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Article

Features of the trace element composition of sockeye salmon (*Oncorhynchus nerka* Walbaum, 1792) from the Eastern Kamchatka bays

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Abstract. This paper is the first study of the trace element content (iron, zinc, copper, nickel, lead, and cadmium) of sockeye salmon caught in Eastern Kamchatka (Avacha and Kamchatka Bays). The results obtained were compared with published data for Sakhalin herds of pink salmon feeding in the open waters of the Pacific Ocean and in the Sea of Japan. The East Kamchatka herds of sockeye salmon are characterized by low concentrations of Ni and Pb, but the content of Zn and Cu are an order of magnitude comparing to pink salmon came here from the open ocean waters and migrating through the Kuril-Kamchatka geochemical impact zone. The content of Zn and especially Cu in the sockeye salmon eggs are several times higher than that in the male testes. Differences in the content of trace elements in salmons are discussed in regard to their biology and ecology, i.e., nature of feeding grounds, where conditions are markedly different and depend on natural and anthropogenic factors.

Keywords: Pacific salmon, Avacha Bay, Kamchatka Bay, geochemical environmental conditions, migration, feeding, Sakhalin-Kuril region, pink salmon, sockeye salmon

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Научная статья

Особенности микроэлементного состава нерки (*Oncorhynchus nerka* Walbaum, 1792) из заливов Восточной Камчатки

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Аннотация. Впервые изучен микроэлементный состав (содержание железа, цинка, меди, никеля, свинца и кадмия) нерки, выловленной в Авачинском и Камчатском заливах. Проведено сравнение полученных данных с опубликованными сведениями для сахалинской горбуши, нагуливавшейся в океане или в Японском море. Показано, что восточно-камчатская нерка отличается низкими концентрациями Ni и Pb, но на порядок большим содержанием Zn и Cu, чем горбуша, пришедшая из океана и прошедшая через Курило-Камчатскую геохимически импактную зону. Количество Zn и особенно Cu в икре в несколько раз превосходит содержание этих элементов в семенниках самцов нерки. Различия в содержании микроэлементов в лососях обсуждаются с позиций их биологии, экологии (характера мест нагула), условия которых заметно различаются и зависят от природных и антропогенных факторов.

Ключевые слова: Тихоокеанский лосось, Авачинский залив, Камчатский залив, геохимические условия среды, миграции, нагул, Сахалино-Курильский регион, горбуша

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Introduction

Traditionally, Pacific salmon of the genus *Oncorhynchus* include 6 species: pink salmon (*Oncorhynchus gorbuscha* (Walbaum, 1792)), chum salmon (*O. keta* (Walbaum, 1792)), sockeye salmon (*O. nerka* (Walbaum, 1792)), coho salmon (*O. kisutch* (Walbaum, 1792)), chinook salmon (*O. tshawytscha* (Walbaum, 1792)), and masu, or cherry trout (*O. masou* (Brevoort, 1876)). In the North Pacific, pink and chum salmons are the most widespread species. Pink, chum and sockeye salmons provide the most of the salmon fishery in Russian Pacific waters. Sockeye salmon, being the third largest species in terms of catch, is the most delicious and so the most valuable. Masu (cherry trout) has the lowest abundance. Being Asian endemic species, it is the most ancient and warm-water species within genera. All other Pacific species of salmons inhabit both coasts of the North Pacific (Asian and American). Sockeye salmon, coho salmon, and chinook salmon are considered cold-water species.

The accumulation of various metals in organs and tissues of commercial aquatic inhabitants should be strictly monitored regardless of their origin. Despite the fact that the marine part of the range of all Asian salmonids is confined to the north-west of the Pacific Ocean, the trace element composition of fish from different populations differs significantly even within the same species. The content of heavy metals in salmon tissues depends on feeding grounds and migration routes.

