Trace Elements Content in the Pink Salmon (*Oncorhynchus gorbuscha* Walbaum, 1792) from Sakhalin-Kuril Region

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The Sakhalin-Kuril region (SKR) is one of the main areas of catch of Pacific salmon in the Far East of Russia. The leading fishing facilities are pink salmon (*Oncorhynchus gorbuscha*) and chum salmon (*O. keta*). In 2016, the catch of these species in the SKR amounted to 105.4 thousand metric tons (74 thousand metric tons of pink salmon and 31.4 thousand metric tons of chum salmon), which was almost one quarter of the production of these salmon in the Far East of Russia. The total capacity of fish-breeding enterprises at the end of 2015 amounted to 956.5 million salmon fry (Report 2016). Most of the plants in the SKR are located in the southern part of Sakhalin and in the Central part of the Iturup Island, on the coast of the Sea of Okhotsk.

In autumn, the Okhotsk pink salmon offspring begin to migrate into the ocean to the Polar front zone. Salmon feed in the spring in the area near Kuril Islands, then head to spawn in native rivers (Shuntov 2001; Temnykh 2004).

The Kuril-Kamchatka region is characterized by the impacts of geochemical conditions that are created by upwelling, underwater and surface volcanism, which carry biogenic and other elements from the depths of the Kuril-Kamchatka trench. The Kuril Island region supplies the surrounding Pacific Ocean waters with a high content of chemicals due to volcanic and seismic activities. Pacific salmon which swim out for the winter and migrate to spawn, encounter these chemicals. This inevitably leaves its "trace" in the microelement composition of fish organs and tissues, which regulates the levels of elements, particularly toxic ones, that are caught in the fishery hydrobionts (Kovkovdova 2011; Kovkovdova et al. 2013; Khristoforova et al. 2014; Khristoforova et al. 2015a; Khristoforova et al. 2015b; Khristoforova et al. 2016; Khristoforova et al. 2018). However, there is limited information about how micronutrient content in active swimmers varies during their extensive migrations, such as Pacific salmon during feeding, wintering and spawning when they pass through geochemically impacted zones.

The purpose of this work is to determine the concentrations of trace elements in the pink salmon tissues returning to the river Reidovaya (Iturup Island) and the river Firsovka (the southern part of the Eastern Sakhalin).

Material and methods

Essential (Zinc and Copper) and non-essential (Nickel, Cadmium, Lead, Arsenic, Mercury) elements were quantified. All of them can be tracers of natural biogeochemical provinces. This was repeatedly noted earlier in the study of the content of heavy metals Fe, Mn, Zn, Cu, Cd, Pb, Ni, Cr in marine benthic organisms from the shallow waters of the Kuril Islands and organisms-fouling navigation buoys (Kavun and Khristoforova 1991; Malinovskaya and Khristoforova 1997; Kavun et al. 2002).

Our study focused on mature pink salmon individuals (*O. gorbuscha* Walbaum, 1792) that spawned in the Reidovaya river and Firsovka in early October 2016 from the fish farms "Reidovy" and "Firsovka" (Fig. 1). The producers were kept in cages at the hatcheries until they sexually matured, at which point three females and three males were selected. All elements except Hg were determined from an acid mineralization according to GOST 26929-94 on an atomic absorption spectrophotometer Shimadzu AA 6800. Data on the mass concentration of Hg was obtained by the method of stripping voltammetry at the analyzer "Tom'analit" (TA-4) (Khristoforova et al. 2015b). The results are presented in $\mu\text{g}\cdot\text{g}^{-1}$ of crude mass (Table. 1). For comparison, our data on the concentrations of elements in pink salmon caught in the ocean waters near the Kuril Islands in July 2013, as well as data on the

ranges of their contents in pink salmon from the Sea of Japan are presented (Kovekovdova 2011). The mean value, standard deviation, and validity of the differences compared (using the Mann–Whitney U-test) were calculated in SPSS Statistics 21 for Mac OS X.

Fig. 1. Location map of the “Firsovka” and “Raidovy” hatcheries in the Sakhalin-Kuril region.

Table 1. Trace elements in organs and tissues of pink salmon of the Sakhalin-Kuril region and comparison areas, $\mu\text{g}\cdot\text{g}^{-1}$ of crude mass ($m \pm \sigma$).

