mercury content in its muscles (water bodies of Vologda Oblast as a case study)

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**Abstract.** The mercury content in muscle tissues of fish from the water bodies of Vologda Oblast varied within  $0.001-2.492~\mu g/g$  wet weight. The minimum average values were recorded for rainbow trout and smelt ( $0.025~and~0.066~\mu g/g$ ), while the maximum average – for asp and smelt ( $0.401~and~0.472~\mu g/g$ ). In 12.1% of the studied non-predatory and 9.5% of predatory fish specimens, mercury concentrations exceeded the RF standard levels established for these groups of species ( $\geq 0.3~\mu g/g~and \geq 0.6~\mu g/g$ , respectively). The proportion of the examined fish, the consumption of which would result in exceeding the permissible weekly mercury intake (RfD according to US EPA) made up 50% for preschool children (2–5 years), 37% for primary school children (6–10 years), 24% for a secondary school age (11–15 years), and 18% for adults.

**Keywords:** freshwater bodies, non-predatory fish, predatory fish, consumption recommendations, calculation of safe doses

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#### Научная статья

# Оценка безопасности употребления в пищу рыбы из водоемов Вологодской области с различным содержанием ртути в мышечной ткани

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Аннотация. Содержание ртути в мышечной ткани рыб водных объектов Вологодской области варьирует в пределах от менее чем 0.001 до 2.492 мкг/г сырой массы. Минимальные средние значения отмечены для радужной форели и снетка (0.025 и 0.066 мкг/г), максимальные средние – для жереха и кильца (0.401 и 0.472 мкг/г). Установлено, что у 12.1% исследованных особей нехищных видов и 9.5% особей хищных видов рыб содержание ртути превышает нормативные уровни, действующие в РФ для этих групп видов (≥ 0.3 мкг/г и ≥ 0.6 мкг/г соответственно). Доля исследованной рыбы, употребление которой приведет к превышению допустимого еженедельного поступления ртути в организм (RfD согласно US EPA) составляет 50% для детей дошкольного возраста (2–5 лет), 37% для детей младшего школьного возраста (6–10 лет), 24% для детей среднего школьного возраста (11–15 лет) и 18% для взрослого населения.

**Ключевые слова:** пресные водоемы, нехищные рыбы, хищные рыбы, рекомендации по потреблению, расчет безопасных доз

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#### Introduction

Currently, the problem of mercury contamination is of global concern. In 2013, more than 120 countries signed the Minamata Convention to protect human health and the environment from mercury contamination<sup>1</sup>. The World Health Organization (WHO) considers mercury among ten major chemical elements posing a threat to public health<sup>2</sup>. In the second half of XX century, WHO developed and recommended safe for human health levels of mercury concentrations in various biosubstrates, the standards for their presence in food, and the reference intake doses3. It is found that fish consumed as food is the main source of mercury intake in the human body (Cottrill et al., 2012). More than 90% of the total mercury in fish muscles is present in the most toxic methylated form (Myers et al., 2007). The majority of methylmercury from the consumed fish (≥ 95%) is easily absorbed through the gastrointestinal tract (Chouvelon et al., 2009). Its content in the human body increases with the proportion of fish in the weekly diet. The cumulative accumulation of mercury in the human body has neurotoxic effects, negatively affects the cardiovascular system, reproductive function and may bring to disruption of embryonic development (Houston, 2011; Rice et al., 2014). The Food and Agriculture Organization of the United Nations (FAO), the European Food Safety Authority (EFSA) and the US Environmental Protection Agency (EPA) recommend to estimate the safety of fish and seafood products in the diet via the calculation of a safe dose of mercury intake in the human body for a certain time (RfD)4. In the Russian Federation, the regulation of mercury intake in the human body is based on limiting the consumption of fish products with mercury copounds not exceeding MAC<sup>5</sup>.

Fishing is one of the traditional activities of the population in Vologda Oblast, rich in a variety of water bodies (Borisov et al., 2019). According to official data, the annual fish catch (up to 30 fish species) in the rivers and lakes of the region in the last decade reaches 2 thousand tons. Bream, smelt, roach, sabrefish, perch, and pikeperch play the greatest role in the structure of industrial catches, while perch, pike, and pikeperch, roach, bream and silver bream - in amateur catches. Fish is not only consumed by the local population, but also exported outside Vologda Oblast. Thus, traditionally frequent consumption of fish from local ponds and streams may put the population at risk from mercury exposure.

This study is aimed at assessing the consumptive safety of fish (from water bodies of Vologda Oblast) with different mercury content in its muscles.

<sup>&</sup>lt;sup>1</sup> UNEP. Minamata Convention Agreed by Nations. Retrieved 19 January 2013. Web page. URL: https://www.unep.org/news-and-stories/press-release/minamata-convention-agreed-nations (accessed: 04.09.2023).

<sup>&</sup>lt;sup>2</sup> WHO. Mercury and health, 2017. Web page. URL: https://www.who.int/news-room/fact-sheets/detail/mercury-and-health (accessed: 04.09.2023).

<sup>&</sup>lt;sup>3</sup> WHO. IPCS. Environmental health criteria 101: Methylmercury, 1993. World Health Organization, Geneva, 1993–2144.

<sup>&</sup>lt;sup>4</sup> UNEP. Executive summary of the document on guidance for identifying populations at risk from mercury exposure. Chiba, Japan, 24–28 January 2011.

<sup>&</sup>lt;sup>5</sup> SanPiN 2.3.2.1078-01. Hygienic requirements for the safety and nutritional value of food products.

#### Material and methods

The work summarizes the results of studies of mercury concentrations in muscle tissue of fish from the reservoirs and watercourses of Vologda Oblast for 2007–2023. A total of 98 different types of water bodies (at 112 sites of all 26 municipal districts), including 38 rivers, 50 lakes, 6 reservoirs, 3 ponds and 1 flooded quarry were studied (Fig. 1, Table 1). Fishing was implemented with fixed gill nets, drift nets, seines, fixed traps, trawls, spinning and fishing rods of various designs. Each fish specimen was thoroughly analyzed. Measurements of commercial length and body weight, sex identification, including selection of fish scale, fin arms and otoliths for subsequent age determination were performed. Muscle samples were taken from the midsection of the body between the lateral line and the dorsal fin, placed in plastic bags and stored at −20 °C.

The mercury content was determined in muscles of 10720 specimens of 34 species and ecological forms of fish (Table 1). All the examined fish specimens were the objects of aquaculture, industrial or amateur fishing and consumed by the population as food thereby being a potential source of mercury intake in the human body.