Earlier, we have studied in detail the content of trace elements in the organs and tissues of pink and chum salmons in the Sakhalin-Kuril region and in Primorye (Khristoforova et al., 2019a, b, 2021; Litvinenko and Khristoforova, 2020; Litvinenko et al., 2021). The results obtained allow us to conclude that most fish migrate to the ocean for wintering through geochemical provinces of the Kuril Ridge and the Kuril-Kamchatka Trough, which are highly productive zones. The Kuril Islands supply a large set of metal ions to the environment through terrestrial and submarine volcanism and post-volcanism, while the deep-sea trench maintains high productivity through upwelling of deep waters containing nutrients and other chemical elements. In nutrient-rich waters of the geochemically impacted zone, salmons can accumulate undesirable toxic elements. Lead is a marker of fish feeding in the ocean and passing through a specific geochemical zone in the Sea of Okhotsk. High content of lead in the salmon organs and tissues specifies particular environment features and properties of this element (Khristoforova et al., 2015). However, a part of pink salmon populations, migrating to the ocean for wintering, stay in the Sea of Japan, evident by its trace element composition. Being a relatively closed water area with shallow straits, the Sea of Japan experiences a noticeable anthropogenic load from the surrounding countries (Russia, Japan, and both Koreas), as evidenced by the increased content of zinc and copper in fish caught in these waters. Increased nickel content in the environment and organisms testifies to hydrocarbon combustion both by ships and onshore thermal power plants and boiler houses[1].

Sockeye salmon, like other salmons, feeds in certain water areas. This indicates its following the preferred water mass in the ocean (Birman, 1967, 1985). Sockeye salmon returns to their native rivers to spawn after spending from one to three years in fresh waters and from one to four years in the sea (Bugaev, 1995; Konovalov, 1980; Shuntov and Temnykh, 2008, 2011). According to numerous studies,

[1] Government of Primorsky Krai, 2021. Impact of economic activities on the environment. Report on the environmental situation in Primorsky Krai in 2020, part 2, 176–177.

main marine feeding areas of the East Kamchatka sockeye salmon are the western part of the Bering Sea and the Kamchatka-Kommandorsky region, from where it goes to the central part of the Bering Sea and the Aleutian waters to overwinter (Bugaev, 2007; Bugaev et al., 2015; Konovalov, 1980; Shuntov and Temnykh, 2008). Because sockeye salmon is characterized by long and indefinite stay in both fresh and marine waters, it is the most difficult salmon species to study and to search for the sources affecting their microelement composition. Limited data is available on the content of some macro- and microelements in the bone tissues of sockeye salmon migrating to spawn from the open waters in Kamchatka waterbodies (Khrustaleva et al., 2020). However, the sources of mineral composition of this fish still remain unknown so far. Our study provides the first data on the content of some heavy metals in the intestines and tissues of this important commercial salmon species performing anadromous migration.

The study aims to determine the content of trace elements in anadromous sockeye salmon from the Avacha and Kamchatka bays of southeastern Kamchatka and to compare it with corresponding indicators for pink salmon from the Sakhalin-Kuril region obtained earlier.

Material and methods

Samples of muscles, liver and gonads of sockeye salmon were collected in the coastal waters of Eastern Kamchatka in July 2021 (Fig. 1). In total, 63 samples from 21 individuals from Avacha Bay and 42 samples from 14 individuals from Kamchatka Bay were obtained. A complete biological analysis of sockeye salmon spawners was performed, then the samples of organs/tissues were frozen at −18 °C and stored until chemical analysis in the Kamchatka Branch of the Pacific Institute of Geography of the Russian Academy of Sciences. Further processing of the samples was carried out in the Institute of the World Ocean of the Far Eastern Federal University, Russia. Samples were prepared for analysis by acid decomposition using a MARS 6 microwave system in highly pure nitric acid (70%) according to generally accepted methods[2]. Metals in organs and tissues were analyzed on a Shimadzu AA-7000 atomic absorption spectrophotometer using flame and flameless atomizers. The accuracy of determining the content of elements, as well as possible contamination of samples during analysis, was controlled by comparison with calibration solutions, including a blank (zero) solution. The accuracy of the method used was confirmed by regular analysis of reference material SRM-1566a (oyster tissue, National Bureau of Standards, USA). A total of 1260 samples were processed. Metal concentrations were expressed as μg/g wet weight. Mean ± standard deviation are given.

Results and discussion

Data on the content of heavy metal ions in both Kamchatka sockeye salmon and Sakhalin pink salmon caught in previous years in Terpeniya Bay (South-Eastern Sakhalin) and Aniva Bay (Southern Sakhalin) are presented to demonstrate the influence of feeding areas on the microelement composition of organs and tissues of salmon (Table 1).