	Zn	Cu	Ni	Cd	Pb	As	Hg
Organs and tissues	Sakhalin island. Hatchery "Firsovka", 06.10.2016, the weight range of fish 780–2100 g						
Muscles	1.74±0.061	0.20±0.040	0.09±0.008	0.08±0.009	0.59±0.050	0.90±0.074	0.03±0.009
Liver	2.86±0.065	0.28±0.012	0.13±0.006	0.19±0.018	0.92±0.035	1.12±0.096	0.09±0.009
Gonads of males	2.76±0.021	0.26±0.014	0.11±0.006		0.87±0.014		0.07±0.003
eggs	2.51±0.058	0.25±0.016	0.12±0.007	0.12±0.012	0.82±0.043	1.09±0.035	0.07±0.004
	Iturup Island. Hatchery "Reidovy". 09.10. 2016, the weight range of fish 1278–2362 g						
Muscles	1.96±0.075	0.24±0.076	0.12±0.007	0.14±0.012	0.67±0.050	0.94±0.064	0.04±0.005
Liver	3.14±0.069	0.32±0.034	0.18±0.009	0.21±0.018	0.96±0.035	1.25±0.098	0.12±0.009
Gonads of males	3.09±0.045	0.33±0.071	0.18±0.009	0.19±0.034	0.89±0.014	1.14±0.085	0.11±0.008
eggs	3.01±0.078	0.29±0.036	0.15±0.008	0.18±0.035	0.84±0.045	1.13±0.086	0.09±0.006
	Ocean waters near the Kuril Islands, July 2013, fish mass range 1168–1458 g						
	(by: Khristoforova et al., 2015)						
Muscles	1.29±0.079	0.108±0.012	Not detect.	0.037±0.005	0.503±0.059	0.930±0.093	0.030±0.009
Liver	2.97±0.089	0.165±0.008		0.152±0.015	0.902±0.108	1.118±0.089	0.120±0.021
Gonads of males	2.43±0.029	0.090±0.010		0.017±0.006	0.297±0.029	0.310±0.017	0.053±0.006
eggs	2.35±0.076	0.087±0.006		0.023±0.006	0.327±0.025	0.337±0.060	0.070±0.010
	Sea of Japan, range of trace elements found in 1992, 2001, 2008						
	(by: Kovekovdova, 2011)						
Muscles	0.57–3.25	0.032–0.087		0.005–0.012	0.012–0.013	0.300–1.370	0.007–0.015
Liver	3.00–4.35	0.119–0.165		0.080–0.145	0.020–0.025	0.450–0.800	0.010–0.025
eggs	2.90–3.90	0.037–0.090		0.001–0.003	0.007–0.020	0.100–0.320	0.003–0.005

Note. Maximum Permissible Concentration (MPC) of toxic elements ($\text{mcg}\cdot\text{g}^{-1}$ of raw mass) in seafood in Russia: Pb—1.0, As—5.0, Cd—0.2, Hg—0.2 (SanPiN ..., 2002); in Canada: Hg—0.5; in the USA: Cd—3, Pb—1.5, As—86.

Results

Mercury (Hg) had the lowest concentrations of all the trace elements. Salmon from Firsovka had Hg concentrations of $0.03 \pm 0.009 \mu\text{g}\cdot\text{g}^{-1}$ in their muscles, and the gonads (male and female) had Hg concentrations of

0.07 ± 0.003 and $0.07 \pm 0.004 \mu\text{g}\cdot\text{g}^{-1}$ in males and females, respectively. In Reidovaya salmon, Hg concentrations in muscles were $0.04 \pm 0.005 \mu\text{g}\cdot\text{g}^{-1}$, while the gonads of males and females had Hg concentrations of 0.11 ± 0.008 and $0.09 \pm 0.006 \mu\text{g}\cdot\text{g}^{-1}$, respectively. Ni and Cd are characterized by minor amounts in the gonads of pink salmon but are found in larger amounts than Hg. Ni was 1.2–1.5 times higher than Cd in the muscles, however in the muscles and gonads of fish from the hatchery “Firsovka,” Cd distribution was almost identical to Ni. In pink salmon from the hatchery “Reidovy,” there were greater concentrations of Cd than Ni, typically 0.14 ± 0.012 in the muscle and 0.19 ± 0.034 and $0.18 \pm 0.035 \mu\text{g}\cdot\text{g}^{-1}$ in the male and female gonads, respectively. Cu was found to be twice the concentration of Ni in the muscles and gonads of salmon, with subsequent increasing concentrations of Pb, As and Zn. The levels of Pb in the fish organs and tissues were as follows: muscle varied from 0.59 ± 0.050 to $0.67 \pm 0.050 \mu\text{g}\cdot\text{g}^{-1}$, male gonads ranged from 0.014 to $0.89 \pm 0.014 \mu\text{g}\cdot\text{g}^{-1}$, and the calf of females was between 0.82 ± 0.043 and $0.84 \pm 0.045 \mu\text{g}\cdot\text{g}^{-1}$. It is important to note that the concentrations of toxic elements in the studied pink salmon individuals did not exceed the maximum Russian permissible concentration in foods (PC) and were below the standards adopted in Canada and the United States. Despite the mercury concentrations in Iturup salmon being five times lower in the muscle and two times below PC in the calf, concentrations of Pb in male and female pink salmon gonads from the island are approaching Russian sanitary standards. Levels of Pb in pink salmon muscle were 1.5 and 1.7 times lower than PC in fish from Iturup and Sakhalin, respectively. Cd concentration is also close to PC and almost reaches its value in the gonads of fish from “Reidovy.” In the gonads of salmon from “Firsovka” and in the fish muscle of fish from both plants, the concentrations of this toxic element were approximately half the acceptable PC. Only concentrations of As were significantly below PC where even the gonads did not exceed $\frac{1}{4}$ of the permissible concentration. Thus, the concentration of Pb and Cd in the pink salmon of the Sakhalin-Kuril region are close to the sanitary standard. The concentrations of these elements in the fish fillet are well below the amount allowed by sanitary standards and do not cause any concerns for consumers (Sanitary rules. 2002).