The mercury content in the samples was determined on a PA-915M mercury analyzer with a PIRO (Lumex) device using the atomic absorption pyrolysis method without preliminary sample preparation (Sholupov et al., 2004). Samples of 10–50 mg were placed on a quartz dispenser and transferred to a thermolysis cell to determine the total mercury content with further combustion at a temperature of about 600 °C for 1–2 minutes. Each sample was analyzed in two replications. The accuracy of analytical measurement methods was monitored after 30 measurements using the certified biological material DORM-4 (with a known mercury content of  $0.41 \pm 0.055 \mu g Hg/g$ ) and DOLT-5 ( $0.44 \pm 0.18 \mu g Hg/g$ ).

To estimate the patterns of mercury accumulation, its content in individual species and trophic groups of fish was compared. The correlation between mercury concentration, length, weight and age of fish was analyzed. The names of fish species were given according to "Ryby v zapovednikakh Rossii" (2010). In terms of trophic specialization, groups of fish (ichthyophages, planktoichthyophages, euryphages, benthophages, phytobenthophages, planktivores) were identified by Yu.V. Slynko and V.G. Tereshchenko (2014) with allowance for specific feeding of fish from the water bodies of Vologda Oblast. During statistical analysis, two types of crucian carp (golden and silver), which did not differ significantly in mercury content, were combined into one group "crucian carp". Because of a significant difference in this indicator, in vendace a large mixed-feeding form "kilets", while in European smelt — a smelt with a short-cycle form and primarily feeding on zooplankton were identified.

Statistical analysis of the results was performed via using the Past 4.0 program (Hammer et al., 2001). For assessing the differences between the mercury content in muscle tissue of fish from different trophic groups, the nonparametric Kruskal–Wallis test (H-test) was applied. Differences were considered significant at a significance level of p  $\leq$  0.05. The relationship between the mercury concentration in muscles of fish and their size / age parameters was estimated based on the Spearman's rank correlation coefficient (Rs). The relationship was statistically significant at p  $\leq$  0.05. When Rs is within 0.3–0.5, the relationship is moderate, from 0.5 to 0.7– noticeable, from 0.7 and above – high.

To estimate a safe dose of fish consumption by the population, mercury concentrations in fish muscles were compared with those established by the RF sanitary and epidemiological rules and regulations (MAC for mercury in freshwater non-predatory and predatory fish: 0.3  $\mu$ g/g and 0.6  $\mu$ g/g wet weight, respectively). A safe dose and the proportion of fish specimens with mercury concentrations exceeding MAC were calculated as well.

Acceptable (safe) weekly fish consumption (CRlim) was defined differentially for each species using the formula (Bloom, 1992):

$$CRlim = \frac{RfD \times BW}{Cm}$$

where CRlim is the permissible weekly consumption of fish (g/week); RfD – the permissible weekly intake of mercury in the human body, BW – a man weight, g; Cm - the concentration of mercury in the consumed fish,  $\mu$ g/g; the EPA reference dose = 0.0007  $\mu$ g/g body weight per week<sup>6</sup>; the FAO reference

<sup>&</sup>lt;sup>6</sup> Guidance for assessing chemical contaminant data for use in fish advisories. Volume 1: Fish sampling and analysis. Third

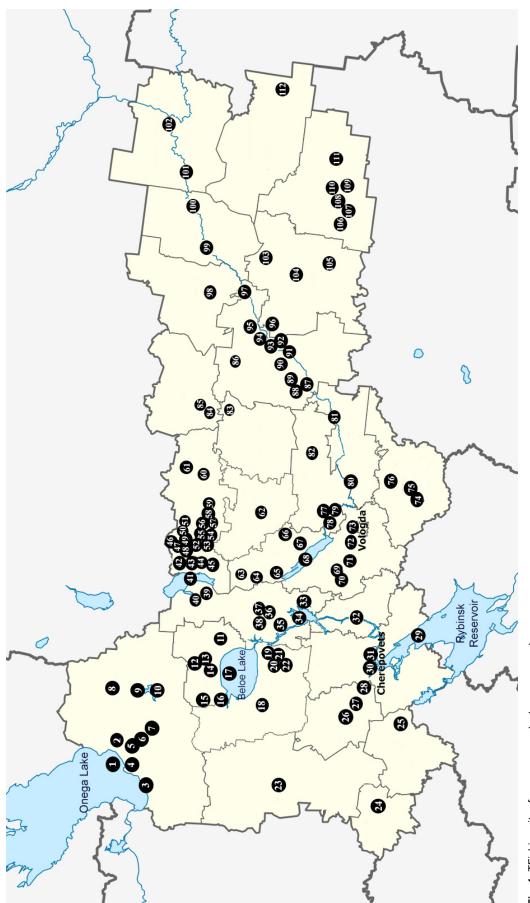


Fig. 1. TFishing sites for mercury content measurement.

**Table 1.** Location, fish species composition and collected material to determine the mercury content in muscle tissue. Types of fish: 1 – sterlet, 2 – zope, 3 – bream, 4 – white-eye, 5 – bleak, 6 – asp, 7 – silver bream, 8 – silver crucian carp, 9 – golden carp, 10 – gudgeon, 11 – chub, 12 – ide, 13 – dace, 14 – sabrefish, 15 – roach, 16 – rudd, 17 – tench, 18 – pike, 19 – European smelt, 20 – smelt, 21 – vendace, 22 – kilets, 23 – whitefish, 24 – whitefish - nelma, 25 – grayling, 26 – rainbow trout, 27 – salmon, 28 – char, 29 – burbot, 30 – ruff, 31 – perch, 32 – pikeperch, 33 – Volga zander, 34 – Amur sleeper.

