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The Content of Metals in Tissues and Organs of Fish of Different Trophic Levels in the Estuary of the Kama River

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Abstract. The content of metals (Fe, Mn, Al, Zn, As, Cu, Cr, Pb, Ni, Cd) in the tissues and organs of bream and pike perch, living in the rivers Mesha and Kama (tributaries of the Volga River) is compared. It is shown that the accumulation of metals in the tissues and organs of fish depends more on their habitats than on the trophic status of the fish. An increased content of Al, Fe, Mn in the gills and liver of the Meshi River fish was found, which is presumably associated with secondary water pollution from bottom sediments. In the tissues and organs of the fish of the Kama River, the content of Cu, Ni, Cr is higher than in the Meshi fish, without significant differences in their content between species (bream and pike-perch), in contrast to the Meshinsky bay, which distinguishes between the accumulation of metals in tissues and organs bream and pike-perch.

1. Introduction

In the aquatic environment, pollutants exist solely in the form of mixtures and their content, as well as transformation, depending on numerous factors, which eliminates the physicochemical assessment of water quality. In this case, the most optimal is to study the response of hydrobionts to the effect [1, 2]. Fish is one of the most suitable biomarkers because they are sensitive to the presence of pollutants, their reaction to changes in the environment is well studied, including through the accumulation of toxicants and pathological changes in their organs [3-6]. In addition, "contaminated" fish poses a threat to human health [7]. The quantitative determination of metals in fish is the most convenient way to assess the content of elements in a bioavailable form and allows identifying elements-markers of anthropogenic pollution of the territory [3, 8].

In an organism, metals can participate in metabolic processes; biosynthesis of DNA and RNA, maintenance of functioning of the hormonal system, but at the raised maintenance they can cause toxic effects [3, 5, 9-16]. Partially the organism can regulate the content of metals and get rid of them because of biotransformation and detoxification mechanisms [4, 16-18]. The interrelationship between the increased content of metals in water and their accumulation in fish is noted [19].

The pathway of metals into the fish body can be through gills from water or through the digestive system with food. In this regard, to study the peculiarities of accumulation of metals in tissues and organs of fish it is advisable to take the inhabitants of the different ecotopes pelagic and benthic zone, which



allows identifying the flow of metals from the bottom sediments during the resuspension and through the benthos. Receipt of elements from benthos can be the dominant way of accumulation, and benthic fish by the most informative species-biomarkers [5, 17, 19-23].

The aim of the work was to assess the content of metals in the tissues and organs of fish of different trophic levels living in the estuary of the Kama River.

2. Material and methods

2.1. Study area

The objects of the study are Meshinsky Bay and the channel part of the mouth of the Kama River. The catchment area of the Meshi River is 4180 km²; the average density of the river network is 0.35 km / km². The catchment area of the Kama River is 507 000 km²; water flow is 3 500 m³ / s.

2.2. Sample collection and laboratory analysis

During the expedition, 17 specimens of bream (*Abramis brama*) and 12 specimens of pikeperch (*Sander lucioperca*) aged 6-9 years were selected from fish caught by a trawl. The age of the fishes was determined from the scales and spikes of the rays of the pectoral fin [24]. The content of elements (Fe, Mn, Al, Zn, As, Cu, Cr, Pb, Ni, Cd) in fish tissues and organs was estimated by atomic emission spectroscopy with inductively coupled plasma on an ICPE-9000 device after wet ashing [25]. For analysis, gills, liver and muscles were used [26].

The fish condition factor was calculated by the following equation (1):

$$CF = Wt/L^3 \times 100 \quad (1)$$

where Wt is the total weight of the fish (grams) and L is the total length (centimetres).

Metal pollution index was calculated by the equation (2):

$$MPI = (Cf_1 \cdot \dots \cdot Cf_n)^{1/n} \quad (2)$$

For statistical analysis was employed Statistica 8.0. Differences in the data were evaluated with Kruskal–Wallis tests. Differences were considered significant when $p < 0.05$. The Spearman correlation analysis (r) was used to verify the influence of water parameters.

To compare the content of metals in the tissues and organs of fish, the data were normalized according to formula (3):

$$X_n = (X_i - X_{\min}) (X_{\max} - X_{\min})^{-1} \quad (3)$$

3. Results and discussions

Morphometric indicators of bream from both habitats were identical. The length of the bream in the Meshinsky Bay averaged 29 ± 2 cm, the mass 544 ± 96 g, along with the riverbed. The Kama is 29 ± 1 cm, weight is 561 ± 34 g. The parameters of the weight and length of pikeperch from the river. The meshes were higher in comparison with the fish from the Kama River: 51 ± 3 cm (length) and 1843 ± 287 g (mass) in the Mecha River compared to 41 ± 3 cm (length), 945 ± 160 g (mass) in the Kama River. The coefficient of fatness (CF) was 2.13 (bream) and 1.42 (pike-perch) for bream and zander of the Meshi and Kama rivers; 2.2 (bream) and 1.33 (pike-perch), respectively. According to the CF index, there were no significant differences depending on the habitat.

