Трансформация экосистем
Ecosystem Transformation

ISSN 2619-0931 Online
www.ecosysttrans.com

DOI: https://doi.org/10.23859/estr-251205
EDN: https://elibrary.ru/ueehxw
UDC [597+574.64] (282.247.413.5):556.555.6

Article

Spatial variability of mercury content in bottom sediments and muscles of bream *Abramis brama* L., 1758 from the Rybinsk Reservoir (Volga River, Russia)

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Abstract. The results of a study on mercury content in bottom sediments (BS) and muscles of bream (*Abramis brama* L., 1758) from four reaches of the Rybinsk reservoir, which differ in hydrological regime, hydrochemical conditions, and biological community structure, are presented. The spatial distribution pattern of Hg in the bottom sediments of the Rybinsk reservoir has remained stable for a long time. The maximum Hg content values in bottom sediments were recorded in the Sheksna reach, and the minimum – in the Mologa reach. The lowest metal concentrations in bream were found in fish caught in the Main and Sheksna reaches, while the highest were in bream from the Mologa reach. Significant differences in Hg content in muscles between different years of the study were revealed for bream from the Main and Sheksna reaches. No significant differences in Hg accumulation in the muscles of females and males were found, nor were significant correlations between Hg content in bream muscles and fish length, weight, sex, or age. A strong relationship was found between Hg concentration in bream muscles and in the reservoir's bottom sediments. In addition, a positive correlation was noted between Hg concentrations in bream muscles and chlorophyll concentration and the pigment index ratio E_{480}/E_{665} in BS, and a negative correlation with the proportion of organic matter. In the studied sample, Hg content in bream muscles and BS did not significantly depend on sediment particle size, water color, transparency, or flow velocity. Hg content in the reservoir's BS was positively correlated with chlorophyll concentration in water and negatively correlated with the concentration of sedimentary pigments in the sediment. Overall, the Hg content in BS and bream muscles falls within the range previously recorded for the Rybinsk reservoir by other authors and does not exceed established standards.

Keywords: heavy metals, fish, granulometry, sedimentary pigments, organic matter, Upper Volga

Funding. The work was carried out within the framework of state assignments No. 124032500015-7 and No. 124032100076-2.

Acknowledgements. The authors express their gratitude to staff members of the IBIW RAS: E.V. Shchedrova for performing the analysis of mercury content in bottom sediments and bream muscles, and T.I. Kritsina for determining the age of bream.

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To cite this article: Lozhkina, R.A. et al., 2026. Spatial variability of mercury content in bottom sediments and muscles of bream *Abramis brama* L., 1758 from the Rybinsk Reservoir (Volga River, Russia). *Ecosystem Transformation* **9** (3), 24–43. https://doi.org/10.23859/estr-251205

Received: 05.12.2025
Accepted: 11.02.2026
Published online: 31.07.2026

DOI: https://doi.org/10.23859/estr-251205
EDN: https://elibrary.ru/ueehxw
УДК [597+574.64] (282.247.413.5):556.555.6

Научная статья

Пространственная вариабельность содержания ртути в донных отложениях и мышцах леща *Abramis brama* L., 1758 Рыбинского водохранилища (р. Волга, Россия)

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Аннотация. Приведены результаты исследования содержания ртути в донных отложениях и мышцах леща *Abramis brama* L., 1758 из четырех плесов Рыбинского водохранилища, различающихся гидрологическим режимом, спецификой гидрохимических условий и структурой биологических сообществ. Характер пространственного распределения Hg в ДО Рыбинского водохранилища длительное время остается стабильным. Максимальные значения уровня содержания Hg в донных отложениях (ДО) зарегистрированы в Шекснинском, а минимальные – в Моложском плесах водохранилища. Наименьшие концентрации металла отмечены у лещей, выловленных в Главном и Шекснинском плесах, максимальные – у лещей, выловленных в Моложском плесе. Значимые различия содержания Hg в мышцах в разные годы исследования выявлены у лещей из Главного и Шекснинского плесов. Не установлено значимых различий накопления Hg в мышцах самок и самцов, а также значимых связей содержания Hg в мышцах леща с его размером, массой, полом и возрастом. Обнаружена сильная взаимосвязь между концентрацией Hg в мышцах леща и ДО водохранилища. Кроме того, отмечена положительная связь концентраций Hg в мышцах леща с концентрацией хлорофилла и соотношением пигментного индекса E_{480}/E_{665} в ДО, отрицательная – с долей органического вещества. В исследованной выборке содержание Hg в мышцах леща и ДО значимо не зависело от размера частиц грунта, показателей цветности, прозрачности и скорости течения. Содержание Hg в ДО водохранилища было положительно связано с концентрацией хлорофилла в воде и отрицательно – с концентрацией осадочных пигментов в грунте. В целом содержание Hg в ДО и мышцах леща находится в диапазоне значений, ранее зарегистрированных для Рыбинского водохранилища другими авторами, и не превышает установленных нормативов.

Ключевые слова: тяжелые металлы, рыба, гранулометрия, осадочные пигменты, органическое вещество, Верхняя Волга

Финансирование. Работа выполнена в рамках государственных заданий № 124032500015-7 и 124032100076-2.

Благодарности. Авторы выражают благодарность сотрудникам ИБВВ РАН Е.В. Щедровой за проведенный анализ содержания Hg в донных отложениях и мышцах леща, Т.И. Крициной за определение возраста леща.

