Трансформация экосистем
Ecosystem Transformation

ISSN 2619-094X Print
ISSN 2619-0931 Online
www.ecosysttrans.com

Review

Trace element composition of commercial fish of the Amur River Basin: A review

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Received: 11.05.2022
Revised: 19.05.2022
Accepted: 20.05.2022
Published online: 15.07.2022

DOI: 10.23859/estr-220511
UDC 574.64

Translated by S.V. Nikolaeva

Abstract. This review presents literature data on the presence of heavy metals in commercial fish species from the Amur River basin. The results of the research show that the trace element composition of fish differs in different parts of the Amur basin; it can exceed permissible concentrations for standardized elements. However, a lack of actual fresh data on heavy metal content of hydrobionts makes it difficult to assess the ecological state of the Amur River or analyze the risks to public health.

Keywords: heavy metals, pollution, pollutants, accumulation, hydrobionts, ichthyophauna, essential and toxic elements, maximum permissible concentrations

To cite this article. Bizborodov, V.O. et al., 2022. Trace element composition of commercial fish of the Amur River Basin: A review. *Ecosystem Transformation* **5** (3), 45–54. https://doi.org/10.23859/estr-220511

Introduction

The Amur River is one of the largest rivers in Russia. As a result of serious anthropogenic pressure, including from China, the problem of heavy metal (HM) pollution in the Amur River basin, as well as their accumulation in hydrobionts (especially fish), becomes especially relevant (Chizhikova et al., 2011). Fish are convenient objects of research, but many are also valuable commercial species. Thus, they can be used to predict various types of impacts on aquatic ecosystems, and the health of the people who use them as food (Kashulin, 2000).

Heavy metals are rare (dispersed, trace) elements (metals) with an atomic mass of more than 50 a.m.u., which are in high exogenous concentrations in environmental objects (soil, water, atmosphere, organisms); they may or may not have certain biological functions in the body (Dabakhov et al., 2005).

It is known that heavy metals in aquatic ecosystems are not subject to decomposition and degradation. In addition, they are able to accumulate in the tissues and organs of hydrobionts, becoming highly toxic to living organisms of all trophic levels, including humans (Kuramshina et al., 2012).

Fish are excellent markers for measuring anthropogenic impact on aquatic ecosystems, in particular, the content of heavy metals and other trace elements in water (Vorobiev and Samilkin, 1980). Despite the scale and seriousness of the problem, the number of works on the study of heavy metals in fish from the basin of the Amur River is small (Chernova et al., 2008; Chukhlebova and Berdnikov, 2011; Chukhlebova and Panasenko, 2010; Luchsheva et al., 2000; Pakusina et al., 2019; Polyakov and Revutskaya, 2015; Revutskaya and Cheglokova, 2015; Zubarev and Burik, 2019; etc.). In addition, the fragmentation of research sites makes it difficult to form a general idea of the state of commercial objects in this area. In this regard, the purpose of our review was to analyze and systematize the available literature data on the content of toxic elements in commercial fish of the basin of the Amur River, as well as to assess the safety of fishery products.

Brief geographical description of the Amur River basin

In the list of the greatest rivers of the world, the Amur is in tenth place, and its basin (after the Yenisei, Ob and Lena) occupies the fourth position among the rivers of Russia. The area of the basin is 1861 thousand km^2, the length of the river is 4444 km (from the confluence of its two sources, Shilka and Argun, 2824 km) (Gotvansky, 2007).

Amur River basin is located within three states (Fig. 1). The Russian part occupies 1003 thousand km^2 of territory; the part belonging to the People's Republic of China (PRC) is 820 thousand km^2, and the part belonging to Mongolia is 32 thousand km^2 (Gotvansky, 2007; Nikolaeva, 2005).

The water regime of the rivers of the Amur River basin is characterized by a rather uneven intra-annual distribution. Winter runoff (from November to March) is usually 5–10 % of the annual value, while in the summer – autumn period it reaches 75–80 % (Simonov et al., 2015).