The results of the study (table 1) showed that the content of Cr, Cu, Ni (figure 1) is significantly higher in all tissues, both bream and pikeperch from the Kama River; the Mn content is reliably lower. Al accumulates mainly in the organs and tissues of bream, which is due to the bottom life. The Fe content is higher in the liver of the Meshi River fish, which may be due to natural causes - the composition of mineral rocks in the river basin, which is indirectly confirmed by the high content of Al and Fe in the gills.

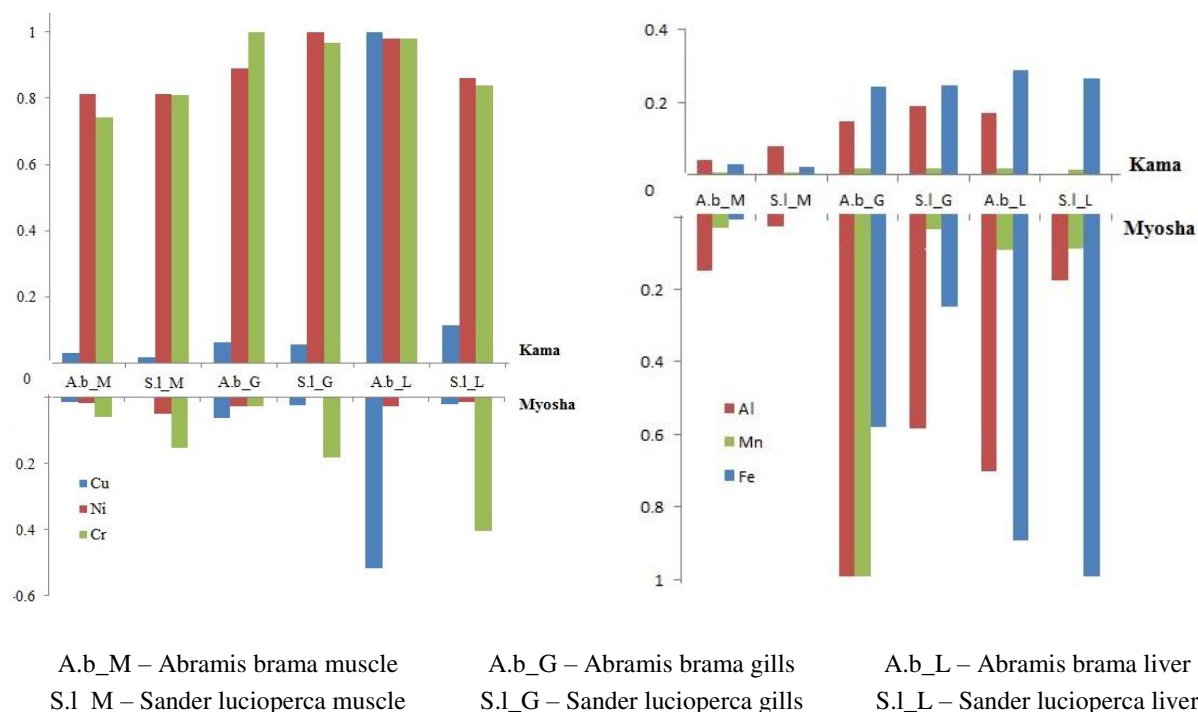


Figure 1. The normalized content of Cu, Ni, Al, Mn, Fe and Cr in tissues and organs of bream and pike-perch from different habitats.

The increased content of Cd and Ni (table 1), mostly of technogenic origin, in the Kama river fish, is probably due to anthropogenic activity in the river basin. The As content is higher in the liver and gills of the Mesha pike perch, unlike the muscles, where its content is higher in the pike perch of the Kama River. Correlation analysis showed a close relationship between Cr and Ni in the liver ($r > 0.8$), Pb and Cr in the gills ($r > 0.6$) of bream, regardless of habitat.