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Для цитирования: Ложкина, Р.А. и др., 2026. Пространственная вариабельность содержания ртути в донных отложениях и мышцах леща *Abramis brama* L., 1758 Рыбинского водохранилища (р. Волга, Россия). *Трансформация экосистем* **9** (3), 24–43. https://doi.org/10.23859/estr-251205

Поступила в редакцию: 05.12.2025
Принята к печати: 11.02.2026
Опубликована онлайн: 31.07.2026

Introduction

Mercury (Hg) and its compounds are highly toxic to all living organisms (Scheuhammer et al., 2012). Hg enters the environment from natural (volcanic eruptions, evaporation from the ocean surface) and anthropogenic (fossil fuel combustion, cement production, oil refining, gold mining) sources (UN Environment..., 2019). The annual emission of the metal into the environment is estimated at about 5–6 thousand tons; anthropogenic sources account for one-third of this amount. The diversity of sources determining the intensity of metal input into terrestrial and aquatic ecosystems suggests both global and local Hg cycling. The local cycle is largely associated with human economic activities and leads to elevated Hg concentrations in ecosystem components located close to the metal source (Boening, 2000). The residence time of Hg in the atmosphere during the global cycle is 6–12 months (Selin, 2009). Such a long period facilitates its transport by air masses over long distances and determines the widespread distribution of the metal.

In natural waters, Hg content is low, on the order of 5–15 ng/L; however, due to atmospheric transport, it enters even water bodies remote from industrial sources, accumulating in bottom sediments (BS) and tissues of aquatic organisms (Fitzgerald and Lamborg, 2007). A significant amount of the metal is retained in bottom sediments, with up to 90% of the total Hg content there being immobile inorganic compounds unavailable to biota (Ulrich et al., 2010). Under favorable conditions, under the action of bacteria in the organic-rich surface layer of sediment, Hg is converted into highly toxic monomethylmercury (CH_3Hg^+), leading to secondary input of the metal into aquatic ecosystems (Hudelson et al., 2020). Methylated compounds are the most toxic among all forms of mercury (Chételat et al., 2020).

Hg content in living organisms increases along the trophic chain and reaches maximum values in representatives of higher trophic levels: predatory fish, piscivorous birds, and mammals (Scheuhammer, 2007). In addition to its systemic toxic effects, Hg has mutagenic, teratogenic, and neurotoxic properties. Accumulating in organs and tissues, Hg can cause a wide range of disorders, including behavioral, reproductive, and physiological-biochemical abnormalities (Beckers and Rinklebe, 2017; Scheuhammer et al., 2015).

The Rybinsk reservoir is one of the largest freshwater artificial reservoirs in Russia, formed in the Mologa-Sheksna lowland after the construction of a hydroelectric dam upstream of the city of Rybinsk on the Sheksna and Volga rivers (Butorin et al., 1975). Based on morphological features of the bed, depth distribution, and water color gradations, four reaches are distinguished in the reservoir: Volga, Mologa, Sheksna, and Main (Ekologicheskie problemy..., 2001).

Bream *Abramis brama* L., 1758 is widely distributed throughout the Volga basin, is one of the abundant species, and forms the basis of the fishery (Ryby Rybinskogo..., 2015). The living conditions of bream in different reaches of the reservoir differ in hydrological and hydrochemical parameters, composition and abundance of representatives of various trophic groups of biological communities, and their distribution over the water area. Moreover, the reaches of the reservoir are subject to varying degrees of anthropogenic pressure (Ekologicheskie problemy..., 2001; Struktura..., 2018).

Previously, the main features of Hg accumulation in the Rybinsk reservoir were established for predatory fish species (perch, pikeperch, pike) (Ekologicheskie problemy..., 2001; Gremyachikh et al., 2019). At the same time, for non-predatory fish, in particular bream, these patterns remain insufficiently studied (Gorbunov et al., 2018; Stepanova and Komov, 1997; Tyutin et al., 2019). Existing studies are limited because they were conducted on small samples and, in most cases, on material only from the Volga reach.

The aim of this work was to study the mercury content in bottom sediments and muscles of bream from different reaches of the Rybinsk reservoir and to identify the main ecosystem parameters affecting metal accumulation in fish.

Materials and methods

In 2016 and 2019, bottom sediments (BS) were sampled at the sites of bream capture (Ryby Rybinskogo..., 2015). Additionally, BS were collected in 2018 along an extended grid of stations across the reservoir (Structure and..., 2018). A modified Ekman-Birge bottom grab (DAK-250) with a sampling area of 1/40 m² was used for sampling. The surface BS layer (7–10 cm thick) was collected in triplicate, air-dried, and ground in an inert mortar with a pestle. A total of 60 BS samples were taken.

Grain-size composition of BS was determined by wet sieving using an electromagnetic shaker "Analysette-3" (Alfred Fritsch & CO, Germany). Individual size fractions were rinsed from the sieves and dried in a water bath. Fractions with particle diameters > 1, 1.0–0.1, 0.1–0.01, and < 0.01 mm were separated and used to calculate the mean particle size. Bulk density, natural moisture, and organic matter (OM) content were determined by conventional methods (Butorin et al., 1975; Teoriya i praktika..., 2006).