Discussion

According to the level of pink salmon stock in the Sakhalin-Kuril region, the three most important areas are the Iturup Island, the Southeastern coast of Sakhalin and the Aniva Bay. In catches on the East coast of Sakhalin and the Southern Kuril Islands, the late (autumn) form of pink salmon dominates (Kaev 2007).

In a previous study, the trace element composition of pink salmon caught in July 2013 in the Kuril Islands waters of the Pacific Ocean during its anadromous migration to the rivers of the Sea of Okhotsk were described (Khristoforova et al. 2015b). However, the present work studied pink salmon in October 2016 as they moved from the ocean into their native river, which would be their second time crossing the very rich waters of the Kuril-Kamchatka Region.

The difference between the trace elements found in the muscle and liver of salmon from the ocean waters near the islands did not exceed twice the amount found in fish from the Firsovka River. Sakhalin fish had much more variation in the levels detected in their tissues, which were 3–7 times higher than the fish from other areas (Table 1). Pink salmon from the Sea of Japan had the lowest concentrations of elements, which were significantly lower than in the fish of the Sakhalin-Kuril region. The greatest differences were found for Pb, whose concentration in muscles, liver and eggs of SKR fish was approximately 50 (49–56), 40 (42–44) and 60 (63–65) times higher, respectively, than in pink salmon from the Sea of Japan.

The exception to these findings was Zn, where greater concentrations were detected in the organs and tissues of pink salmon from the the Sea of Japan compared to fish in the SKR, which is a consequence of the anthropogenic influence on the Sea of Japan.

During winter, the fish that reproduce in the rivers of the Sakhalin-Kuril basin feed in the Sea of Japan and in the North-West Pacific Ocean. From the feeding area in the Sea of Japan, pink salmon migrate to spawn in the rivers of Northern Primorye, Western Sakhalin, the Amur basin, as well as Eastern Sakhalin, the southern Kuril Islands and the rivers flowing into the Aniva Bay. However, they mainly reproduce in the rivers of the first three regions. Fishing is based on the late oceanic group, which are selected based on the study of salmon.

Therefore, as the Asian pink salmon leave the nursery and return to spawn, not all of them will pass through the impact zone on the Kuril Island, or specifically pass by it on the seaside (the Sea of Japan) (Khristoforova et al. 2015b).

Pacific salmon (specifically Sakhalin-Kuril pinks) often feed in a high-altitude area (145 to 165°E and South to 40°N) where there is an abundance of zooplankton (Birman 1974). These zooplankton, which have absorbed copious amounts of phytoplankton growing on biogenic and other elements supplied by volcanism and upwelling in this area, transmit the microelements in their biomass to organisms of the next trophic level, including Pacific salmon.

The pink salmon that spawned in October migrated through the rivers of Reidovaya and Firsovka, which means that they were feeding in the North-Western Pacific Ocean and passed through the impacted geochemical zone twice. The transfer of trace elements through trophic levels explains why these salmon had significantly higher concentrations of all trace elements (except Zn) compared to the Japanese pink salmon.

Immature pink salmon that were caught in the ocean waters near Kuril Islands in July 2013 had to swim from the Sea of Okhotsk to the Southeast zone of the subarctic front from the southern and central parts of the Kuril Ridge (Shuntov and Temnykh 2011). These fish were captured on the outskirts of the geochemical impact zone and can not have accumulated the same levels of microelements compared to mature fish that came to spawn in the rivers Reidovaya and Firsovka.

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