The mean long-term annual module of the runoff of the Amur River, is 6.1 l/(s × km²), which corresponds to a water discharge at the mouth of 11330 m^3/s, or 357 km^3/year. The volume of runoff from the territory of neighboring countries (PRC and Mongolia) totals 28 %. The interannual amplitude of the annual volumes of the Amur runoff reaches 314 km^3 (Kalugin and Motovilov, 2018).

The Amur River basin is located in the temperate climate zone, where the monsoon character of the atmospheric circulation clearly prevails in conjunction with cyclonic activity. Summer precipitation of the monsoon type covers enormous areas (100–200 thousand km^2 and more). Their duration is 20–30 days, and the amount of water from a rainy day often exceeds the monthly norm by 2–3 times (200–400 mm). Due to abundant precipitation, as well as the presence of permafrost and impervious rocks, the Amur mountain river is characterized by rapid surface runoff. This, in turn, leads to an increased rise in the water level (1–3 m/day) and the formation of heavy rain-floods.

The rivers of the Amur River basin according to the conditions of the water regime belong to the Far Eastern type, which is clearly characterized by the rain type of nutrition. Its share in the basin of the Upper and Middle Amur is 50–70 %, in the basin of the Lower Amur it is 60–85 %. Snow supply accounts for 5–10% of the runoff, while underground recharge accounts for 10–20% (Simonov et al., 2015).

Fig. 1. Amur River Basin.

The most intense sedimentation is characteristic of the Middle Amur Lowland. The surface of the bottom of the river valley rises here by 1.7–1.8 mm/year, or 17–18 cm per 100 years (Simonov et al., 2016).

Annual water consumption values for the Amur basin differ between the countries where it is located. For example, the volume of annual water consumption in its Russian part, where fewer than 5 million people live, reached 1.18 km^3 in 2010, while in the Chinese part of the basin (with a population of about 70 million people) this figure was 36 km^3.

The per capita values for water consumption in the Amur River basin are also very different. They are 734.5 m^3/person in Inner Mongolia Autonomous Region and 712.9 m^3/person in Heilongjiang Province, while in Jilin Province these values are several times lower. In the Russian part of the Amur River basin, water consumption per capita averages 216 m^3/person in a year. This difference is primarily due to the use of water for agriculture (Simonov et al., 2015).

Trace elements in fish in the Amur River Basin: overview by site

Aquatic biological resources, in particular fish, are widely used for food due to their high content of protein, polyunsaturated fatty acids, vitamins and trace elements. However, it is necessary to control the trace element composition, since the accumulation of heavy metals in the tissues of aquatic organisms leads to an increase in their concentrations, which means that the consumption of such organisms is highly undesirable and can lead to various pathologies (Shulgin et al., 2007). Therefore, it is very important to regularly assess the quality of commercial fish in terms of the content of essential (iron, cobalt, copper, chromium, manganese, zinc, etc.) and non-essential (arsenic, cadmium, mercury, lead, etc.) elements in them.

For convenience and a more accurate comparison of the results, it was decided to divide the basin of the Amur River into districts (Fig. 2).

Trace element composition in the fish of the Nizhneamursky site

Studies of HM concentrations in the internal organs of Gibel carp, also called Prussian carp *Carassius auratus gibelio* (Bloch, 1782) from various water bodies of the river basin. The maximum values in the Amur fish were noted in the organs responsible for the processes of reproduction and deposition of substances, i.e., in the gonads and the liver. Iron accumulated in the greatest amounts, the maximum concentration was observed in the liver of fish from the main channel

Fig. 2. Schematic map of research locations from 2000 to 2019: I –Verkhneamursky, II – Nizhneamursky; III –Lake Khanka. Sampling points: 1 – Gryaznushka River, 2 – Kozmodemyanovskoe Reservoir, 3 – Tambov Reservoir, 4 – Ushumun River, 5 – Bira River, 6 – Vertoprashikha River, 7 – Solonechnaya River, 8– Urmi River, 9 – In River, 10 – Lake Khanka, 11 – main channel of the Amur River (village of Sinda), 12 –Kharpi River, 13 – village of Malmyzh, 14 – village of Belgo, 15 – Limury River, 16 – Lake Udyl.

of the Amur (537.2 ± 93.0 mg/kg wet weight); in addition, an increased content of copper was recorded in their liver, and the concentration of cadmium exceeded the MPC[1] and reached 0.4 mg/kg. The zinc content in fish is close to that of iron; in fish gonads, the zinc concentration varied over a wide range, from 2.6 mg/kg (main stream) to 37.41 mg/kg wet weight (Lake Udyl). The content of other metals in the organs of carp from Lake Udyl and Limury River was the smallest (Chukhlebova and Panasenko, 2010).