Pigments in BS were used as indicators of plant-derived organic matter. Concentrations of chlorophyll *a* (Chl *a*) and its degradation products (pheopigments, Ph) were determined spectrophotometrically in a 90% acetone extract. Chl+Ph concentrations were calculated using Lorenzen's equations per 1 g dry BS. The ratio E_{480}/E_{665} (analogous to the E_{480}/E_{664} index used for phytoplankton) – the ratio of optical densities of the extract at 480 nm (a carotenoid absorption maximum where Chl absorption is minimal) and 665 nm (Chl absorption maximum) – was used as an indicator of the ratio of yellow to green pigments (Sigareva, 2012).

Bream is a predominantly freshwater benthivore and does not migrate over long distances within riverine sections and reservoirs. This allows sampling with reference to specific zones within the range of local populations. It is known that bream in the Rybinsk reservoir form a single population consisting of local herds (groupings) (Ryby..., 2015). These differ in the scale of migration during spawning and feeding periods; both sedentary and mobile individuals that travel long distances in search of food occur.

Bream were caught using a bottom trawl in four reaches of the reservoir: Mologa, Main, Volga, and Sheksna (at stations Protivye, Pervomayka, Vsekhsvyatskoye, Volkovo, Koprino, Myaksa, and Lyubets) (Struktura i..., 2018). To assess Hg content in bream muscles, 43 individuals (18 females and 25 males) were collected in August 2016, and 66 fish (38 females, 13 males, and 15 juveniles) in October 2019. Immediately after capture, weight, Smith length, and body length to the end of the squamation were measured, and sex was determined. Weight of fish without abdominal organs was measured, and scales were taken for age determination (Pravdin, 1966). Dorsal muscle samples (15–20 g) were taken from the left side below the dorsal fin. Muscles were placed in plastic bags, frozen, and stored at −14 °C until analysis.

Prior to analysis, BS and muscle samples were dried at +40 °C to constant weight. Hg concentrations (μg/g dry weight) were determined by pyrolysis atomic absorption spectrometry using a RA-915+ spectrometer with a PYRO attachment (Lumex, Russia). Analytical accuracy was controlled using certified biological materials DORM-2 and DOLM-2 (Institute for Environmental Chemistry, Ottawa, Canada) and certified soil reference samples SDPS GSO 2498-83-2500-83 (NPO Taifun, Obninsk, Russia). Measurements were performed in triplicate; the lower detection limit for Hg was 0.002 μg/g. The coefficient of variation for repeated measurements ranged from 0.05 to 2.5%. When comparing our data with literature values where Hg content was measured in wet samples, recalculation to dry weight was performed (Campbell et al., 2008).

Statistical analysis was performed using STATGRAPHICS Centurion XV.I. Data are presented as medians (Me), means and their standard errors (x ± SE). Differences between parameters were assessed using the Kruskal-Wallis H-test (non-parametric ANOVA). Correlation analysis (Spearman's rank correlation coefficient, r_s) was used to identify relationships and evaluate their strength and direction. Differences were considered statistically significant at $p < 0.05$.

Results

Hg content in the bottom sediments (BS) of the Rybinsk reservoir ranged from 0.001 to 0.361 mg/kg (CV = 74%) (Table 1). The mean and median concentrations were 0.093 and 0.086 mg/kg, respectively. Mean Hg concentrations were higher in the BS of the Sheksna reach and lower in the Mologa and Main reaches (Fig. 1**A**). Due to the high variability of Hg concentrations in BS, differences between the reaches were not significant ($p > 0.05$). Maximum mercury concentrations were recorded in the BS of the Sheksna reach, and minimum in the sediments of the Mologa and Main reaches (Fig. 1**A**).

Based on grain-size composition, four sediment types were distinguished: sands, silty sands, sandy silts, and clayey silts. Clayey silts predominated among the studied BS samples. All sediment types occurred in each reach. Different sediment types differed significantly in Hg content ($p < 0.001$). Significantly higher Hg concentrations were found in clayey silts compared to sands (Table 2). Sandy silts formed a homogeneous group with both sands and clayey silts in terms of Hg content. Hg content in individual BS types was highly variable (CV = 38–85%).

The OM fraction in the BS of the reservoir ranged from 2 to 56% (CV = 57–70%) (Table 1). Significant differences in OM content in BS between reservoir reaches were observed. Maximum OM concentrations were recorded in the Main reach and minimum in the Volga reach (Fig. 1**B**).

Different sediment types differed significantly in OM content ($p < 0.001$). The OM fraction in clayey silts was significantly higher compared to other BS types (Table 2). OM concentrations in individual BS types were highly variable (CV = 34–55%).

Sedimentary pigment concentrations in the BS of the Rybinsk reservoir varied widely (Fig. 1**C**, Table 3). In the BS of the Mologa reach, Chl concentration was higher than in the BS of the Sheksna reach ($p < 0.05$). At the same time, sedimentary pigment content (Chl+Ph) in BS did not differ significantly between reaches. The values of the pigment index E_{480}/E_{665} indicated different degrees of chlorophyll and carotenoid degradation in BS. The mean values of the E_{480}/E_{665} index were minimal for the Main reach and maximal for the Volga reach, suggesting a lower degree of transformation of the algal pigment complex in BS of the lacustrine part of the reservoir.

The distribution of sedimentary pigments over the reservoir bed was consistent with the distribution of different BS types. Mean Chl+Ph concentrations increased in the sequence: sand → silty sand → sandy silt → clayey silt (Table 2).