Iron, copper, and zinc, being indispensable elements, have the maximum concentration in the mineral composition of both sockeye and pink salmons. Metals are most concentrated in the liver, which is undoubtedly due to its functional role as an accumulator and detoxicant organ. The presence of iron indicates a terrigenous influence; this element may enter the organism of fish in large quantities in freshwater bodies. Copper and zinc, in addition to being naturally occurring, are characteristic components of domestic effluents and enter watercourses as a result of economic activity, reflecting anthropogenic impact on biotopes (Khristoforova et al., 2018a).

Copper is an important essential element, but it has a toxic effect on aquatic organisms if its concentration exceeds the body's needs. The toxicity of this element is highly dependent on water quality (Playle et al., 1992; Sciera et al., 2004). In fish and terrestrial vertebrates, the liver is the main organ involved in Cu metabolism (Cousins, 1985; Crosell and Wood, 2002). Once captured by the gills and absorbed, copper is excreted through the liver, stored in Cu-protein complexes, or excreted in bile (Handy, 1996; Crosell and Wood, 2002).

Zinc, as well as other trace elements, enter the fish body from water through the gills and with food; it is absorbed in both freshwater and marine fish in the gastrointestinal tract (Spry et al., 1988). Soluble forms of zinc in water are also a potential source of this mineral for salmon and anadromous fish as they

[2] GOST 26929–94, 1994. Raw materials and food products. Sample preparation Mineralization to determine the content of toxic elements.

Fig. 1. Sampling sites for sockeye salmon (Kamchatka) and for pink salmon (Sakhalin).

drink seawater. In fish, zinc is excreted through bile, by the intestinal mucosa (in feces), and through the gills (Lall and Bishop, 1977; Pentreath, 1973).

When analyzing the data, it is obvious that lead content in the tissues of East Kamchatka sockeye salmon is significantly lower than that in pink salmon from the Sea of Okhotsk (Table 1). At the same time, sockeye salmon is characterized by much higher levels of zinc and copper, as well as iron and cadmium in the ovaries and liver, although the cadmium content in the liver varies greatly. Low lead content in sockeye salmon suggests that the fish did not pass through the impact zone and did not feed in the Kuril waters, but migrated to open waters (most likely the Bering Sea) from their bays and returned to them before entering the rivers. As we have found earlier, the microelements' content in pink salmon caught in the Firsovka River (Terpeniya Bay) indicate its wintering area in the ocean. High content of Zn, Cu, and Ni has been revealed in pink salmon from the Aniva Bay wintering in the Sea of Japan, which indicates both the anthropogenic impact on the water area of this closed sea and the high traffic of ships operating on hydrocarbon fuel (Litvinenko et al., 2021). When the latter is burned, a large set of chemical elements are released into the environment, among which Ni and V noticeably predominate (Khristoforova et al., 2018a, b).

Iron dominates in the liver of both Kamchatka sockeye salmon and Aniva pink salmon, being as well the most common microelement in the environment and biota. The lowest content has been observed for cadmium, especially in muscles, but it also noticeably in the liver of both fish species, exceeding the maximum permissible concentration (MPC) for seafood severalfold[4]. The lowest content of trace

Table 1. The content of trace elements (µg/g wet weight) in sockeye salmon from the bays of southeastern Kamchatka and in pink salmon from the bays of southern Sakhalin. The highest concentrations of each element in organs and tissues are marked in bold; "–" – the indicator was not determined. Maximum permissible concentration in seafood (µg/g wet weight): Pb – 1.0, Cd – 0.2[3].

