ORGANOCHLORINE COMPOUNDS
IN FLOUNDERS OF GENUS HIPPOGLOSSOIDES GOTTSCHE, 1835
FROM THE FAR EASTERN SEAS OF RUSSIA

© 2020 M. M. Donets¹, V. Yu. Tsygankov¹,², M. D. Boyarova¹,
A. N. Gumovsky¹, Yu. P. Gumovskaya¹, and N. K. Khristoforova²,³

¹School of Biomedicine, Far Eastern Federal University, Vladivostok, Russian Federation
²School of Natural Sciences, Far Eastern Federal University, Vladivostok, Russian Federation
³Pacific Institute of Geography FEB RAS, Vladivostok, Russian Federation
Email: maksim.donecz@mail.ru

Received by the Editor 30.09.2019; after revision 20.11.2019; accepted for publication 27.03.2020; published online 31.03.2020.

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are global superecotoxicants belonging to a group of persistent organic pollutants (POPs). Fish and seafood are an important source of high-grade protein and polyunsaturated fatty acids, especially for residents of coastal areas. Up to 90 % of all pollutants enter the human body through food. Final depot of POPs in environment is marine ecosystems; therefore, POPs can accumulate in various objects of marine fisheries. The paper presents information on the concentrations of OCPs [HCH isomers (α-, β-, γ-), as well as DDT and its metabolites (DDD and DDE)], and polychlorinated biphenyls (PCBs) in muscles of flounders of genus Hippoglossoides Gottsch, 1835 from the Far Eastern seas of Russia (the Sea of Okhotsk, the Tatar Strait, and the Sea of Japan). Lipids were extracted from fish tissue samples with a mixture of hexane and acetone, followed by destruction of fatty components by concentrated sulfuric acid. OCPs and PCBs were separated by column chromatography with polar and non-polar solvents. Xenobiotics were quantified by gas chromatography–mass spectrometry. To assess quality of this methodology, a standard addition method was used. The average reproducibility of analyte concentrations varied 94.6 to 103.7 %, and it indicates reliability of the data obtained as well as effectiveness of methods applied. Average concentrations of \( \sum \text{DDT}, \sum \text{HCH}, \sum \text{OCP} (\sum \text{DDT} + \sum \text{HCH}), \) and \( \sum \text{PCB} \) were: (62 ± 89), (50 ± 52), (100 ± 125), and (92 ± 45) ng·g⁻¹ of lipids in the samples from the eastern part of the Sea of Okhotsk; (20 ± 17), (36 ± 37), (54 ± 41), and (99 ± 43) ng·g⁻¹ of lipids from the southern part of the Sea of Okhotsk; (40 ± 29), (62 ± 36), (102 ± 50), and (1616 ± 1177) ng·g⁻¹ of lipids from the Sea of Japan, respectively. In the samples from the Tatar Strait, the average levels of \( \sum \text{HCH}, \sum \text{OCP}, \) and \( \sum \text{PCB} \) were (221 ± 182), (224 ± 180), and (455 ± 317) ng·g⁻¹ of lipids, respectively. DDT was detected in three samples. In the flounders from the eastern part of the Sea of Okhotsk, the highest concentrations of DDT and average concentrations of HCH were recorded, which may be due to the location of a “repository” of pesticides on the Kamchatka Peninsula, where OCPs are buried. The entrance of PCBs into the waters of the southern part of the Sea of Okhotsk can be associated both with intensive shipping and effluents from landfills that carry residual amounts of PCBs into the ecosystem. The southern part of the Sea of Okhotsk is the cleanest of the areas studied and is characterized by the lowest content of DDT, HCH, and PCB in organisms. DDT was practically absent in the flounders from the Nevelsky Bay (the Tatar Strait). At the same time, they showed the highest level of HCH, represented only by β-isomer, which indicates a prolonged circulation of the toxicant in the ecosystem. According to the decree of the Government of the Sakhalin Region, on the territory of Sakhalin there are landfills for out-of-use or banned pesticides; storage of them was performed (at the time of the decree entering the force) with violations that could lead to serious environmental
pollution. Most likely, they became the source of pollution of the Tatar Strait. Another source of HCH pollution is currents that carry the waters of the Sea of Japan through the Nevelsky Bay into the Sea of Okhotsk. High levels of PCBs in the waters of the bay may result from intensive shipping and possible impact of household waste dumps on the Sakhalin Island. Flounders from the Sea of Japan are characterized by the highest POPs pollution. The entrance of OCPs into the sea may be due to surface runoffs, river flows, storage leaks of pesticides banned for use, and atmospheric transport from Asian countries where the use of some OCPs is still permitted. The determined levels of PCBs are an order of magnitude higher than those in the flounders from the Sea of Okhotsk and the Tatar Strait, which may be due to active shipping in Sea of Japan waters, influence of operating oil and coal ports in the city of Nakhodka, as well as local pollution of the coastal zone (so called wild beaches). Thus, we have studied the accumulation of organochlorine pesticides (HCH and DDT) and polychlorinated biphenyls in the muscles of flounders from the Far Eastern seas of Russia. With the existing global background of POPs formed on the planet, the levels of these compounds in the flounders of the southern part of the Sea of Okhotsk can be taken as background ones. The Sea of Japan is subject to the greatest anthropogenic pressure, and PCB concentrations are significantly higher in this area than in the Far Eastern seas of Russia and in the compared regions of the world as a whole. 