No.	Water body	Municipal district	Fish species	Number of species	Number of specimens
1	Lake Onega	Vytegorsky	3, 7, 15, 18, 19, 21, 22, 23, 25, 26, 27, 28, 29, 30, 31, 32	16	495
2	Lake Tudozero	Vytegorsky	3, 7, 15, 16, 18, 23, 29, 31, 32	9	113
3	River Megra	Vytegorsky	3, 15, 16, 18, 25, 29, 31	7	22
4	Lake Velikoye	Vytegorsky	3, 7, 9, 14, 15, 16, 18, 29, 31, 32	10	224
5	Vytegorsk Reservoir	Vytegorsky	3, 6, 7, 12, 14, 15, 16, 18, 31, 32, 33	11	104
6	Belousovsk Reservoir	Vytegorsky	3, 5, 7, 14, 15, 18, 31, 32, 33	9	161
7	Novinkinsk Reservoir	Vytegorsky	2, 3, 4, 6, 7, 12, 14, 15, 18, 30, 31, 32	12	77
8	Lake Kemskoye	Vytegorsky	2, 18	2	57
9	Lake Kuzhozero	Vytegorsky	3, 15, 31, 32	4	16
10	Kovzha Reservoir	Vytegorsky	3, 15, 18, 21, 29, 31, 32	7	148
11	Lake Volotskoye	Vashkinsky	3, 8, 15, 16, 30, 31, 32	7	77
12	Lake Borovskoye	Vashkinsky	15, 31	2	27
13	Lake Ananino	Vashkinsky	3, 15, 18, 19, 29, 30, 31	7	90
14	Lake Svyatozero	Vashkinsky	3, 7, 12, 15, 16, 18, 19, 29, 30, 31	10	144
15	Lake Yarbozero	Vashkinsky	3, 7, 12, 15, 16, 30, 31	7	51
16	River Kema	Vashkinsky	3, 6, 18, 29, 32	5	13
17	Lake Beloye	Vashkinsky, Belozersky	2, 3, 4, 6, 7, 9, 10, 12, 14, 15, 16, 17, 18, 20, 21, 29, 30, 31, 32, 33	20	851
18	Lake Andozero	Belozersky	3, 7, 14, 15, 16, 18, 31, 32	8	103
19	Lake Kozhino	Belozersky	3, 15, 16, 17, 18, 31	6	48
20	Lake Lozskoye	Belozersky	3, 7, 12, 15, 16, 18, 31, 32	8	42
21	Lake Motkozero	Belozersky	3, 7, 15, 16, 18, 29, 31, 32	8	71
22	Lake Azatskoye	Belozersky	3, 7, 9, 15, 16, 18, 26, 31, 32	9	152
23	Lake Serkhlovskoye	Babaevsky	18, 31	2	27
24	Lake Sinichye	Chagodo- schensky	18, 31	2	49
25	River Mologa	Ustyuzhensky	1, 2, 3, 4, 7, 8, 10, 11, 12, 14, 15, 18, 30, 31, 32, 33	16	474
26	River Kolp'	Kaduisky	12, 15, 18, 31	4	21
27	River Suda	Kaduisky	3, 7, 11, 15, 18, 29, 30, 31	8	153

No.	Water body	Municipal district	Fish species	Number of species	Number of specimens
28	River Andoga	Kaduisky	2, 3, 7, 15, 29, 31	6	19
29	Rybinsk Reservoir	Cherepovetsky	3, 7, 8, 12, 15, 18, 21, 29, 30, 31, 32, 33	12	366
30	River Yagorba	Cherepovetsky	2, 3, 6, 12, 15, 30, 31, 32	8	52
31	River Sheksna (Cherepovets)	Cherepovetsky	2, 3, 6, 7, 11, 12, 15, 18, 29, 31, 32	11	224
32	River Sheksna (village Poteryaevo)	Sheksninsky	2, 3, 6, 7, 12, 14, 15, 18, 31, 32, 33	11	161
33	Lake Uzbinskoye	Kirillovsky	15, 31	2	31
34	Sheksna Reservoir	Kirillovsky, Sheksninsky	1, 2, 3, 4, 5, 6, 7, 8, 9, 12, 14, 15, 16, 17, 18, 21, 26, 29, 30, 31, 32, 33	22	848
35	quarries near the village of Kovrizhnovo	Kirillovsky	3, 15, 31	3	18
36	Lake Il'inskoye	Kirillovsky	3, 9, 18, 31	4	24
37	Lake Spasskoye	Kirillovsky	3, 9, 15, 18, 31	5	48
38	Lake Borodaevskoye	Kirillovsky	3, 9, 12, 15, 18, 31	6	61
39	Lake Veshchozero	Kirillovsky	3, 5, 7, 12, 15, 29, 30, 31	8	173
40	Lake Svyatoye	Kirillovsky	3, 5, 7, 15, 18, 19, 21, 29, 30, 31, 32	11	252
41	Lake Vozhe	Kirillovsky,	3, 5, 7, 12, 15, 18, 29, 30, 31, 32	10	980
42	Lake Danislovo	Vozhegodsky	15, 31	2	18
43	Lake Beketovskoye	Vozhegodsky	9	1	58
44	River Ilmenets	Vozhegodsky	13, 25	2	16
45	Lake Munskoye	Vozhegodsky	9	1	37
46	Lake Orekhovo	Vozhegodsky	15, 31	2	39
47	Lake Pertozero	Vozhegodsky	3, 9, 15, 18, 26, 30, 31	7	148
48	Lake Sienskoye	Vozhegodsky	15, 31	2	29
49	Lake Morenno	Vozhegodsky	15	1	11
50	Lake Svyatoye	Vozhegodsky	3, 9, 15, 18, 31	5	114
51	Lake Salozero	Vozhegodsky	15, 31	2	65
52	River Vozhega	Vozhegodsky	3, 7, 12, 13, 15, 18, 25, 29, 30, 31	10	193
53	Lake Gagatrino	Vozhegodsky	31	1	25
54	Lake Korgozero	Vozhegodsky	3, 15, 31	3	60
55	Lake Monozero	Vozhegodsky	31	1	35
56	Lake Chunozero	Vozhegodsky	15, 18, 31	3	48
57	Lake Dolgoye	Vozhegodsky	3, 15, 18, 30, 31	5	62
58	Lake Tamenskoye	Vozhegodsky	31	1	18
59	Lake Bolshoye Yakhrengskoye	Vozhegodsky	15, 31	2	20