Table 1 shows the annual changes in the concentrations of heavy metals in the muscles of fish from the main channel of the Amur River (village of Sinda) (Chukhlebova and Berdnikov, 2011; Chukhlebova and Panasenko, 2010). In the period 2006–2008 the content of HM in the muscles of Amur fish species remained at the same level (with a predominance of zinc), which indicates a constant anthropogenic impact on the ecosystem. The concentrations of normalized HMs (for example, lead and cadmium, evidence of industrial pressure on the environment) were within the permissible values (except for the concentration of Cd in the tissues of the spotted steed *Hemibarbus maculatus* (Bleeker, 1871), caught in the summer and autumn of 2007, as well as concentrations of Pb in Gibel carp and Ussuri catfish *Pseudobagrus ussuriensis* (Dybowski, 1872), caught in autumn of the same year). Since for the river basin of the Amur River is characterized by high water and frequent floods in the summer-autumn period; it can be assumed that the migration of cadmium and lead occurs in the tissues of hydrobionts, which are the basis of the food supply for these fish species (Chukhlebova and Berdnikov, 2011).

E.N. Chernova et al. (2008) studied the content of heavy metals in the organs of Gibel carp from the reservoirs of southern Primorye. The paper also provides data on the Harpi River, part of the Amur River basin. High levels of biophilic elements (zinc and iron) were recorded in scales, skin, kidneys, gills and in kidneys, gills, liver and spleen, respectively. Of the normalized elements, only cadmium and lead were determined; their concentrations in fish meat used for food did not exceed the MPC.

Based on the presented results, it can be concluded that the Nizhneamursky region is subject to heavy metal pollution. In the tissues of the fish caught here, single cases of exceeding the MPC for cadmium and lead were recorded. Thus, eating fish from this area cannot be considered completely safe for human health.

[1] TR CU 021/2022. Technical Regulations of the Customs Union "On food safety".

Trace element composition in the fish of the Verkhneamursky site

The main the catchment area of the Amur River is made up of small rivers; consequently, the deterioration of their water quality has a negative impact on the river ecosystem as a whole. Therefore, it is necessary to study the content of trace elements in the waters of small rivers and hydrobionts inhabiting them (Platonova et al., 2013).

V.Yu. Polyakov and I.L. Revutskaya (2015) studied the concentration of the most dangerous, ecotoxic HMs (Hg, Pb, Cd, As) in fish caught in 2010 and 2012 in the Urmi and In rivers (Table 2). It shows that a predominance of mercury over other elements (0.2369 mg/kg) was observed in the organs of fish, although the MPC was not exceeded. This ratio is attributed to several factors: geochemical features of the underlying surface, runoff from agricultural fields, and/or the result of atmospheric transport. Minor changes in the concentrations of cadmium, lead and arsenic were also noted. Their maximum concentrations did not exceed the permissible ones and amounted to 0.018, 0.036, and 0.0226 mg/kg, respectively.

In 2019, a study was conducted showing the effect of drainage reclamation on the accumulation of HMs in hydrobionts, in particular, in the gills of the Lagowski's minnow *Phoxinus lagowskii* (Dybowski, 1869) living in the tributaries of the middle reaches of the Amur River (Ushumun, Gryaznushka, Vertoprashikha, Solonechnaya rivers) (Zubarev and Burik, 2019). The Ushumun river basin completely lacks objects of economic activity; its hydrological, hydrogeological and hydrochemical regimes are in a natural state, so this reservoir acted as a background area.