**Keywords:** DDT, HCH, PCB, flounder, genus *Hippoglossoides*, Far Eastern seas of Russia

Organochlorine pesticides (hereinafter OCPs) and polychlorinated biphenyls (hereinafter PCBs) belong to a group of persistent organic pollutants (hereinafter POPs) and are global superrecotoxicants [1]. Distribution of these compounds is due to transport by air and water, as well as bioaccumulation and biomagnification (an increase in concentration of toxicants in organisms with transition to higher levels of the food chain) [10, 11, 22, 26]. OCPs enter the environment through atmospheric transport from Asian countries where the use of DDT (for controlling disease carrier insects) and HCH (as a remedy for lice and scabies) is still permitted [21]. OCPs sources are landfills and pesticides burials, from which they are washed away by atmospheric precipitation and groundwater, entering marine ecosystems through river flows and surface runoffs. OCPs are known to get into freshwater bodies, including spawning grounds, through biotransport by migrating organisms [18]. PCBs enter ecosystems mainly during incineration of domestic and industrial waste, ignition of old transformers, evaporation from plasticizers, as well as leaks with other industrial wastes and leaks from PCBs-containing oils [13, 19, 20].

Fish and seafood are an important source of high-grade protein and polyunsaturated fatty acids, especially for residents of coastal areas. Up to 90 % of all pollutants enter the human body with food. The final depot of POPs in the environment is marine ecosystems; therefore, these substances can accumulate in various objects of marine fisheries [17, 22, 26].

The Far Eastern seas (the Sea of Japan, the Sea of Okhotsk, and the Bering Sea) are the main fishing zones of the Russian Federation. Flounders caught in the Far East are among the most important objects for fishing accounting for 9.5 % of the total fish catch in the region [2]. Catch volume, species diversity, and low market price predetermine their special significance in nutrition structure of local population. One of the most important types of flounders is halibut flounder of genus *Hippoglossoides* Gottsche, 1835 which is widespread in the Sea of Okhotsk, the Sea of Japan, and the Tatar Strait. We carried out preliminary monitoring of POPs content in flounders of the Sea of Okhotsk and made an assumption about possible use of the obtained concentrations of POPs as background ones for the Far Eastern seas [17].

The aim of the work is to assess levels of accumulation and biotransformation of OCPs and PCBs in halibut flounder from various regions of Far Eastern seas of Russia (the Sea of Okhotsk, the Tatar Strait, and the Sea of Japan).