Hg content in the reservoir BS was significantly positively correlated with water chlorophyll concentration and significantly negatively correlated with sedimentary pigment concentration in BS (Table 4). No significant correlations were found between Hg content in BS and water color, transparency, flow velocity, or BS OM, Chl, and E_{480}/E_{665} ratio.

Bream length ranged from 185 to 365 mm, body weight from 142 to 1145 g. The mean age of individuals ranged from 4+ to 10+ years. Overall, bream samples from different reservoir reaches did not differ significantly in length, weight, or age (Table 5).

Hg concentrations in bream muscles from different reservoir reaches differed significantly (Table 5). Regardless of the year of study, low metal concentrations were found in the muscles of bream caught in the Main and Sheksna reaches, and the highest in the Mologa reach (Fig. 1**D**). Significant differences in Hg content in bream muscles between the study years were observed for the Main and Sheksna reaches. In October 2019, metal concentrations in fish muscle from these reaches were 1.7 and 1.4 times higher, respectively, compared to August 2016 (Table 5). No significant correlations were found between Hg concentration in muscles and bream length, weight, or age (r_s = 0.082, 0.071, and 0.002, respectively; $p > 0.05$).

No significant differences in Hg accumulation in muscles were found between male and female bream (Fig. 2). Hg content in muscles of females from the Mologa reach was significantly higher compared to females from other reaches. Minimal Hg concentrations were observed in muscles of males from the Main and Sheksna reaches, and maximal in males from the Mologa reach.

A negative correlation was found between Hg levels in bream muscles and in BS ($r_s = -0.74$). At the same time, no statistically significant correlations were found between Hg concentrations in muscles and parameters such as sediment particle size, water color, transparency, and flow velocity (Table 4). A positive correlation of Hg content in bream muscles was observed with chlorophyll concentration and the E_{480}/E_{665} ratio in BS, and a negative correlation with the OM fraction. In addition, Hg content in reservoir BS correlated positively with water chlorophyll concentration and negatively with sedimentary pigment concentration in the sediment.

Table 1. Mercury and organic matter contents in bottom sediments of the reaches of the Rybinsk reservoir, 2018. Superscript letters indicate significant differences between the reaches at p < 0.05.

Reach	n	X ± SD	Median	Min–Max	CV, %
		mercury content, μg/g			
Mologa	9	0.069 ± 0.050	0.081	0.011–0.160	72
Main	9	0.070 ± 0.055	0.096	0.007–0.142	78
Volga	12	0.096 ± 0.053	0.094	0.017–0.182	56
Sheksna	30	0.106 ± 0.081	0.085	0.001–0.361	74
		organic matter content, %			
Mologa	9	11.3 ± 7.9^{ab}	9.7	4.0–29.1	70
Main	9	19.7 ± 16.5^{b}	20.9	3.3–56.1	84
Volga	12	10.9 ± 6.9^{a}	9.5	2.0–22.5	63
Sheksna	30	13.9 ± 7.9^{ab}	12.3	2.6–38.0	57

Табл. 2. Contents of mercury, organic matter, and sedimentary pigments in different types of bottom sediments of the Rybinsk reservoir, 2018. Notations as in Table 1.

Type of BS	n	X ± SD	Median	Min–Max	CV, %
		mercury content, μg/g			
Sand	4	0.013 ± 0.005^{a}	0.013	0.007–0.017	38
Silty sand	7	0.019 ± 0.017^{a}	0.014	0.001–0.052	85
Sandy silt	10	0.062 ± 0.037^{ab}	0.049	0.011–0.117	60
Clayed silt	39	0.123 ± 0.065^{b}	0.109	0.021–0.361	53
		organic matter content, %			
Sand	4	3.8 ± 1.3^{a}	3.9	2.2–5.1	34
Silty sand	7	4.5 ± 2.2^{a}	4.0	2.0–7.7	48
Sandy silt	10	9.3 ± 2.8^{a}	10.0	5.5–14.2	30
Clayed silt	39	17.6 ± 9.7^{b}	14.2	3.6–56.1	55
		sedimentary pigment content (Chl+Ph), μg/g dry sediment			
Sand	4	9.0 ± 5.0	5.7	2.8–21.7	96
Silty sand	7	10.8 ± 2.8	8.6	2.2–23.3	64
Sandy silt	10	31.1 ± 6.1	22.6	19.3–72.0	59
Clayed silt	36	100.8 ± 14.7	71.2	15.9–488.8	86