No.	Water body	Municipal district	Fish species	Number of species	Number of specimens
60	Lake Pogorelovo	Vozhegodsky	31	1	13
61	Lake Chernoye	Vozhegodsky	9, 15	2	16
62	River Kubena (Kharovsk town)	Kharovsky	13, 31	2	20
63	River Uftyuga (Panikha village)	Ust-Kubinsky	11, 13, 15, 18, 30, 31	6	55
64	River Uftyuga (Bogorodskoye village)	Ust-Kubinsky	3, 7, 12, 13, 15, 24, 31	7	45
65	River Uftyuga (Tavlash village)	Ust-Kubinsky	3, 7, 12, 15, 18, 24, 29, 30, 31, 32	10	116
66	Lake Glukhoye	Ust-Kubinsky	15, 18	2	9
67	River Kubena, (Ustye village)	Ust-Kubinsky	3, 5, 7, 12, 15, 18, 30,	8	125
68	Lake Kubenskoye	Ust-Kubinsky, Vologdsky	3, 5, 7, 9, 12, 13, 15, 16, 18, 24, 29, 30, 31, 32	14	656
69	Lake Dmitrovskoye	Vologdsky	15, 18, 30, 31	4	88
70	Lake Koskovskoye	Vologdsky	9, 15, 18, 31	4	79
71	River Ema	Vologdsky	5, 10, 13, 15, 30, 31	6	25
72	Siberian Pond (Vologda)	Vologdsky	34	1	15
73	River Vologda	Vologdsky	3, 7, 12, 15, 18, 30, 31, 32	8	166
74	pond on R.Sinichka	Gryazovetsky	34	1	15
75	River Nurma	Gryazovetsky	31	1	10
76	River Lezha	Gryazovetsky	5, 15, 31	3	65
77	ponds (Sokol town)	Sokolsky	15, 18, 31	3	5
78	Lake Ozerko	Sokolsky	9	1	18
79	River Sukhona (Sokol town)	Sokolsky	3, 7, 12, 15, 18, 31	6	46
80	River Sukhona (Shuiskoye village)	Mezhdure- chensky	3, 6, 7, 12, 15, 18, 30, 31	8	110
81	River Sukhona (Kozhukhovo village)	Mezhdure- chensky	1, 3, 4, 7, 11, 12, 15, 18, 31, 32	10	106
82	River Votcha	Sokolsky	25	1	31
83	River Kiyug	Syamzhensky	13, 25	2	12
84	River Kostyuga	Verkhovazhsky	25	1	25
85	River Vaga	Verkhovazhsky	13, 15, 25	3	21
86	Lake Glubokoye	Totemsky	3, 12, 15, 18, 31	5	28
87	River Sukhona (Yubileiny settlement)	Totemsky	3, 7, 12, 15, 31	5	25
88	River Tiksna	Totemsky	13, 25	2	17
89	River Vopra	Totemsky	13	1	10
90	River Tsareva	Totemsky	13	1	11

No.	Water body	Municipal district	Fish species	Number of species	Number of specimens
91	River Sukhona (Ustye village)	Totemsky	1, 3, 4, 7, 11, 12, 15, 30, 31	9	39
92	River Pechen'zhitsa	Totemsky	13	1	20
93	River Sukhona (Tot'ma town)	Totemsky	1, 3, 4, 7, 12, 13, 15, 18, 29, 31	10	121
94	River Eden'ga	Totemsky	12, 13, 25	3	72
95	River Noren'ga	Totemsky	13	1	10
96	River Leden'ga	Babushkinsky	13	1	10
97	River Sukhona (Kochen'ga village)	Totemsky	3, 4, 7, 12, 15, 31	6	35
98	River Sheben'ga	Tarnogsky	25	1	15
99	River Sukhona (Nyuksenitsa village)	Nyuksensky	1, 4, 15, 30, 31	5	38
100	River Sukhona (Vostroye village)	Nyuksensky	4, 7, 11, 12, 15, 18, 30, 31, 32	9	58
101	River Sukhona (Poldarsa village)	Velikoustyugsky	1	1	31
102	River Sukhona (Veliky Ustyug)	Velikoustyugsky	4, 11, 12, 13, 15, 31	6	16
103	Lake Babye	Babushkinsky	31	1	8
104	River Yurmanga	Babushkinsky	25	1	5
105	River Yuza	Babushkinsky	13	1	17
106	River Unzha	Nikolsky	5, 13, 31	3	20
107	River Lundonga	Nikolsky	12, 13, 15, 25, 31	5	47
108	River Bolshoy Karnysh	Nikolsky	13, 15	2	20
109	River Pyrnug	Nikolsky	25	1	10
110	River Zemtsovka	Nikolsky	25	1	50
111	River Yug	Nikolsky	31	1	6
112	River Yeontala	Kichmengsko- Gorodetsky	25	1	26

dose = 0.0016  $\mu$ g/g body weight per week<sup>7</sup>; the average weight of an adult ≈ 70 kg; the average weight of children of a secondary school age (11–15 years) ≈ 42 kg, of a primary school age (6–10 years) ≈ 26 kg, a preschool age (2–5 years) ≈ 16 kg<sup>8</sup>.

MAC of mercury in fish at a given level of consumption (number of servings per week) is calculated using the formula<sup>6</sup>:

$$SV = \frac{RfD \times BW}{CR}$$

edition, 2000. EPA, Washington, DC, USA.

<sup>&</sup>lt;sup>7</sup> Committee on toxicity of chemicals in food consumer products and the environment. Updated COT statement on a survey of mercury in fish and shellfish, 2003.

<sup>&</sup>lt;sup>8</sup> WHO. Weight-for-age (5–10 years), 2007. Web page. URL: https://www.who.int/tools/growth-reference-data-for-5to19-years/indicators/weight-for-age-5to10-years (accessed: 10.09.2023).

where SV is MAC of mercury in fish at a given level of consumption ( $\mu$ g/g); RfD is the permissible weekly intake of mercury; BW is a man weight, g; CR – a weekly fish consumption (g/week); the EPA reference dose = 0.0007  $\mu$ g/g body weight per week. Weekly fish consumption was calculated taking into account a serving weight for a certain age group of the population (for adults – 150 g; for children of 11–15 year old – 110 g, for 6–10 year old – 90 g and 2–5 year old children – 70 g<sup>9</sup>) and the number of servings per week (1, 2 and 3 pieces).

#### **Results and discussion**

The mercury content in muscles of fish from Vologda water bodies varied widely: from 0.001 µg/g wet weight in muscles of roach, silver bream and dace to 2.492 in perch. The minimum average metal concentrations were recorded in rainbow trout and European smelt, whereas the maximum ones - in asp and smelt (Fig.2). In some specimens of rainbow trout and smelt, maximum mercury concentrations reached 0.1 µg/g; in tench, whitefish, Amur sleeper, grayling, crucian carp they varied as 0.2–0.4µg/g; in sterlet, bleak, vendace, Volga zander, whitefish, gudgeon, rudd, char – from 0.4 to 0.6 μg/g; blue bream, dace, chub, burbot, ide, salmon and kilets - from 0.6 to 0.8 µg/g; white-eye, sabrefish and smelt – from 0.8 to 1.0 µg/g. Maximum concentrations exceeded 1.0 µg/g in bream, roach, silver bream, pikeperch, ruff and asp, 1.5 μg/g excess was in pike and 2.0 μg/g – in perch. The average mercury concentrations in muscles of fish from the water bodies of Vologda Oblast were comparable to those in fish from freshwater bodies and watercourses of Russia and the world (Allen-Gil et al., 1997; Arantes et al., 2016; Kalkan et al., 2015; Komov et al., 2014; Li et al., 2015; Milanov et al., 2016; Nemova et al., 2014; Pal and Ghosh, 2013; Siraj et al., 2016). Thus, according to the European Food Safety Authority, freshwater fish species accumulate on average the following concentrations of mercury: roach – 0.12, perch – 0.17, bream – 0.23, and pike – 0.39 μg/g wet weight (Cottrill et al., 2012). Our findings suggest that this indicator for roach caught in Vologda water bodies makes up 0.18, perch – 0.33, bream – 0.13, and pike- 0.38 µg/g.