**MATERIAL AND METHODS**

Flounders of genus *Hippoglossoides* (Gottsche, 1835) were caught in the eastern (off the coast of Kamchatka) and southern (off the coast of the Kuril Islands) parts of the Sea of Okhotsk, in the Nevelsky
Bay off the southwest coast of Sakhalin Island (the Tatar Strait), and in the Rifovaya Bay of Peter the Great Bay (the Sea of Japan) in summer (2016–2018) (Table 1, Fig. 1). Age of the fish ranged 0.6 to 1 year. Muscle (fillet) of fish was analyzed for the content of OCPs and PCBs. Frozen (−20 °C) tissue samples were delivered to the laboratory and homogenized before chemical analysis.

| Sampling area                   | Sampling year | Number of samples | Weight, g* | Lipids, %* |
|---------------------------------|---------------|-------------------|------------|------------|
| Southern part of the Sea of Okhotsk | 2016         | 10                | 219–402    | 0.03–2.07  |
|                                 |               |                   | 294 ± 52   | 0.72 ± 0.64|
| Eastern part of the Sea of Okhotsk | 2016         | 10                | 160–415    | 0.06–0.47  |
|                                 |               |                   | 230 ± 82   | 0.20 ± 0.13|
| The Tatar Strait                | 2017         | 15                | 289–510    | 0.03–0.6   |
|                                 |               |                   | 368 ± 72   | 0.17 ± 0.16|
| The Sea of Japan                | 2018         | 9                 | 122–250    | 0.04–1.06  |
|                                 |               |                   | 195 ± 45   | 0.62 ± 0.31|

Note: * – range, min–max (above the bar); mean ± standard deviation (under the bar).

Lipids were extracted from muscle homogenates of individual specimens (10–20 g) using a mixture of n-hexane and acetone, followed by destruction of fatty components by concentrated sulfuric acid [23]. Next, the extract obtained was separated by nonpolar (for PCB) and polar (for OCP) solvents by column chromatography with Florisil® sorbent.

Fig. 1. Map of sampling sites of flounders: 1 – the Rifovaya Bay, Peter the Great Bay, the Sea of Japan; 2 – the Nevelsky Bay, the Tatar Strait; 3 – southern part of the Sea of Okhotsk (off the coast of the Kuril Islands); 4 – eastern part of the Sea of Okhotsk (off the coast of Kamchatka)
To prepare standard solutions of OCPs and PCBs, standard samples (Dr. Ehrenstorfer and Accu-Standard) of α-HCH, β-HCH, γ-HCH, \(p,p'\)-DDT, \(o,p'\)-DDT, \(p,p'\)-DDD, \(o,p'\)-DDD, \(p,p'\)-DDE, and \(o,p'\)-DDE, as well as mixture of PCB congeners 28, 52, 155, 101, 118, 143, 153, 138, 180, and 207 with established metrological characteristics (content of main substances of 99.4–99.6%, determination error of 0.4%) were used. To calibrate the chromatoo-mass spectrometer, working standard solutions of OCP and PCB with a concentration of 10 ng·ml\(^{-1}\) were prepared by diluting standard solutions with an appropriate volume of \(n\)-hexane. Pesticides Library was also used. The main mass content of organochlorine compounds in the biomaterial was determined with Shimadzu GC MS-QP 2010 Ultra gas chromatoo-mass spectrometer equipped with AOC-5000 autosampler (detailed characteristics were indicated previously [27]). A SLB-5 capillary column was used for the study, as well as helium as a gas carrier (flow rate of 1 ml per minute). Temperatures of injector and detector were of +250 °C and +150 °C, respectively. The heating program was the following: increase in temperature to +100 °C for 4 minutes, heating to +310 °C at the rate of 7 °C per minute, and maintaining the final temperature for 6 minutes. Test mixture in a volume of 2 μl was added without separation, followed by opening the separation port after 1 minute. The ionization of substances in the gas phase was carried out in the electronic ionization mode (EI mode). Selected ion monitoring (SIM) was designed according to settings and detection limits of the device. Two ions (\(M^+\) and \([M+2]^+\)) were monitored for each chlorination level. To identify the test compound as supporting criteria, the exit time, mass, and relative content of the supporting ion were used. Measurement uncertainty of less than ±20% was considered as acceptable. Peak areas were measured using GCMS Postrun Analysis.