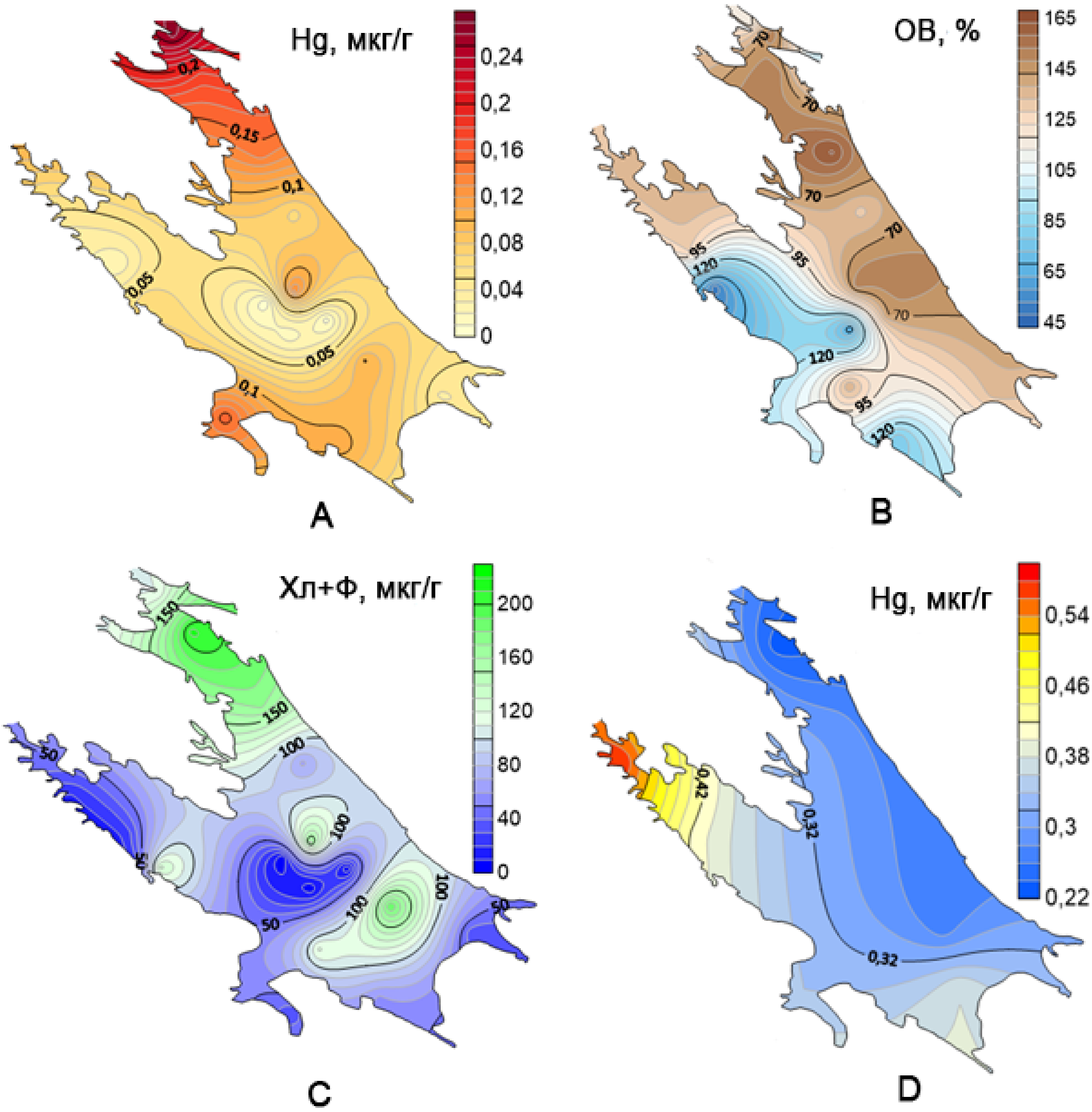

Fig. 1. Spatial variability of some components of bottom sediments of the Rybinsk reservoir: **A** – mercury, **B** – organic matter, **C** – sedimentary pigments; **D** – spatial variability of mercury concentration in bream muscles. I – Mologa, II – Main, III – Volga, IV – Sheksna reach.

Table 3. Sedimentary pigment content in bottom sediments of the reaches of the Rybinsk reservoir, 2018. Notations as in Table 1. The numerator shows the X ± SD; the denominator shows the minimum and maximum values.

Reach	n	Chl, µg/g dry sediment	Ph, µg/g dry sediment	Chl+Ph, µg/g dry sediment	E_{480}/E_{665}
Mologa	9	21.4 ± 39.7[b] 0.9–125.4	76.9 ± 101.8 5.9–323.5	98.4 ± 140.6 6.8–448.8	3.0 ± 0.7[ab] 2.3–4.4
Main	9	20.9 ± 20.9[ab] 59.4–59.0	88.3 ± 77.2 2.4–195.7	109.2 ± 96.6 2.8–255.1	2.5 ± 0.5[a] 1.6–3.5
Volga	11	7.7 ± 6.3[ab] 0.7–23.4	58.6 ± 40.3 5.5–154.0	66.2 ± 46.5 6.2–177.4	3.1 ± 0.5[b] 2.3–4.0
Sheksna	28	7.2 ± 7.6[a] 0.8–26.0	44.7 ± 44.8 1.4–323.5	52.0 ± 51.2 2.2–448.8	2.9 ± 0.9[ab] 1.4–5.8

Table 4. Correlations between Hg content in bottom sediments and bream *Abramis brama* muscles with some parameters from the fishing sites in the Rybinsk reservoir. Statistically significant differences are shown in bold; the range of the parameter is given in parentheses. * – according to: Mineeva and Semadeni, 2020.

Parameter	Correlation coefficient, r_s	
	bottom sediments	bream muscles
particles of bottom sediments > 0.01 (2.1–93.7 %)	0.14	−0.33
particles of bottom sediments < 0.01 (0.9–41.8 %)	0.20	−0.33
organic matter in BS (1.9–38.9 %)	0.31	**−0.77**
Chl in BS (0.4–125.4 µg/g dry sediment)	−1.00	**0.74**
Chl+Ph in BS (9.2–275.6 µg/g dry sediment)	**−0.74**	0.26
E_{480}/E_{665} ratio in BS (2.04–2.70)	−0.32	**0.58**
Chl in water* (10.1–28.5 мкг/л)	**0.82**	−0.51
water color (40–240 Pt-Co)	−0.09	0.35
water transparency (80–170 cm)	−0.27	0.47
flow velocity (0.1–0.89 m/s)	−0.23	0.37

Table 5. Length, weight, age, and mercury content in the muscles of bream from the reaches of the Rybinsk reservoir. The numerator shows the X ± SE; the denominator shows the minimum and maximum values in the sample. Superscript letters indicate statistically significant differences within each column at $p \leq 0.05$; * – median age values are given in the numerator.