Despite the fact that primarily interspecific differences in the accumulation of elements due to physiological characteristics, an important role is played by environmental factors. In terms of metal content in tissues and organs, pikeperch and bream from the Kama River differ less in comparison with fish from the Meshinsky Bay. A significant difference ($p < 0.05$) noted the content of Al, Cu and Zn in liver and Cu in the muscle of pikeperch and bream from the river Kama. The absence of differences in the content of elements in the gills due to the similarity of the composition of water at different depths, as well as predominantly sandy type of bottom sediments in the studied area of the Kama river, which have a reduced ability to sorb metals, therefore, do not pose a threat to secondary water pollution. Bream and pikeperch of the Meshinsky Bay differ significantly in the content of As, Cr and Cu in the liver; Cu, Fe, Mn and Zn in gills; As, Al, Cu, Fe and Mn - in muscles. It should be noted that Cu is more accumulated in the tissues and organs of bream (figure 1), and As and Cr in the pikeperch liver. The As content is larger in the tissues and organs of the pike perch on all the sites examined. The increased content of Fe and Zn in the gills of bream can be associated with their increased content in the bottom water and the peculiarities of migration of these metals at the boundary of water-bottom sediments when the oxygen regime changes.

The calculated metal pollution index (MPI) (table1) showed that unlike the fish of the Meshi River, characterized by the accumulation of metals mainly in the liver, the fish of the Kama River accumulates metals in all tissues evenly.

Table 1. Average content of elements in tissues and organs (mg/kg of dry weight).

Elements	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	MPI
the Myosha river bay											
Bream muscle	12.38±2.18 ^e	4.63±0.51 ^e	< 0.001	0.55±0.12 ^{b,d}	1.03±0.09 ^{b,c}	26.82±2.25 ^e	3.69±0.46 ^{b,c,d}	0.12±0.05 ^{b,d}	0.13±0.04 ^d	14.64±0.49 ^d	2.1
Bream gills	53.99±6.29 ^{b,d}	8.85±1.54	0.06±0.04	0.46±0.05 ^{b,d}	3.09±0.29 ^e	340.67±21.53 ^{b,c,d}	75.25±6.04 ^{b,c,d}	0.18±0.08 ^{b,d}	0.43±0.14	43.70±1.22 ^e	4.5
Bream liver	39.62±10.38 ^d	29.08±3.00 ^{b,c}	0.27±0.09	0.39±0.11 ^{b,c,d}	22.34±2.90 ^{b,c,d}	513.24±29.09 ^d	8.19±0.80 ^{b,d}	0.19±0.08 ^{b,d}	1.77±1.17	73.62±11.95	7.0
Pike-perch muscle	6.19±0.53 ^a	2.02±0.56 ^a	< 0.001	0.81±0.16 ^{d,b}	0.46±0.03 ^{d,ab}	18.64±2.10 ^{ab}	0.81±0.12 ^{d,ab}	0.33±0.10 ^{d,e}	0.16±0.04	13.62±0.80	1.5
Pike-perch gills	33.72±7.78 ^{d,b}	13.78±2.83	0.05±0.03	0.88±0.22 ^{d,b}	1.45±0.09 ^{ab}	158.3±17.32 ^{d,a}	3.87±0.33 ^{a,ab}	0.01±0.009 ^{d,b}	0.10±0.07	36.87±1.27 ^{a,b}	2.0
Pike-perch liver	13.61±5.00	121.27±16.89 ^{d,ab}	< 0.001 ^b	1.49±0.34 ^{d,ab}	1.41±0.32 ^{d,ab}	567.86±40.28 ^{d,b}	8.02±3.32 ^d	0.10±0.009 ^{d,b}	0.58±0.35	62.79±5.26 ^b	7.3
riverbed of the Kama River											
Bream muscle	6.51±0.54	5.00±1.38	< 0.001	2.41±0.17 ^{a,c}	1.71±0.19 ^{a,d,e}	35.64±4.04 ^e	1.28±0.1 ^{a,c}	5.17±0.32 ^{a,c}	3.97±2.75	14.92±1.81	5.0
Bream gills	11.79±0.83 ^{a,c}	7.91±1.34	< 0.001	3.12±0.43 ^{a,c}	3.14±0.39 ^e	153.09±9.29 ^a	2.20±0.09 ^{a,c}	5.66±0.26 ^{a,c}	2.85±2.09	48.42±5.22 ^e	8.5
Bream liver	13.01±1.43 ^d	6.72±1.74 ^{a,c}	0.51±0.14 ^e	3.07±0.31 ^{a,c}	42.80±6.61 ^{a,d,e}	177.60±12.95 ^e	2.17±0.11 ^a	6.22±0.63 ^{a,c}	1.83±0.93	81.68±1.97 ^{d,e}	8.6
Pike-perch muscle	8.37±1.67	5.60±2.01	0.01±0.00	2.59±0.16 ^{c,a}	1.14±0.11 ^{c,b}	30.85±2.75	1.30±0.1 ^{ca}	5.17±0.46 ^{ca}	2.25±0.79 ^a	12.42±0.60 ^a	4.5
Pike-perch gills	13.90±2.10 ^{ca}	5.36±1.56	< 0.001	3.03±0.51 ^{ca}	2.90±0.28	154.89±13.18 ^{ca}	2.14±0.23 ^{ca}	6.36±1.11 ^{c,a}	0.55±0.40	48.20±2.22	5.7
Pike-perch liver	4.54±0.62 ^{ba}	15.35±7.27 ^c	0.14±0.08	2.68±0.26 ^{ca}	5.33±0.55 ^{c,ba}	165.70±25.84 ^{ca}	1.92±0.17 ^{ca}	5.48±0.51 ^{ca}	1.38±1.25	50.12±4.57 ^b	5.3