To assess the quality of the methodology applied, the method of standard additives was used. Known amounts of test compounds were added to the muscle tissue of 10 flounder samples. Sample preparation and study of mixed samples were carried out using the method described above. The results showed that average reproducibility of analyte concentrations varied 94.6 to 103.7 %, which indicates reliability of the data obtained as well as efficiency of methods applied. Detection limits were calculated as 3 standard deviations of 10 samples in samples mixed with the standards. For analytes that were not identified in mixed samples, the detection limits were determined as an amount of analyte in the sample in relation to minimum concentration of calibration standard. For the OCPs investigated, the detection limits were: α-HCH – 0.2–0.3; β-HCH – 0.1–0.2; γ-HCH – 0.3–0.5; \(p,p'\)-DDT – 0.6–0.7; \(o,p'\)-DDT – 0.2–0.6; \(p,p'\)-DDD – 0–0.1; \(o,p'\)-DDD – 0.1–0.2; \(p,p'\)-DDE – 0.1–0.2; \(o,p'\)-DDE – 0.1–0.4 ng·g\(^{-1}\). For PCB congeners, the detection limits were: 28 – 0.5–0.6; 52 – 0.4–0.7; 155 – 0.1–0.5; 101 – 0.6–0.8; 118 – 0.7–0.8; 143 – 0.2–0.7; 153 – 0–0.1; 138 – 0.2–0.3; 180 – 0.5–0.6; 207 – 0.7–0.8 ng·g\(^{-1}\).

Statistical analysis of the results was made using IBM SPSS Statistics software. The reliability of the data was assessed using two-sided Kruskal – Wallis test with a significance level of \(p \leq 0.05\). The results are presented as follows: concentration range, mean value ± standard deviation.

RESULTS

Eastern and southern parts of the Sea of Okhotsk. A concentration range of \(\Sigma\)OCP (\(\Sigma\)DDT + \(\Sigma\)HCH) in the flounders from the eastern part of the Sea of Okhotsk varied widely 14 to 434 ng·g\(^{-1}\) of lipids with an average concentration of \((100 \pm 125)\) ng·g\(^{-1}\) of lipids. Total levels of HCH and DDT ranged 14 to 158 [average of \((50 \pm 52)\)] and 0.6 to 276 [average of \((62 \pm 89)\)] ng·g\(^{-1}\) of lipids, respectively. A range of OCP concentrations in fish from the southern part of the Sea of Okhotsk was 11–141 ng·g\(^{-1}\) of lipids with an average concentration of \((54 \pm 41)\) ng·g\(^{-1}\) of lipids, which was lower than in the waters off the coast.
of Kamchatka. Total levels of HCH and DDT in fish varied 3 to 103 [average of (36 ± 37)] and 1 to 45 [average of (20 ± 17)] ng·g⁻¹ of lipids, respectively, i.e. they were also lower than off the coast of Kamchatka.

Of the HCH isomers in fish from the eastern part of the Sea of Okhotsk, the β-isomer with a concentration of 14–158 [average of (49 ± 51)] ng·g⁻¹ of lipids was the most frequently recorded one (Fig. 2). Meanwhile, α-HCH was detected in only one sample with a concentration of 8 ng·g⁻¹ of lipids. Concentrations of γ-HCH were below the detection limits in all samples.

![Fig. 2. Average concentration of pollutants in the flounders from the eastern and southern parts of the Sea of Okhotsk (error bars represent standard deviation value)](image)

In the eastern part of the Sea of Okhotsk, of DDT and its metabolites concentrations of o,p'-DDT, p,p'-DDT, and p,p'-DDE were below the detection limits in all samples. The levels of o,p'-DDD and p,p'-DDD ranged 6 to 45 [average of (23 ± 19)] and 13 to 276 [average of (72 ± 114)] ng·g⁻¹ of lipids (Fig. 2), respectively. Meanwhile, o,p'-DDE was identified in two samples at concentrations of 0.55 and 41.68 ng·g⁻¹ of lipids.