Reach	n	Smith length, mm	Length, mm	Weight, g	Eviscerated weight, g	Age*, years	Hg, µg/g dry weight
				August 2016			
Mologa	9	351 ± 4^{b} / 328–363	324 ± 4^{b} / 298–342	752 ± 27^{b} / 625–872	670 ± 24^{b} / 547–776	9 / 7–9	0.578 ± 0.045^{c} / 0.419–0.735
Main	10	353 ± 4^{a} / 335–369	324 ± 4^{b} / 305–341	751 ± 31^{b} / 599–889	664 ± 25^{b} / 534–783	8.5 / 7–9	0.204 ± 0.018^{a} / 0.128–0.290
Volga	9	339 ± 5^{b} / 319–359	313 ± 4^{ab} / 297–331	669 ± 34^{ab} / 541–820	597 ± 31^{ab} / 483–730	8 / 8–9	0.330 ± 0.485^{b} / 0.162–0.597
Sheksna	14	332 ± 6^{ab} / 303–372	305 ± 5^{a} / 282–338	637 ± 33^{a} / 475–867	572 ± 28^{a} / 434–759	8 / 7–9	0.220 ± 0.019^{a} / 0.138–0.334
				October 2019			
Mologa	20	329 ± 9 / 205–380	302 ± 9 / 185–350	627 ± 48 / 142–953	556 ± 41 / 129–850	7^{b} / 5–10	0.498 ± 0.046^{b} / 0.207–0.880
Main	18	310 ± 9 / 235–370	284 ± 8 / 215–340	511 ± 42 / 207–875	457 ± 37 / 185–770	7^{a} / 4–8	0.337 ± 0.023^{a} / 0.216–0.588
Volga	7	331 ± 20 / 250–395	303 ± 19 / 228–365	671 ± 133 / 248–1145	553 ± 101 / 235–942	7^{ab} / 4–10	0.376 ± 0.045^{ab} / 0.265–0.617
Sheksna	21	316 ± 7 / 255–362	292 ± 6 / 233–332	555 ± 37 / 260–885	489 ± 31 / 231–735	7^{ab} / 4–9	0.297 ± 0.022^{a} / 0.154–0.572
				Mean			
Mologa	29	336 ± 7 / 205–380	309 ± 6 / 185–350	666 ± 35 / 142–953	592 ± 31 / 129–850	8 / 5–10	0.523 ± 0.035^{c} / 0.207–0.880
Main	28	325 ± 7 / 235–370	298 ± 6 / 215–341	597 ± 37 / 207–889	531 ± 32 / 185–783	7 / 4–9	0.289 ± 0.020^{ab} / 0.128–0.588
Volga	16	336 ± 9 / 250–395	309 ± 8 / 228–365	670 ± 59 / 248–1145	578 ± 46 / 235–942	8 / 4–10	0.350 ± 0.033^{b} / 0.162–0.617
Sheksna	35	323 ± 5 / 255–372	297 ± 4 / 233–338	588 ± 26 / 260–885	522 ± 23 / 231–759	8 / 4–9	0.266 ± 0.016^{a} / 0.138–0.572