The content of iron, manganese, zinc, copper, and lead in the gills of the Lagowski's minnow in the upper reaches of the rivers was within the permissible range, but under the influence of drainage reclamation, the concentrations of all HMs increase in the lower reaches, especially lead (2.5–3 MPC) and iron (Fig. 3). The average content of manganese was 11.5 mg/kg, however, significant fluctuations in the concentration of the metal in the lower reaches of the rivers were recorded, 18–31 mg/kg. In the gills of fish from the lower reaches of the Vertoprashikha and Solonechnaya rivers, high concentrations of lead were found, significantly exceeding the MPC for commercial fish (Zubarev and Burik, 2019).

The results of HM studies in the muscles of Gibel carp *Carassius gibelio* (Bloch, 1782) showed that the concentrations of trace elements did not reach the MPC for fish and were ranked as follows: Cd < Pb < Mn < Cu < Fe < Zn. However, in the muscles of the fish from the Kozmodemyanovskoye reservoir in the

Table 1. Seasonal changes in the concentrations of heavy metals in the muscles of fish from the main channel of the Amur River (village of Sinda) (Chukhlebova and Berdnikov, 2011; Chukhlebova and Panasenko, 2010);). "–" – element not found; * – maximum concentrations exceeded the MPC for foodstuffs.

Species	Fishing season	Trace element, mg/kg wet weight											
		Cd			Pb			Cu			Zn		
Spotted steed	Winter 2006/2007	0.1			0.01–0.08			0.53–1.44			9.65–20.4		
Amur pike	Winter 2006/2007	0.01–0.09			0.02–0.04			0.54–1.46			12.4–22.3		
Predatory carp	Winter 2006/2007	0.01–0.07			0.04			0.72–2.36			1.78–6.78		
		spring	summer	autumn	spring	summer	autumn	spring	summer	autumn	spring	summer	autumn
Spotted steed	April – October 2007	0.001–0.04	0.13–0.26*	0.02–0.26*	0.01–0.05	0.001–0.07	0.02–0.06	0.43–1.98	0.001–1.04	0.24–0.71	3.48–14.80	1.57–20.30	6.15–16.90
Gibel carp	April – October 2007	0.001–0.02	0.001–0.04	0.001–0.02	0.001–0.02	0.001–0.06	0–0.05	0.29–0.84	0.24–0.99	0.24–8.06	2.33–4.88	6.87–20.98	16.90–42.48
Ussuri catfish	April – October 2007	0.001–0.01	0.02–0.07	0–0.11	0.001–0.04	0.015–0.03	0.05–1.72*	0.11–3.40	0.17–0.82	0.36–3.33	3.01–6.82	4.58–6.95	11.48–17.41
Silver carp	April – October 2007	0.03–0.09	0–0.11	–	0.001–0.03	0–0.03	0.02–0.06	0.64–1.41	0.001–5.73	0.66–1.61	0.96–5.06	0.001–22.20	13.18–29.42
Gibel carp	May – October 2008	0.01 ± 0.009			0.03 ± 0.01			0.4 ± 0.1			17.1 ± 5.3		
MPC		0.2			1.0			–			–		