In fish from the southern part of the Sea of Okhotsk, HCH was represented by α- and β-isomers with concentrations of 2–12 [average of (5 ± 4)] and 1–96 [average of (40 ± 37)] ng·g⁻¹ of lipids, respectively (Fig. 2). The levels of γ-HCH were below the detection limits in all samples. Of DDT and its metabolites, concentrations of o,p'-DDT were below the detection limits in all the fish studied. Meanwhile, p,p'-DDT, p,p'-DDD, and o,p'-DDE were determined singly at concentrations of 7, 23, and 33 ng·g⁻¹ of lipids, respectively. The content of o,p'-DDD ranged 2 to 45 ng·g⁻¹ of lipids, with an average concentration of (17 ± 18) ng·g⁻¹ of lipids. Concentrations of p,p'-DDE varied in the range of 1–7 [average of (4 ± 2)] ng·g⁻¹ of lipids.

The sum of PCB concentrations in the flounders from the eastern part of the Sea of Okhotsk varied 24 to 279 [average of (125 ± 91)] ng·g⁻¹ of lipids. PCBs were mainly represented by 101 and 153 congeners; 28, 52, 155, 118, 138, and 180 congeners were identified fragmentarily (in one or two samples) at the following concentrations: 28 – of 41 and 19; 52 – of 33; 155 – of 71; 118 – of 21 and 71; 138 – of 108 and 35;
Concentrations of PCB 207 were below the detection limits in all samples studied. The concentrations of PCB 101 and PCB 153 varied 11 to 81 [average of (42 ± 27)] and 49 to 117 [average of (49 ± 37)] ng·g⁻¹ of lipids, respectively.

The sum of PCB levels in the samples ranged 25 to 150 [average of (99 ± 43)] ng·g⁻¹ of lipids. PCBs were represented by 28, 101, 118, 153, and 138 congeners at concentrations of 6–12, 5–30, 15–50, 18–55, and 34–51 ng·g⁻¹ of lipids, respectively. The average levels were (9 ± 2), (18 ± 9), (38 ± 13), (35 ± 15), and (44 ± 7) ng·g⁻¹ of lipids (Fig. 2). PCBs 52, 155 and 180 were found fragmentary at following concentrations: 52 – of 14 and 5; 155 – of 17; 180 – of 17 and 12 ng·g⁻¹ of lipids. The amounts of PCB 143 and PCB 207 were below the detection limits in all samples.

**Nevelsky Bay, the Tatar Strait.** In fish from the Tatar Strait, of OCPs mainly β-HCH was detected within a wider range of concentrations of 37–555 ng·g⁻¹ of lipids (average of (224 ± 180) ng·g⁻¹ of lipids). DDT and its metabolites were found in three samples and represented by p,p'-DDD (of 15 ng·g⁻¹ of lipids) and p,p'-DDE (of 6 and 19 ng·g⁻¹ of lipids) (Fig. 3). The sum of PCB concentrations in the flounders was within the range of 193–1384 ng·g⁻¹ of lipids (with an average value of (455 ± 317) ng·g⁻¹ of lipids). PCB congeners 28, 52, 155, 101, 118, 143, 153, 138, and 180 were found in the flounders from the Tatar Strait. PCB 207 concentrations were below the detection limits in all samples. Levels of PCB congeners were found in ranges: for 28 – 4–61; 52 – 3–287; 155 – 3–78; 101 – 23–108; 118 – 20–326; 143 – 25–56; 153 – 38–291; 138 – 8–423; 180 – 28–106 ng·g⁻¹ of lipids. The average concentrations were (29 ± 21), (80 ± 83), (30 ± 28), (45 ± 23), (85 ± 80), (44 ± 13), (118 ± 72), (121 ± 109), and (59 ± 29) ng·g⁻¹ of lipids. PCB 101 was detected in all the samples studied.