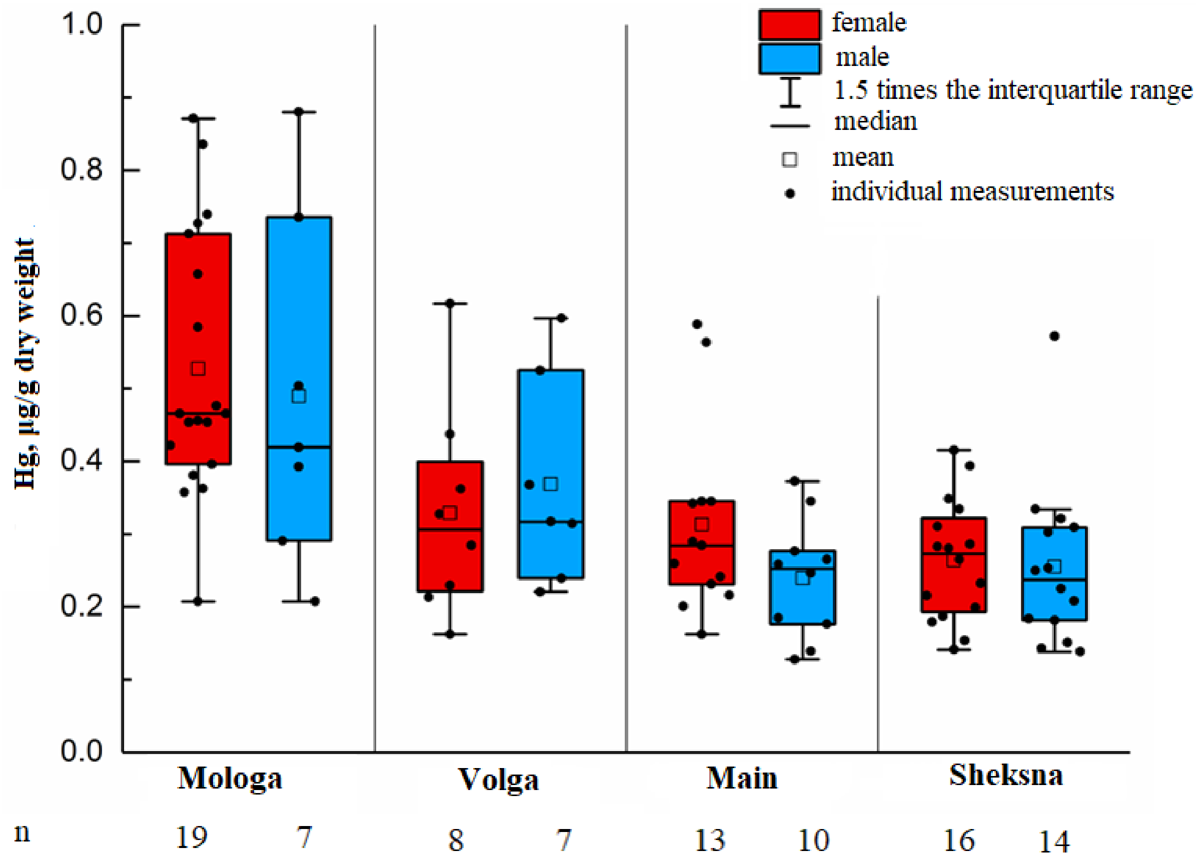

Fig. 2. Mercury content in the muscles of female and male bream from the Rybinsk reservoir in 2016 and 2019. Different letter indices indicate significant differences between individuals of the same sex from different reaches of the reservoir ($p \leq 0.05$).

Discussion

The spatial distribution pattern of Hg in the bottom sediments (BS) of the Rybinsk reservoir has remained stable for a long time. The highest metal content is recorded near the city of Cherepovets and gradually decreases downstream along the Sheksna river up to the dam area of the reservoir, reaching concentrations of 0.100 µg/g (Chuiko et al., 2015). In the BS of the Uglich reservoir, located upstream, average Hg concentrations were 2.5 times higher compared to the BS of the Rybinsk reservoir (Udodenko et al., 2018a). In contrast, in the BS of the Gorky and Cheboksary reservoirs, located downstream, Hg concentrations were 1.5 times lower (Udodenko et al., 2018b).

Hg content in BS depends on the origin of sedimentary material, the quantity and composition of organic matter (OM), water pH, etc. (Dickson et al., 2019). In BS, Hg is present in a form unavailable to biota, but part of the metal is bound to OM components or sorbed onto fine-particle surfaces (He et al., 2019). Hg enters the trophic web primarily as methylmercury, most of which is produced by microorganisms (Hudelson et al., 2020). The rate of methylmercury production in aquatic ecosystems is determined by the physicochemical parameters of water, BS, and suspended matter (pH, quantity and composition of dissolved substances, oxygen content, etc.) (Ullrich et al., 2007). At the same time, it has been shown that the rate of methylmercury formation is weakly correlated with the total Hg content in the environment. Thus, under certain conditions, BS can be a source of Hg input into local food webs.

The results of the present study are consistent with previously published data on bream caught from the Rybinsk reservoir (Gorbunov et al., 2018; Stepanova and Komov, 1997; Tyutin et al., 2019), which, however, were based on limited sample sizes (< 30 specimens) and mainly concerned the Volga reach. Comparison with data from other reservoirs of the Volga basin revealed both similarities and significant differences. For example, Hg concentrations in bream muscle reported by A.V. Gorbunov et al. (2018) for reservoirs of the Volga basin (mean 0.045 µg/g wet weight, or ~0.225 µg/g dry weight) are comparable to our values (0.353 μg/g dry weight). In contrast, the values obtained by T.I. Moiseenko et al. (2005) for the Ivankovo reservoir (0.019 ± 0.003 μg/g dry weight) are approximately 18 times lower. Probable reasons for such discrepancies include the temporal factor (sampling in August–September 2000) as well as differences in sample preparation and analytical methods.

In our study, regardless of the year of observation, low metal concentrations were recorded in the muscles of bream caught from the Sheksna and Main reaches, and the highest in those from the Mologa reach. Significant differences in Hg content in bream muscles between years were registered for the Sheksna and Main reaches. In October 2019, metal concentrations in bream muscle from these reaches were 1.7 and 1.4 times higher, respectively, compared to August 2016. Earlier, B.A. Flerov (1990) noted that in autumn, bream may migrate to the Sheksna reach for wintering from uncontaminated areas of the Rybinsk reservoir. Thus, due to bream migration during the year, a single sample may contain both individuals residing in industrially polluted areas and those that have moved there from cleaner locations. A study of heavy metal (Cd, Pb, Al, Cr, Cu, Mn, Fe, Co, Ni, V) accumulation in bream muscle from the Rybinsk reservoir revealed intensive accumulation of Al, Fe, and Co in individuals caught from the Sheksna reach (Payuta et al., 2023a).