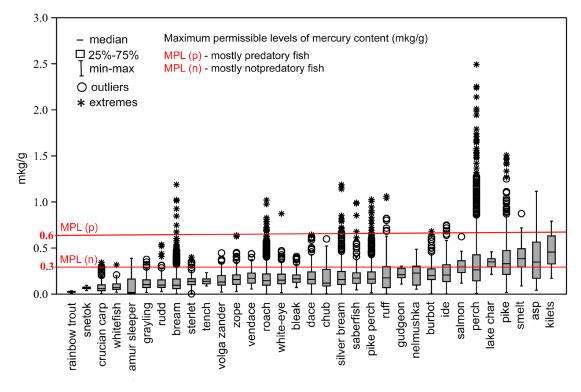


Fig. 2. Mercury content (µg/g, wet weight) in muscles of different fish species from water bodies of Vologda Oblast.

<sup>9</sup> SanPiN 2.3/2.4.3590-20. Sanitary and epidemiological requirements for the organization of public catering for the population.

Trophic specialization is one of the crucial factors determining the mercury content in muscle tissues of fish. Mercury concentrations increase in organs and tissues exponentially with each higher trophic level that is a peculiar feature of this metal migration in the food chain (Bloom, 1992). Hence, the mercury levels in predatory fish can exceed the background concentrations by hundreds of thousands or even millions of times (Croteau et al., 2005).

By feeding habits, Vologda fish can be split in two large groups: peaceful and predatory. Predatory, or ichthyophagous, feed mostly on other fish species; in the early stages of development, their main food is large invertebrates, especially insect larvae. Among the studied fish species, this group includes perch, pike, pikeperch, asp, burbot, salmon, and Volga zander. The second, more numerous group consists of peaceful species. Depending on the predominant feeding component, they are divided into planktivores, benthophages, phytobenthophages, euryphages and species of a mixed feeding type (Slynko and Tereshchenko, 2014). Planktivores (zope, bleak, vendace and smelt) primarily feed on zooplankton, benthophages (white-eye, bream, dace, sterlet, ruff, whitefish) consume benthic organisms, while phytobenthophages (roach, rudd, silver bream, crucian carp, tench) - mainly benthos and plants. Euryphages (ide, grayling, chub, Amur sleeper), which along with various groups of benthic invertebrates also consume fish in large quantities, are distinguished by the greatest diet diversity. A similar position is occupied by planktoichthyophages; adults often feed on juvenile fish (Siberian fish) and are capable of forming ecological groups with a predatory type of feeding (smelt and kilets).

Significant differences in the mercury content were established when comparing trophic groups of fish. The least concentrations  $(0.025 \pm 0.002 \ \mu g/g)$  were recorded in rainbow trout kept in cages and fed with specialized high-calorie artificial food. No significant differences were noted between ichthyophages and planktoichthyophages, as well as benthophages and phytobenthophages, which have similar feeding spectrum. The highest mercury concentrations were observed in planktoichthyophages  $(0.271 \pm 0.009 \ \mu g/g)$  and predators  $(0.304 \pm 0.004 \ \mu g/g)$  (Table 2). Thus, predatory fish, as the largest longest-lived and occupying a high position in the food chain, contain more mercury and pose the greatest human health hazard.

**Table 2.** Mercury content ( $\mu$ g/g ,wet weight) in fish muscles of different trophic groups from water bodies of Vologda Oblast. N – the sample size, AM – the arithmetic mean, SE – the arithmetic mean error, Min – the minimum concentration, Max – maximum concentration; letters indicate statistically significant differences between mercury concentrations in muscle tissue of fish of different trophic groups (H-test) at a significance level of p  $\leq$  0.05 (Kruskal–Wallis test).

NI-	Too a bis amassa	Fish anadias	NI.		Hg,	μg/g		
No.	Trophic group	Fish species	N	AM	SE	Min	Max	H-test
1	Artificial food	rainbow trout	13	0.025	0.002	0.010	0.036	а
2	Planktivores	vendace, zope, bleak, smelt	650	0.150	0.003	0.027	0.638	b
3	Benthophages	whitefish, ruff, bream, dace, white-eye, sterlet, whitefish-nelma, gudgeon	2434	0.168	0.003	0.001	1.184	С
4	Phytobentho- phages	silver bream, golden crucian carp, silver crucian carp, rudd, tench, roach	2564	0.172	0.003	0.001	1.184	С
5	Euryphages	ide, grayling, Amur sleeper, chub	626	0.188	0.005	0.002	0.749	d
6	Plankto- ichthyophages	saberfish, smelt, kilets	336	0.271	0.009	0.045	0.992	е
7	Ichthyophages	pike, pikeperch, Volga zander, salmon, asp, burbot, perch, char	4097	0.302	0.004	0.003	2.492	e

**Table 3.** Size-age dependence of mercury content in fish muscles. N – the sample size, Rs – the Spearman's rank correlation coefficient. A significant correlation (Rs  $\geq$  0.3 at p  $\leq$  0.05) between the mercury content in muscles and size/age of fish is shown in bold.