**Rifovaya Bay, Peter the Great Bay, Sea of Japan.** Concentrations of OCP (ΣHCH + ΣDDT) in the flounders from the Rifovaya Bay ranged 38 to 193 ng·g⁻¹ of lipids with an average value of (102 ± 50) ng·g⁻¹ of lipids. HCH and DDT isomers, as well as its metabolites, were found in all the samples studied. The levels of ΣHCH and ΣDDT varied 29 to 134 and 9 to 88 ng·g⁻¹ of lipids, respectively; average concentrations were (62 ± 36) and (40 ± 29) ng·g⁻¹ of lipids. In the flounders from the Sea of Japan, all HCH isomers were detected.
were found. Levels of α-, β-, and γ-isomers were within the ranges of 0.4–5, 27–127, and 0.9–6 ng·g⁻¹ of lipids, respectively. Average concentrations were: for α-HCH – of (2 ± 1); β-HCH – (59 ± 35); γ-HCH – (2 ± 2) ng·g⁻¹ of lipids (Fig. 4). The β-isomer was found in all the samples studied.

![Graph showing average concentration of pollutants in flounders from the Sea of Japan](image)

**Fig. 4.** Average concentration of pollutants in the flounders from the Sea of Japan (error bars represent standard deviation value)

Of DDT and its metabolites in the flounders, o,p’-DDT was not detected, while p,p’-DDT was found in only one sample (6 ng·g⁻¹ of lipids). The concentration ranges of o,p’-DDD, p,p’-DDD, o,p’-DDE, and p,p’-DDE were 1–38, 6–52, 1–34, and 4–47 ng·g⁻¹ of lipids, respectively. Average levels were (12 ± 12), (19 ± 18), (7 ± 10), and (16 ± 16) ng·g⁻¹ of lipids (Fig. 4). The concentration of PCBs ranged 421 to 3716 ng·g⁻¹ of lipids; average concentration was of (1616 ± 1177) ng·g⁻¹ of lipids. PCBs were represented by 28, 52, 101, 118, 143, 153, 138, and 180 congeners. PCB 207 concentrations were below the detection limits in all the samples studied. Congener levels varied as follows: 28 – 3–405; 52 – 7–287; 101 – 40–207; 153 – 3–11; 118 – 53–581; 143 – 11–46; 153 – 126–849; 138 – 126–936; 180 – 28–1835 ng·g⁻¹ of lipids. Average concentrations were (54 ± 132), (54 ± 88), (6 ± 3), (117 ± 58), (241 ± 183), (26 ± 15), (387 ± 265), (429 ± 279), and (318 ± 579) ng·g⁻¹ of lipids, respectively.

**DISCUSSION**

In the Far East, monitoring of POPs content in marine and onshore facilities was not carried out regularly until 2012. Currently, monitoring is carried out regularly throughout the Far Eastern seas. Data on the content of OCPs and PCBs in Pacific salmon, birds, and mammals were accumulated [16, 17, 18, 22, 24, 25, 26, 27, 28].

Flounders (Pleuronectidae family) are among the most common representatives of the bottom ichthyofauna that inhabit the entire shelf and continental slope of the seas. The main feature of flounders’ biology is their lifestyle: they lie on the ground or swim in the bottom layer, remaining within their area and migrating seasonally to deeper regions [8]. Thus, they can be bioindicators of local pollution.
Flounders of genus *Hippoglossoides* belong to a group of flounders with mixed type of nutrition: both typical benthic (shrimps, bivalves, etc.) and plankton animals (hyperiids, sagittae, etc.) can be found in their food. Also, juveniles of smelt, herring, and other small fish species often become the food of flounders. The food composition is strongly dependent on the area. In warmer areas of the Far Eastern seas (the Sea of Japan, the southern part of the Tatar Strait), mainly flathead flounder (*Hippoglossoides dubious* Schmidt, 1904) is found, while in colder waters (the Sea of Okhotsk, the Bering Sea) it is Bering flounder (*Hippoglossoides robustus* Gill & Townsend, 1897). In the southeast of Sakhalin and in the Sea of Japan, molluscs dominate the diet; in the southeastern part of the Bering Sea, flounders feed mainly on echinoderms and chillums in the lower shelf, as well as plankton in shallow water [6, 8]. Both species belong to the same genus, are similar in environmental and biological characteristics, and can be used as bioindicators. Differences in the accumulation of POPs in flounders from different regions may be due to anthropogenic pressure on the habitat area or bioaccumulation of organisms included in the diet.