Organ / tissue	Zn	Cu	Ni	Cd	Pb	Fe
Sockeye salmon, Avacha Bay, 2021; body weight of 1200–2330 g						
Muscles	5.33 ± 0.63	0.62 ± 0.13	0.43 ± 0.09	0.010 ± 0.007	0.10 ± 0.08	7.91 ± 3.35
Liver	**47.18 ± 5.51**	**260.71 ± 95.31**	0.39 ± 0.19	**1.310 ± 0.560**	0.22 ± 0.09	**250.29 ± 73.17**
Testes	18.63 ± 1.35	0.91 ± 0.12	0.31 ± 0.18	0.011 ± 0.005	0.34 ± 0.06	7.62 ± 3.22
Ovaries	**46.35 ± 4.26**	**59.16 ± 6.27**	0.61 ± 0.27	0.034 ± 0.020	0.08 ± 0.04	**33.63 ± 7.16**
Sockeye salmon, Kamchatka Bay, 2021; body weight of 1650–3280 g						
Muscles	6.20 ± 2.28	0.99 ± 0.37	0.31 ± 0.15	0.006 ± 0.003	0.16 ± 0.06	6.85 ± 4.42
Liver	**41.4 ± 9.38**	**173.57 ± 88.93**	0.33 ± 0.12	**0.820 ± 0.650**	0.21 ± 0.08	**171.52 ± 55.71**
Testes	20.89 ± 3.66	1.69 ± 0.77	0.28 ± 0.15	0.014 ± 0.008	0.27 ± 0.09	**25.34 ± 6.49**
Ovaries	**40.70 ± 11.03**	**60.84 ± 12.47**	0.32 ± 0.15	0.010 ± 0.006	0.21 ± 0.06	**23.37 ± 6.42**
Pink salmon, Sakhalin Island, Terpeniya Bay, 2016; body weight of 780–2100 g (Khristoforova et al., 2019a)						
Muscles	1.74 ± 0.06	0.20 ± 0.04	0.09 ± 0.01	0.080 ± 0.000	**0.59 ± 0.05**	–
Liver	2.86 ± 0.06	0.28 ± 0.01	0.13 ± 0.01	0.190 ± 0.020	**0.92 ± 0.04**	–
Testes	2.76 ± 0.02	0.26 ± 0.01	0.11 ± 0.01	0.120 ± 0.010	**0.87 ± 0.01**	–
Ovaries	2.51 ± 0.06	0.25 ± 0.02	0.12 ± 0.01	0.110 ± 0.020	**0.82 ± 0.04**	–
Pink salmon, Sakhalin Island, Aniva Bay, 2019; body weight of 1027–1508 g (Litvinenko et al., 2022)						
Muscles	**6.45 ± 0.89**	0.21 ± 0.16	**0.83 ± 0.17**	0.008 ± 0.008	0.15 ± 0.03	4.7 ± 1.0
Liver	**37.29 ± 6.72**	**44.20 ± 28.69**	**0.77 ± 0.25**	0.570 ± 0.307	0.19 ± 0.06	84.7 ± 31.4
Testes	**16.57 ± 1.32**	0.29 ± 0.13	**0.71 ± 0.24**	0.016 ± 0.001	0.24 ± 0.05	9.8 ± 2.8
Ovaries	**24.55 ± 2.19**	5.39 ± 0.27	**1.20 ± 0.17**	0.006 ± 0.012	0.25 ± 0.07	22.1 ± 2.2

[3] SanPiN 2.3.2.1078-01, 2002. Hygienic requirements for the safety and nutritional value of food products.

elements is observed in muscles, regardless of the geographical location where sockeye salmon was caught. In the eggs, the content of Zn, Cu and Fe is significantly higher than in muscles, which is consistent with the previous studies (Scalecki et al., 2020; Topus et al., 2017). There are also significant differences in the concentration of some elements depending on fish sex: the content of Zn and especially Cu in eggs is several times higher than in the male testes (Fig. 2).

According to the obtained results, anadromous sockeye salmon from Avacha and Kamchatka bays have higher concentrations of iron, copper and zinc comparing to Sakhalin pink salmon, especially those coming to the Firsovka River (Terpeniya Bay). This may indicate a more intense anthropogenic and terrigenous load on the breeding and feeding areas of sockeye salmon (Fig. 3). Different levels of metal ion concentrations in salmon reflect geographical differences in environmental conditions (Khristoforova et al., 2019a); however, no clear statement can be made about the river or lake system, where the sockeye salmon grew. There is no doubt that its environment has been affected by the terrigenous runoff of numerous rivers draining a vast territory, volcanogenic influence, and surely the anthropogenic load from the largest cities of Petropavlovsk-Kamchatsky, Elizovo, Vilyuchinsk located in the southeast of the Kamchatka Peninsula. The impact of these factors is noticeable, at least at the level of trends. In addition, the influence of active volcanoes (Vilyuchinsky, Avachinsky, and Koryaksky), located around the Avachinsky Bay, is also found by higher concentrations of metals (primarily Fe, Cu, and even Cd) in the soft tissues of Avachinsky Bay sockeye salmon stock compared to that from Kamchatka Bay (Khrustaleva et al., 2020). The volcanogenic impact on the environment was also noted for the soils of Kamchatka: the total content of copper in the soils of the southeast of this peninsula ranges from 13 to 100 mg/kg (averaging 33 mg/kg), which is almost 1.5 times higher than the clarke number (20 mg/kg) (Zavarikhina and Litvinenko, 2011).