Species	NI NI	mercury/a	age of fish	mercury/m	nass of fish	mercury/le	ngth of fish
,	N	Rs	Р	Rs	р	Rs	р
Rainbow trout	13	_	_	0.283	0.347	0.072	0.813
Smelt	30	_	_	0.412	0.023	0.388	0.033
Crucian carp (gold and silver)	171	0.491	0.000	0.035	0.646	0.032	0.674
Whitefish	69	0.425	0.000	0.134	0.270	0.202	0.094
Amur sleeper	34	0.171	0.332	0.323	0.062	0.198	0.261
Grayling	214	0.396	0.000	0.288	0.000	0.345	0.000
Rudd	169	0.173	0.032	0.003	0.959	0.001	0.985
Bream	1305	0.358	0.000	0.347	0.000	0.351	0.000
Sterlet	297	0.371	0.000	0.292	0.000	0.278	0.000
Tench	33	0.107	0.572	0.106	0.554	0.122	0.498
Volga zander	150	0.043	0.625	0.148	0.069	0.156	0.055
Zope	318	0.566	0.000	0.380	0.000	0.418	0.000
Vendace	164	0.211	0.089	0.520	0.000	0.427	0.000
Roach	1554	0.255	0.000	0.117	0.000	0.197	0.000
White-eye	135	0.219	0.010	0.162	0.052	0.183	0.032
Bleak	138	0.277	0.006	0.135	0.112	0.050	0.555
Dace	322	0.547	0.000	0.473	0.000	0.480	0.000
Chub	16	0.482	0.006	0.800	0.000	0.803	0.000
Silver bream	637	0.326	0.000	0.361	0.000	0.398	0.000
Sabrefish	220	0.283	0.000	0.329	0.000	0.406	0.000
Zander	721	0.434	0.000	0.473	0.000	0.478	0.000
Ruff	258	0.404	0.000	0.132	0.033	0.139	0.524
Gudgeon	14	0.442	0.017	0.654	0.028	0.646	0.031
Whitefish	34	0.126	0.308	0.153	0.384	0.024	0.891
Burbot	231	0.530	0.000	0.472	0.000	0.479	0.000
lde	362	0.407	0.000	0.429	0.000	0.447	0.000
Perch	2339	0.576	0.000	0.564	0.000	0.587	0.000
Salmon	21	0.174	0.430	0.266	0.149	0.256	0.338
Char	15	0.130	0.641	0.242	0.383	0.403	0.135
Pike	543	0.504	0.000	0.461	0.000	0.476	0.000
Smelt	99	0.481	0.013	0.451	0.000	0.477	0.000
Asp	77	0.872	0.000	0.772	0.000	0.822	0.000
Kilets	17	0.445	0.007	0.385	0.030	0.637	0.005

Age and life expectancy also affect mercury levels in fish. Mercury concentrations in organs and tissues are generally higher in long- than in short-lived species. They are higher in slow-growing than in fast-growing species, as well as in larger and older fish than in young ones (Ivanova et al., 2023; Soltani et al., 2021; Sonesten, 2003; Stepanova and Komov, 1997). The reliable correlations between the mercury content in muscle tissue and age were established for 19 studied species, while with body length for 18 and with body weight – for 17 species (Table 3). A significant positive relationship between mercury content and age was noted for crucian carp, whitefish, grayling, bream, sterlet, blue bream, dace, chub, silver bream, pikeperch, ruff, gudgeon, burbot, ide, perch, pike, smelt, carp, and asp. The best correlation was found for ichthyophages. Thus, the Spearman's rank correlation coefficient (Rs) between mercury concentrations and size-age indicators (age, weight, length) for pikeperch was 0.434–0.478, pike – 0.461–0.504, burbot – 0.472–0.530, perch – 0.564–0.587, asp – 0.722–0.872. At the same time, in most peaceful species (rudd, tench, roach, vendace, white-eye, bleak) and euryphages (Amur sleeper, sabrefish) such a correlation was absent or weakly expressed.

The comparison of mercury concentrations in fish muscles with those established by the RF hygienic rules and regulations for food products safety indicated that mercury concentrations exceeded MAC (< 0.6  $\mu$ g/g) in 4.5% of predatory fish species from water bodies of Vologda Oblast. Most often high concentrations were found in kilets (29.4%), asp (20.8%), pike (12.9%) and perch (11.9%), not so often – in smelt, char, chub, ruff, salmon, white bream, sabrefish, pikeperch and sporadically – in ide, burbot, dace, roach, white-eye and bream (Table 4) had mercury concentrations corresponding to the recommended levels for non-predatory freshwater fish (0.3  $\mu$ g/g). Only three species (rainbow trout, smelt, tench) demonstrated the recommended metal content (within 0.3  $\mu$ g/g). In 3% of whitefish, sterlet, grayling, Amur sleeper and in 10% of rudd, Volga zander, vendace, bream, blue bream, gudgeon, and white-eye this indicator was above 0.3  $\mu$ g/g. In other peaceful fish species (i.e. bleak, roach, bream, sabrefish, silver bream), the proportion of specimens with a high mercury content was 10–20%, and in whitefish, ruff, chub and ide it even exceeded 20%. In general, MAC excess was revealed in 12.1% of specimens of peaceful species and in 9.5% of predatory ones.

Maximum permissible concentrations for food products reflect just average statistical values being often ineffective in assessing the risks to public health associated with alimentary intake of toxic elements and their compounds in food. Therefore, when calculating and making recommendations, it is better to use the criterion of a safe dose of mercury intake in the human body, or RfD (a reference dose), which takes into account the coefficients of absorption and excretion of mercury in the body, the amount of mercury intake with the minimal negative effect on health <sup>10</sup>.

The FAO Joint Expert Committee, which assesses contaminants in food, has established a safe weekly intake of methylmercury at  $0.0016~\mu g/g$  body weight per week. The most stringent guidelines have been currently set by EPA: a safe daily dose is  $0.0007~\mu g/g$  body weight per week. WHO recommendations are aimed at preserving the adults health, while US regulations (EPA) – to prevent the negative effects of mercury on the nervous system of a developing fetus (Bell, 2017; Grandjean and Budtz-Jørgensen, 2007).

With allowance for the EPA recommendations, the safe permissible weekly consumption of rainbow trout (artificially grown in the reservoirs of Vologda Oblast) for adults is about 2000 g per week, for children of a secondary school age – 1200 g, a primary school age – 700 g and a preschool age – almost 500 g. Wild fish eating is less safe. Depending on a fish type, it varies within 104–740 g for adults, 62–444 g for children of a secondary and 39–275 g of a primary as well as 24–169 g for preschool children. According to FAO recommendations, the calculated levels of safe weekly consumption of fish from Vologda water bodies are almost 2.3 times higher, amounting to 237–1692 g per week for adults, 142–1015 g for children of 11–15 years, 88–628 g of 6–10 year olds and 54–387 g for 2–5 year old children (Table 5).

Based on the calculated number of servings per week of fish with different mercury levels (not

<sup>&</sup>lt;sup>10</sup> UNEP. Executive summary of the document on guidance for identifying populations at risk from mercury exposure. Chiba, Japan, 24–28 January 2011.