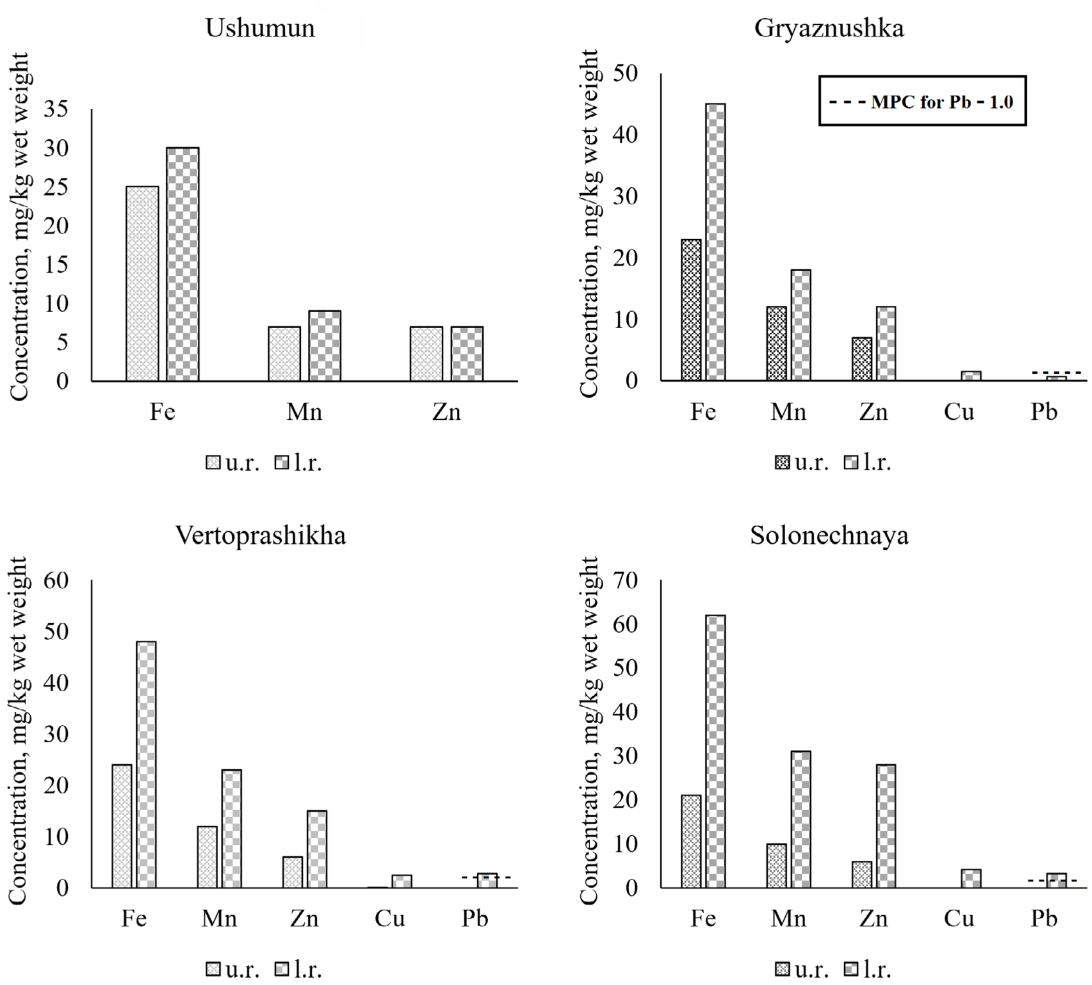

Fig. 3. Heavy metal concentrations in the gills of the Lagowski's minnow (*Phoxinus lagowskii*) (Zubarev and Burik, 2019); u.r. – upper reaches, l.r. – lower reaches.

fall of 2015, a lead concentration was recorded reaching 1–1.2 mg/kg, which exceeds the MPC values for fish[2], making it potentially hazardous to human health (Pakusina et al., 2019).

Thus, the trace elements in the fish of the Verkhneamursky site does not allow us to consider them safe to eat. Cases of exceeding the MPC for normalized elements associated with anthropogenic activities have been recorded. However, the conclusion about the safety of fish products can be considered preliminary, since the data from studies of small rivers do not give a general impression of the Amur river.

Trace elements in the fish of Lake Khanka

Lake Khanka is the largest Far Eastern lake, which is an important part of the freshwater fisheries resources and belongs to the catchment area of the Amur River (Turanov et al., 2019). As a result of increasing water pollution due to agricultural and industrial development of the territory, the stocks of fish products are gradually decreasing. Nevertheless, Lake Khanka continues to play a large role in the fisheries of Primorsky Krai (Luchsheva et al., 2000) and is an international natural object (part of it belongs to China). Therefore, it is extremely necessary to monitor the content of heavy metals in the commercial fish of the lake.