The letters indicates significant differences

a – Abramis brama from the Myosha river

b – Abramis brama from the Kama river

c – Sander lucioperca from the Myosha river

d – Sander lucioperca from the Kama river

Analysis of the content of metals in the tissues and organs of the fish made it possible to identify 3 clusters (figure 2): the first cluster includes bream and pike perch of the Kama River; second and third clusters, formed by bream and pike-perch Meshinsky Bay.

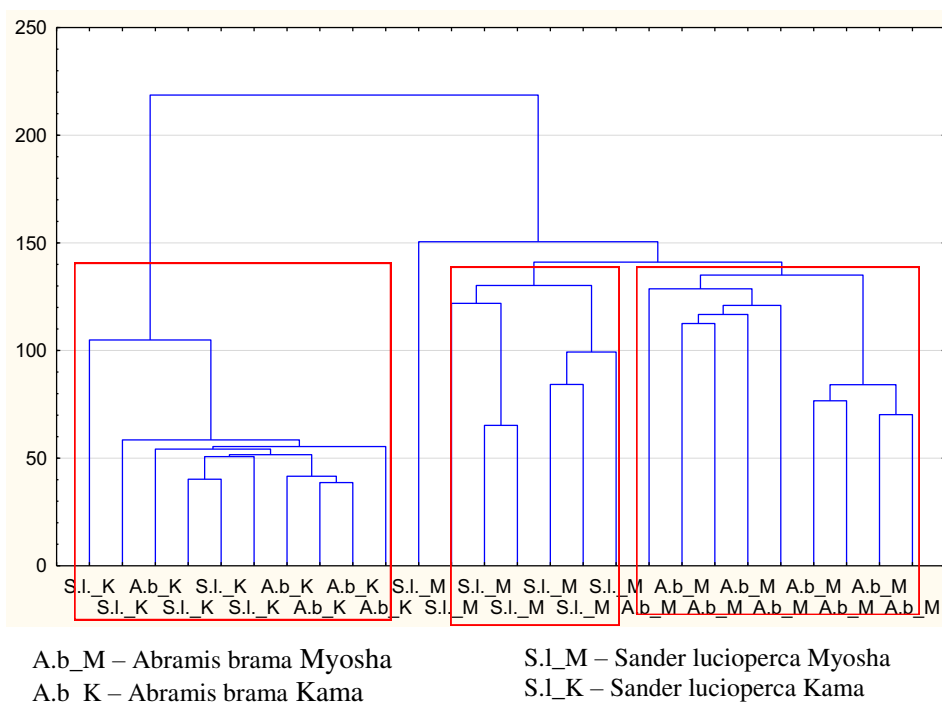


Figure 2. Cluster analysis.

The isolation of the first cluster is due to the high content of Cu, Cr and Ni in the muscles and liver of pikeperch and the bream of the Kama River. The division of data into 2 and 3 clusters is associated with the specific differences in the accumulation of metals in the Meshinsky Bay, where special habitats for the bottom and pelagic fish are formed. Al, Fe, Mn enter the water from predominantly muddy bottom sediments, which leads to an increase in their content in the tissues and organs of the fish.

4. Conclusion

The results of the study showed that the accumulation of metals in the tissues and organs of fish depends more on their habitats than on the trophic status of fish. The increased content of Al, Fe, Mn in the gills, muscles, liver of bream and pikeperch, living in the Meshinsky Bay, where silt bottom sediments are noted and possible secondary contamination of water by these metals with oxygen regime change is revealed. In the tissues and organs of the Kama river fish, the content of Cu, Ni, Cr is higher than in the Mesh fish, without significant differences in their content between species (bream and pike-perch).

Two ecotopes (bottom and pelagic) are distinguished in the Meshinsky Bay, which forms various conditions for the entry and accumulation of metals in the tissues and organs of bream and zander. Differences between the content of metals in the tissues and organs of bream and pikeperch of the Kama River are not significantly different. The absence of differences in the content of metals is due to the similarity of the composition of water at different depths, and predominantly the sandy type of bottom sediments in the investigated section of the Kama River, which has a reduced ability to sorb metals.

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