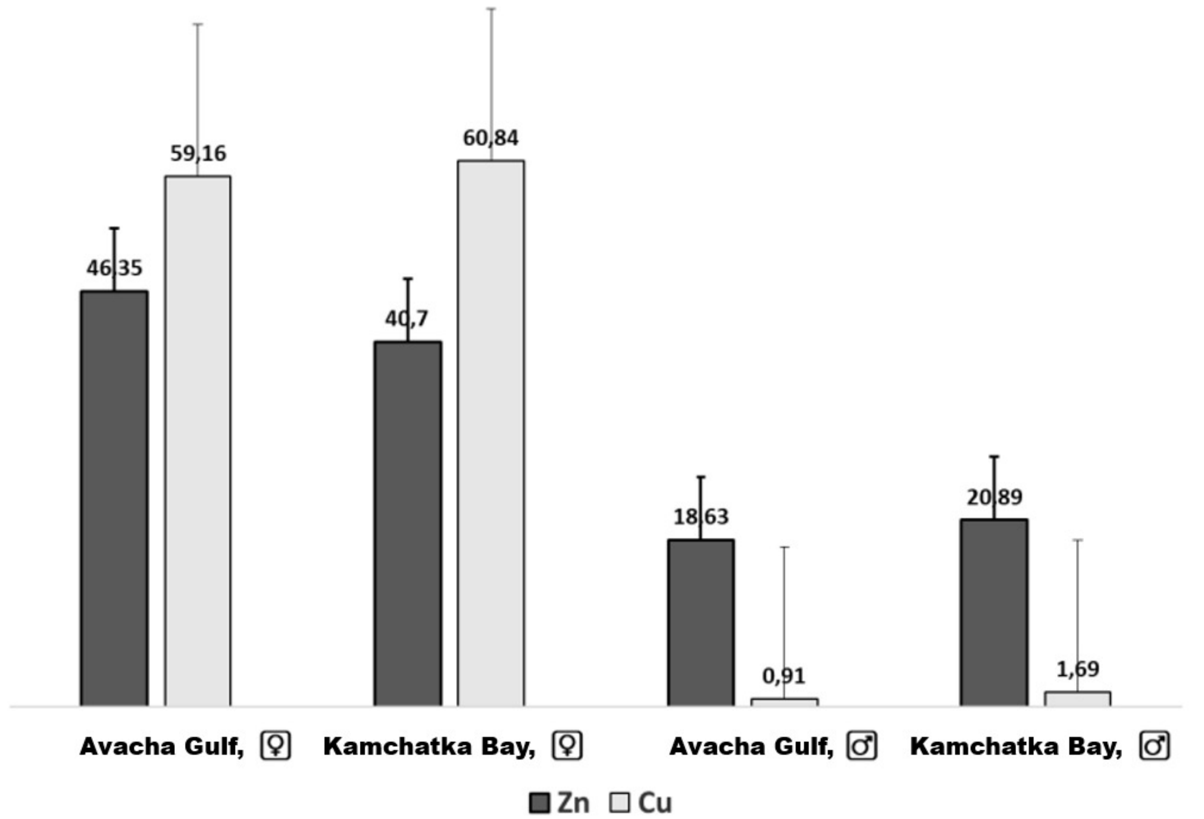

Fig. 2. Content of trace elements (µg/g wet weight) in the liver and gonads of sockeye salmon females and males sampled in the southeastern bays of Kamchatka.

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[4] SanPiN 2.3.2.1078-01, 2002. Hygienic requirements for the safety and nutritional value of food products.