Two studies of the trace element composition in the organs and tissues of the Gibel carp *Carassius auratus gibelio* from water bodies in the south of Primorsky Krai, including Lake Khanka (Chernova et al., 2008; Marchenko et al., 2006). In the first study, scales, muscles, skin, gonads, kidneys, gills, liver, and spleen were examined for heavy metal content (Marchenko et al., 2006); in the second publication, only muscles were the object of study (Chernova et al., 2008). In general, the concentration of heavy metals in the muscle tissue of Gibel carp in 2006 and 2008 were similar and were characterized by an insignificant spread of values (Fig. 4). The opposite picture was observed in the organs. The content of metals varied over a wide range, exceeding the MPC

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

Table 2. Heavy metal concentrations in fish samples caught in the Urmi and In rivers in 2010 and 2012 (Polyakov and Revutskaya, 2015).

Species	Concentration, mg/kg wet weight							
	Pb		Cd		Hg		As	
	2010	2012	2010	2012	2010	2012	2010	2012
Amur grayling	< 0.0003	< 0.0003	< 0.0003	0.0118 ± 0.002	0.1672 ± 0.0251	0.0777 ± 0.012	< 0.0005	< 0.0001
Gibel carp	< 0.0003	< 0.0003	< 0.0003	0.018 ± 0.002	0.1772 ± 0.0266	0.0968 ± 0.015	< 0.0005	0.0094 ± 0.003
Asiatic trout	< 0.0003	0.1808 ± 0.0271	< 0.0003	0.0103 ± 0.002	0.1461 ± 0.0219	0.0994 ± 0.0149	< 0.0005	< 0.0001
Northern pike	0.0024 ± 0.0006	< 0.0003	< 0.0003	0.018 ± 0.002	0.2186 ± 0.0328	0.0777 ± 0.012	< 0.0005	< 0.0001
Northern snakehead	< 0.0003	< 0.0003	0.0015 ± 0.0004	0.003 ± 0.0006	0.1808 ± 0.0271	0.2369 ± 0.036	< 0.0005	< 0.0001

Table 3. The content of mercury in commercial fish species from the Lake Khanka, mg/kg wet weight (Luchsheva et al., 2000). – the maximum concentrations exceeded the MPC for food products.

Species	Organs				
	Liver	Gut	Kidneys	Gills	Muscles
Silver carp	0.11–2.95*	0.07–0.40*	0.04–0.42*	0.03–0.26	0.02–0.16
Amur carp	0.08–3.15*	0.04–0.66*	0.07–2.30*	0.03–0.71*	0.04–0.60*
Spotted steed	0.09–0.31*	0.06–0.87*	0.05–0.78*	0.06–0.45*	0.06–0.30*
Amur catfish	0.09–0.68*	0.02–0.51	0.10–0.32	0.07–0.42	0.17–0.56
Amur pike	0.18–0.73*	0.10–0.96*	0.10–0.79*	0.03–0.25	0.08–1.18*
Predatory carp	0.10–3.25*	0.05–0.89*	0.15–1.34*	0.06–1.77*	0.08–1.30*

for cadmium in scales, gills, and kidneys (0.28, 0.34, and 0.52 mg/kg wet weight, respectively). Of the biophilic elements, iron (in the gills and spleen) and zinc (in the kidneys, skin, gills and scales) were noted in high concentrations, which indicates an anthropogenic impact on this area.

Pollution of the aquatic environment and aquatic organisms with mercury is one of the serious environmental problems of our time. Fish, which are the final link in the food chain in most freshwater ecosystems, are capable of accumulating mercury concentrations thousands of times higher than the content of this element in the aquatic environment. In addition, more than 90 % of the mercury in fish organs and tissues is found in the most toxic organic forms (Kocharyan et al., 1989; Kuzubova et al., 2000; Lucotte et al., 1999; Sukhenko, 1995). Therefore, knowledge about the amount of this metal in the organs and tissues of commercial fish is of fundamental importance (it is known that fish and other aquatic organisms that are the main source of methylmercury for humans (Myers et al., 2007)).