Fish size and age largely determine their Hg content (Wiener et al., 2002). Unlike other trace elements, Hg accumulation in the body is generally positively correlated with fish length and weight (Dang and Wang, 2012; Hanna et al., 2015). However, in our study, no significant correlations were found between metal concentration in bream muscle and fish length, weight, or age. Earlier, Gorbunov et al. (2018) also noted the absence of a relationship between Hg concentration in muscle and body weight of bream from the Volga basin.

No significant differences in metal accumulation in muscles between females and males were found in this study (Fig. 2). Generally, Hg concentrations in female bodies are higher because they need to consume more food to cover the energy costs of egg production, but only a small portion of the metal is transferred to the eggs and eliminated from the body during spawning (Nicoletto and Hendricks, 1988).

We observed a negative correlation between Hg content in bream muscles and in BS of the reservoir reaches ($r_s = -0.74$). Earlier, using the example of drainage-free neutral and acidic lakes in the Darwin state nature biosphere reserve (Vologda Oblast), a negative relationship was also shown between Hg concentrations in fish muscles and its content in BS. At the same time, maximum metal concentrations in BS were characteristic of neutral lakes, while in fish muscles they were characteristic of acidic lakes (Stepanova and Komov, 2004).

Hg methylation in water layers plays an important role because the water volume is generally much larger than the volume of surface BS (Bezel et al., 1983). The vast majority of Hg in the water column is associated with suspended matter (the Hg accumulation coefficient by suspended matter is 1.34–1.88 × 10^5). Thus, suspended particles (less than 20–0.45 μm) contain 10^5 times more Hg than in dissolved form (Moore and Ramamoorthy, 1987).

Phytoplankton plays an important role in reservoir ecosystems. Through photosynthesis, it creates the main pool of OM, thereby participating in the main processes of transformation and transport of trace metals (including Hg) in aquatic ecosystems. In the Rybinsk reservoir, the highest mean chlorophyll a concentrations are observed in the Volga and Sheksna reaches, intermediate in the Main Reach, and low in the Mologa reach (Semadeni, 2023). Thus, the distribution of chlorophyll a in water corresponds to the spatial distribution pattern of sedimentary pigments in BS (Fig. 1**C**).

The Mologa and Sheksna reaches are fed mainly by runoff from wetland areas of highly colored surface waters containing significant amounts of dissolved OM. In the presence of larger amounts of highly colored OM, Hg forms stable complexes with humic substances (Linnik and Nabivanets, 1986; Sukhenko, 1995). Earlier, it was shown that the presence of wetlands in the catchment, water humification, and low pH values are often associated with Hg accumulation in fish organs and tissues (Moiseenko and Gashkina, 2016; Rask et al., 2021).

The amount of Hg entering the human body with food in the Russian Federation suggests limiting the consumption of fish with metal concentrations above the regulatory values: 0.30 mg/kg for non-predatory and 0.60 mg/kg for predatory freshwater fish[1]. In our study, Hg concentrations recalculated to wet weight were 0.10 ± 0.01 mg/kg wet weight for the Mologa reach, 0.06 ± 0.00 mg/kg for the Main

[1] SanPiN 2.3.2.1078-01. Hygienic requirements for safety and nutritional value of food products.

reach, 0.07 ± 0.01 mg/kg for the Volga reach, and 0.05 ± 0.00 mg/kg for the Sheksna reach. Earlier, when assessing the accumulation levels of trace metals (Cd, Pb, Al, Cr, Cu, Mn, Fe, Co) in bream muscle, the safety of its consumption by humans was also noted (Payuta et al., 2023a). Moreover, no potential non-carcinogenic risk to human health from the concentrations of the same trace metals in bream muscle was demonstrated (Payuta et al., 2023b). Thus, the obtained results indicate no health risk for humans consuming bream from the Rybinsk reservoir. The exception is individual specimens from the Mologa reach: according to calculations based on WHO/FAO, European Food Safety Authority, and US Environmental Protection Agency recommendations, restrictions should apply to 3%, 1%, and 0% of fish caught for children aged 2–5 years, 6–10 years, and adults, respectively (Gremyachikh et al., 2022).

Conclusions

The spatial distribution of Hg in the bottom sediments (BS) and muscles of bream from the Rybinsk reservoir exhibits pronounced heterogeneity. The maximum Hg concentrations in BS were observed in the Sheksna reach, and the minimum in the Mologa reach. At the same time, Hg content in the BS of the Rybinsk reservoir is 2.5 times lower than in the upstream Uglich reservoir, but 1.5 times higher than in the downstream Gorky and Cheboksary reservoirs.

Regardless of the year of observation, the lowest Hg concentrations in bream muscles were recorded in individuals from the Sheksna and Main reaches, and the highest in those from the Mologa reach. No statistically significant differences in Hg accumulation were found between males and females; however, in the Mologa reach, individuals of both sexes were characterized by higher metal content compared to the other reaches of the reservoir. Correlation analysis revealed no significant relationships between Hg accumulation and fish length, weight, or age.

A significant negative correlation was found between Hg content in bream muscles and in BS (r_s = −0.74). Hg concentration in muscles correlated positively with the content of chlorophyll and sedimentary pigments (Chl+Ph) in BS and negatively with the proportion of organic matter.

In contrast, Hg content in the reservoir BS was positively correlated with chlorophyll concentration in water and negatively correlated with sedimentary pigment concentration in the sediment. Water color, transparency, and flow velocity parameters did not significantly affect the studied variables.

In most cases, Hg content in the BS and bream muscles of the Rybinsk reservoir is comparable to data from other researchers and does not exceed established standards.

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