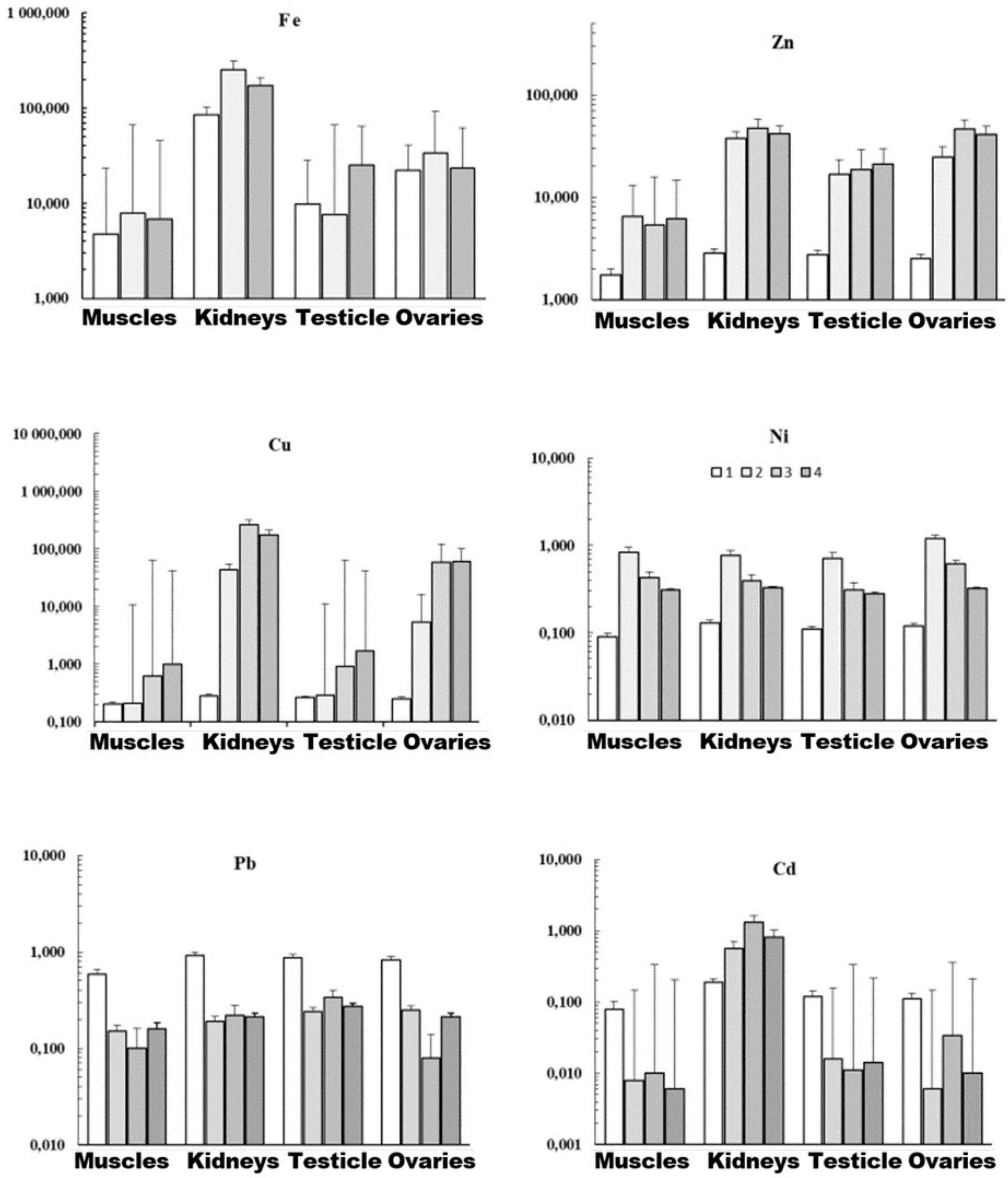

Fig. 3. Content of trace elements (μg/g wet weight) in the organs and tissues of pink salmon and sockeye salmon, μg/g fresh weight.

Conclusions

The microelement composition of sockeye salmon from two East Kamchatka bays is affected by both terrigenous and volcanogenic, as well as anthropogenic factors. Apparently, these impacts mainly during the freshwater period of its ontogenesis, before the fish enter the sea.

Previous studies on the content of certain metals in the tissues and organs of pink salmon, as well as current results on East Kamchatka sockeye salmon allow us to confirm that the marine habitats of these species do not coincide and that environmental conditions differently the formation of their mineral composition.

It is also important to emphasize that volcanic activity affects the trace element composition of both pink salmon and sockeye salmon. For pink salmon wintering in the ocean, the impact of volcanism and upwelling occurs during their migration through the geochemically active and nutrient-rich Kurilo-Kamchatka zone; it is revealed by a marked predominance of lead. At the same time, for sockeye salmon with a long period of stay in fresh water bodies and watercourses draining the areas adjacent to terrestrial volcanoes of Kamchatka, this influence is primarily detected by the increased content of copper and zinc in their organs and tissues.

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