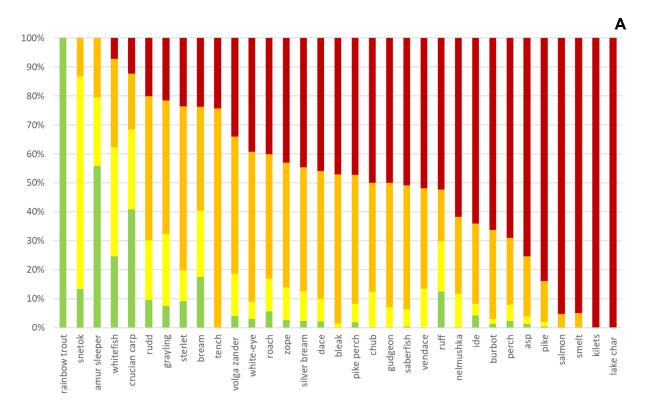
**Table 4.** The ratio of mercury content in peaceful and predatory fish of water bodies of the Vologda region with sanitary and hygienic standards of the Russian Federation.

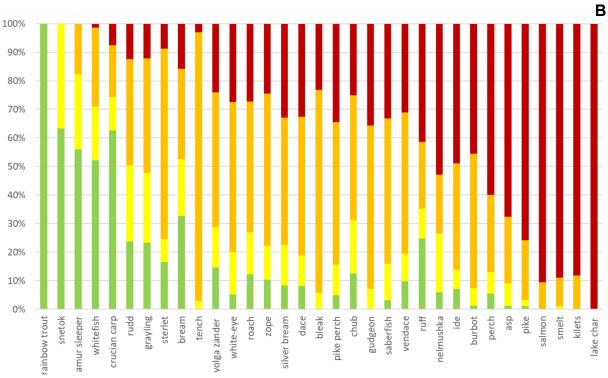
Fish species	N	with Hg	individuals content ≤ θ μg/g	with Hg	individuals content = 599 µg/g	Number of with Hg co µg	
		ind.	%	ind.	%	ind.	%
			Artificia	l feed			
Rainbow trout	13	13	100.0	0	0.0	0	0.0
			Peacefu	l views			
Smelt	30	30	100.0	0	0.0	0	0.0
Tench	33	33	100.0	0	0.0	0	0.0
Whitefish	69	68	98.6	1	1.4	0	0.0
Grayling	214	210	98.1	4	1.9	0	0.0
Sterlet	297	291	98.0	6	2.0	0	0.0
Crucian carp	171	167	97.7	4	2.3	0	0.0
Rotan	34	33	97.1	1	2.9	0	0.0
Rudd	169	162	95.9	7	4.1	0	0.0
Vendace	164	155	94.5	9	5.5	0	0.0
Bream	1305	1215	93.1	81	6.2	9	0.7
Sinets	318	296	93.1	20	6.3	2	0.6
Gudgeon	14	13	92.9	1	7.1	0	0.0
White-eye	135	122	90.4	12	8.9	1	0.7
Bleak	138	124	89.9	14	10.1	0	0.0
Roach	1554	1367	88.0	168	10.8	19	1.2
Dace	322	277	86.0	40	12.4	5	1.6
Chekhon	220	189	85.9	26	11.8	5	2.3
Gustera	637	534	83.8	84	13.2	19	3.0
Whitefish	34	25	73.5	9	26.5	0	0.0
Ruff	258	195	75.6	50	19.4	13	5.0
Chub	16	12	75.0	3	18.8	1	6.3
lde	362	258	71.3	98	27.1	6	1.7
Smelt	99	30	30.3	62	62.6	7	7.1
Kilets	17	3	17.6	9	52.9	5	29.4
Total	6610	5809	87.9	709	10.7	92	1.4
			Predatory	species			
Bersh	150	143	95.3	. 7	4.7	0	0.0
Zander	721	608	84.3	95	13.2	18	2.5
Burbot	231	187	81.0	41	17.7	3	1.3
Salmon	21	12	57.1	8	38.1	1	4.8
Perch	2339	1329	56.8	731	31.3	279	11.9
Pike	543	234	43.1	239	44.0	70	12.9
Asp	77	32	41.6	29	37.7	16	20.8
Palia	15	4	26.7	10	66.7	1	6.7
Total	4097	2549	62.2	1160	28.3	388	9.5
TOTAL	10720	8371	78.1	1869	17.4	480	4.5

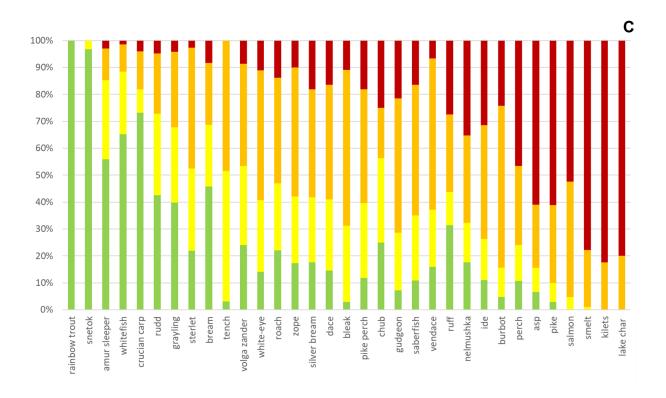
Table 5. Consumptive safety of fish from water bodies of Vologda Oblast, g/week.