L.N. Luchsheva et al. (2000) studied the content of mercury in the organs and tissues of commercial fish from Lake Khanka. A significant accumulation of this metal in fish was recorded. In particular, in 22 % of cases, mercury concentrations exceeded the MPC for freshwater fish (0.6 and 0.3 mg/kg wet weight for predatory and non-predatory species) (Table 3). The minimum concentrations of mercury (0.02 mg/kg) were found in the intestines of the Amur catfish *Parasilurus asotus* (Linnaeus, 1758) and the muscles of the silver carp, also called Amur silver carp, *Hypophthalmichthys molitrix* (Valenciennes, 1844), the maximum concentrations were found in the liver of the common carp *Cyprinus carpio* Linnaeus, 1758 and predatory carp *Chanodichthys erythropterus* Basilewsky, 1855 (3.15 and 3.25 mg/kg wet weight, respectively). The authors suggest that such high concentrations of mercury in the fish of Lake Khanka are associated with the flow of organic metal compounds with the drain waters of rice paddies.

Thus, according to the food safety standards of Russia, eating fish from the Lake Khanka cannot be considered safe. However, it is important to take into account that today the considered works are out of date, and for a correct conclusion it is necessary to conduct new studies.

Conclusions

One of the most significant and acute environmental problems worldwide is the pollution of aquatic ecosystems. Every year, the anthropogenic pressure increases, various pollutants enter the reservoirs, capable of migrating over long distances, accumulating hydrobionts, in particular fish, and being transmitted along trophic chains, the final link of which is a person. Heavy metals entering water bodies with runoff and washouts from the territories of cities, industrial enterprises, agricultural lands, etc., serve as an important object of environmental monitoring.

The Amur River basin is located within three states, and the river itself plays a leading role in fisheries among the inland waters of Russia. Despite the international status of the Amur and Lake Khanka, there is very little information on the trace element composition of commercial fish, and some of it is already out of date. However, according to available data, the concentrations of some heavy metals in fish tissues exceed the MPC, and their consumption can be dangerous. Therefore, it is necessary to regularly monitor the water area for the content of normalized elements and assess the safety of fishery products.

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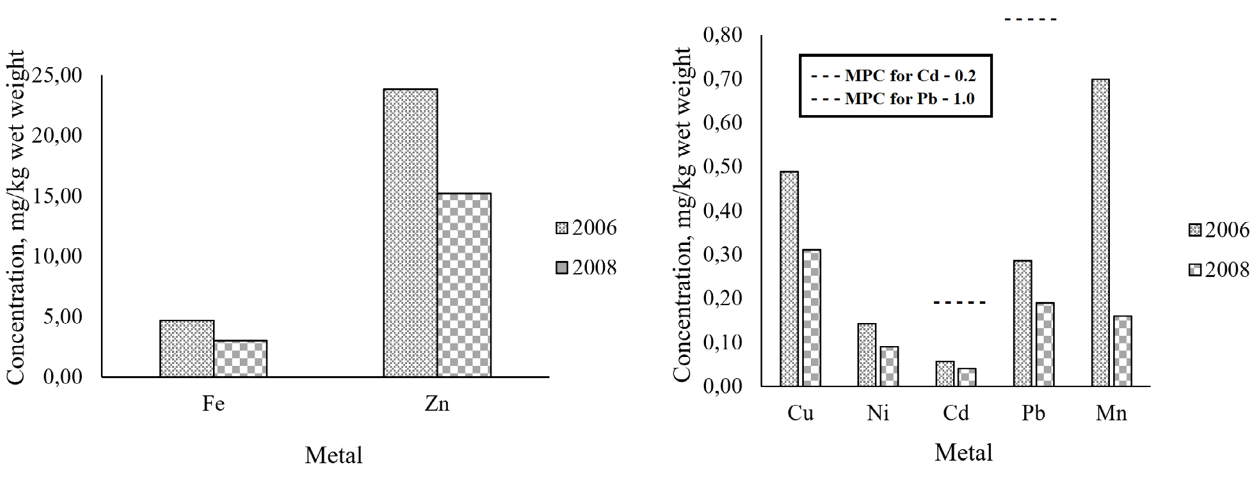

Fig. 4. Interannual changes in the concentration of HM in the muscles of Gibel carp (*Carassius gibelio*) (Chernova et al., 2008; Marchenko et al., 2006).

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