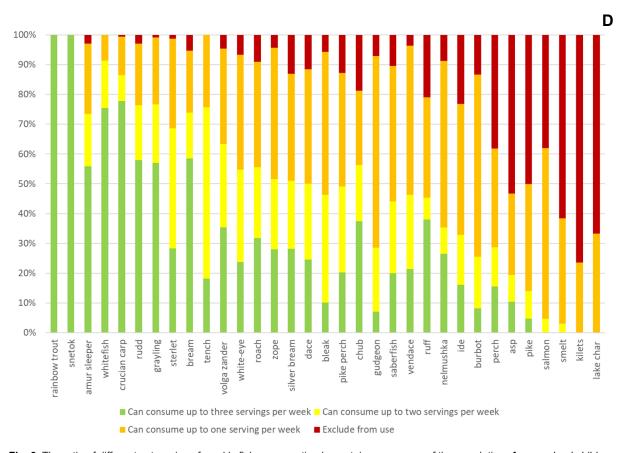
Fish species	z	Average mercury	Children of 2 years old	ildren of 2–5 years old	Children of 6 years old	Children of 6–10 years old	Children	Children of 11–15 years old	Ad	Adults
	<u>:</u>	content in fish, µg/g	EPA	FAO	EPA	FAO	EPA	FAO	EPA	FAO
Rainbow trout	13	0.025	455	1040	739	1690	1194	2730	1991	4550
Smelt	30	990.0	169	387	275	628	444	1015	740	1692
Carp	171	0.083	135	309	220	502	355	811	592	1352
Common whitefish	69	0.085	131	300	213	488	345	788	575	1313
Amur sleeper	34	0.092	122	280	199	455	321	734	536	1224
Grayling	214	0.122	92	209	149	340	240	549	401	915
Rudd	169	0.124	06	206	147	335	237	541	395	902
Bream	1305	0.130	98	197	140	320	226	517	377	861
Sterlet	297	0.136	82	187	133	304	215	491	358	819
Tench	33	0.141	80	182	129	296	209	478	349	797
Volga zander	150	0.152	73	167	119	272	192	439	320	732
Zope	318	0.168	29	152	108	248	175	400	292	299
Vendace	164	0.174	64	147	105	239	169	386	282	644
Roach	1554	0.177	64	145	103	236	167	382	278	989
White-eye	135	0.178	63	144	102	234	165	378	275	629
Bleak	138	0.181	62	141	100	229	162	370	270	617
Dace	322	0.189	29	135	96	220	155	355	259	591

Fish species	z	Average mercury	Children of 2–5 years old	of 2–5 s old	Children year	Children of 6–10 years old	Children year	Children of 11–15 years old	Adults	lts
	_	content in fish, µg/g	EPA	FAO	EPA	FAO	EPA	FAO	EPA	FAO
Chub	16	0.192	58	134	92	217	153	351	256	585
Silver bream	637	0.198	99	129	92	210	148	339	247	292
Sabrefish	220	0.202	26	127	06	206	146	334	243	556
Zander	721	0.203	22	126	06	205	145	331	242	552
Ruff	258	0.213	53	120	85	195	138	315	230	526
Gudgeon	4	0.217	52	118	84	192	135	309	226	516
Whitefish	8	0.218	51	117	84	191	135	308	225	514
Burbot	231	0.226	49	113	80	184	130	297	217	495
lde	362	0.236	47	108	77	176	125	285	208	474
Salmon	21	0.308	36	83	29	135	92	218	159	363
Perch	2339	0.331	34	78	22	127	06	205	149	341
Char	15	0.344	33	74	53	121	98	195	143	326
Pike	543	0.378	30	89	48	110	78	178	130	296
Smelt	66	0.392	59	92	46	106	75	171	125	286
Asp	77	0.401	28	64	45	104	73	167	122	279
Kilets	17	0.472	24	54	39	88	62	142	104	237









**Fig. 3.** The ratio of different categories of weekly fish consumption by certain age groups of the population: **A** –preschool children (2–5 years), a serving is 70 g; **B** –primary school children (6–10 years) – 90 g; **C** – secondary school children (11–15 years) – 110 g, **D** –adults – 150 g.

		Age	group	
Consumption level	Children of 2–5 years	Children of 6–10 years	Children of 11–15 years	Adults
up to 3 servings per week	≤ 0.05	≤ 0.07	≤ 0.09	≤ 0.11
up to 2 servings per week	≤ 0.08	≤ 0.10	≤ 0.14	≤ 0.16
no more than 1 serving per week	≤ 0.17	≤ 0.21	≤ 0.28	≤ 0.33
to exclude from diet	> 0.17	> 0.21	> 0.28	> 0.33

Table 6. MAC of mercury in fish (µg/g, wet weight) for different age groups with regard for recommended servings per week.

exceeding EPA RfD standards), fish from local reservoirs was categorized in 4 groups: "can be consumed up to 3 servings per week", "up to 2 servings per week", "no more than 1 serving per week", "must be excluded from a diet" (Table 6).

A comparison of our results with EPA recommendations (Table 6) shows that at a mercury content of > 0.33  $\mu$ g/g in Vologda fish, the adult population should completely exclude fish from the diet or eat no more than one serving per week (0.16–0.33  $\mu$ g/g or 18 and 34%). For children of different age, these indicators are the following: for 2–5 years – 50 and 34%, for 6–10 years – 37 and 38%, for 11–15 years – 24 and 35%, respectively.

A comparison of fish species suggests that 20–40% of perch, salmon and ide, 40–60% of pike and asp, and 60–80% of kilets, char and smelt contain hazardous mercury concentrations to adult health (Fig. 3). Dangerous for preschool children mercury content was detected in 60–80% of pike, asp, perch, burbot, ide, whitefish and in 40–60% of pikeperch, bleak, dace, silver bream, blue bream and roach. In this regard, the local population should limit a regular consumption of these types of fish. Kilets, char, salmon and smelt must be completely excluded from the diet of preschoolers. Eating of rainbow trout and smelt is the safest for all categories of the population.

#### Conclusion

Mercury concentrations in fish from water bodies of Vologda Oblast varied widely. For instance, the range between the minimum and maximum values made up three orders of magnitude. The lowest concentrations (0.001  $\mu$ g/g wet weight) were found in muscles of roach, silver bream and dace, whereas the highest (> 1.5  $\mu$ g/g) – in pike and perch. The maximum average concentrations were noted in typical predatory species (pike, perch, asp, salmon, char) and predatory forms (kilets, smelt) of peaceful species. Rainbow trout (grown in cage farms on artificial feed) and smelt, a typical planktivore, had the least average concentrations of mercury. It is known that mercury accumulation in fish muscles depends on the trophic specialization of individual species, fish age and size. Being the largest long-lived and occupying top levels in the food chain, predatory fish contain more mercury, and thereby at regular consumption in food they are most dangerous to human health.

An important point is that estimation results of a consumptive safety of fish depend on the applied calculation method based on either a safe dose of mercury intake in the human body for a certain time or a safe mercury concentration in fish. The excess in MAC of mercury in muscles has been revealed in 9.5% of the studied predatory and in 12.1% of peaceful fish caught in different reservoirs of Vologda Oblast. In terms of a safe dose of mercury intake in the human body, the amount of unsafe fish consumed by adults in the region under study is 1.5 times (23%) greater of the RF standards for mercury. For adults, it is recommended to exclude up to 18% of fish from the diet, for children of a secondary school age – up to 24%, for primary school – 37% and preschool age children – almost 50%.

Thus, the federal rationing system is relevant only for limiting the peaceful fish consumed by adults. The standards adopted in the Russian Federation do not actually limit the consumption of fish harmful to the health of children.

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