In the flounders in the eastern part of the Sea of Okhotsk, the highest concentrations of DDT and moderate concentrations of HCH were detected. This may be due to location of a “repository” of pesticides on the Kamchatka Peninsula, where aldrin, dieldrin, hexachlorobenzene, and other OCPs are buried [3, 5]. DDD was the most common metabolite of DDT; HCH was represented by the most stable β-isomer. It indicates a prolonged circulation of both toxicants in the ecosystem and decomposition of initial compounds to more stable forms. Leakage from the reservoirs buried and evaporation of toxicants with subsequent atmospheric transport are probably the main reasons of environment and biota pollution in this area, since agriculture on the western side of the Kamchatka Peninsula is poorly developed. Currently, as there are no garbage processing plants in Kamchatka, garbage is buried at special landfills [3, 9], and leakages are quite possible. It is known that due to their chemical stability, insulating properties, and thermal stability, PCBs were used in various industries for production of thermal insulation, rubber, plastic, as well as dyes, pigments, and carbonless copy paper [19]. Entrance of polychlorinated biphenyls into Sea of Okhotsk waters off Kamchatka can result from both intensive shipping and effluents from the landfills that carry residual amounts of PCBs into the ecosystem.

The southern part of the Sea of Okhotsk is the cleanest of the areas studied and is characterized by the lowest content of DDT, HCH, and PCB in organisms. The south of the Sea of Okhotsk is located far from all surface sources of pollution. In addition, the region is characterized by active hydrodynamics and water exchange with the Pacific Ocean through the Kuril straits, which can contribute to the redistribution of POPs in the waters. The concentrations of all POPs found in the flounders from the southern part of the Sea of Okhotsk are the lowest, compared with those of the Sea of Japan, the Tatar Strait, and the eastern part of the Sea of Okhotsk. Thus, the hypothesis that the levels of pollutants in the muscles of flounders from the south of the Sea of Okhotsk are background ones for the Far Eastern seas of Russia [17] has been proved.

Interesting scientific information is provided by the data on OCP content in the muscles of flounders from the Nevelsky Bay (the Tatar Strait). DDT was hardly identified in the samples studied: only one sample contained *p,p*-DDD, while two samples contained *p,p*-DDE. This suggests that the area is not seriously polluted with the pesticide. At the same time, the highest level of HCH was detected in the muscles of flounders from the Tatar Strait (Fig. 5); HCH was represented only by β-isomer, which indicates the long-term circulation of this toxicant in the ecosystem.
Organochlorine compounds in flounders of genus *Hippoglossoides* Gottsche, 1835…

Fig. 5. Concentrations of α-HCH (A), β-HCH (B), and ∑HCH (C) in the muscles of the flounders from the areas studied (error bars represent standard deviation value).

The Nevelsky Bay is located far from large agricultural enterprises from the side both of Sakhalin Island and the mainland. However, according to the decree of the Government of the Sakhalin Region dated September 22, 2008, there are landfills for out-of-use or prohibited pesticides on the island, the storage of which was performed (at the time of the decree entering the force) with violations that could lead to serious environmental pollution [4, 7]. Most likely, it was the landfills that became the source of pollution of the Tatar Strait, and it led to the release of HCH into the ecosystem of the strait. This is also indicated by the detection of β-isomer of HCH, which is considered to be the most stable one. Another source of HCH pollution is currents that carry the waters of the Sea of Japan through the Nevelsky Strait into the Sea of Okhotsk.

PCB levels in fish from the Nevelsky Bay are several times higher than those from the Sea of Okhotsk, but noticeably lower than those of Sea of Japan flounders (Fig. 6). High concentrations of polychlorinated biphenyls can be related to intensive shipping and possible impact of landfills on Sakhalin Island (according to 2007 data, there were 54 authorized landfills and 37 unauthorized ones in the region [4]). The Tatar Strait is an economically important area with active fishing and variety of cargo transportation. Influence of warm currents of the Sea of Japan and cold currents of the Sea of Okhotsk, as well as limited water exchange with the open sea and with the ocean due to the “tightness” of the strait water body between the mainland and the island, are the factors contributing to the accumulation of pollutants in this region. Thus, the main source of PCBs in the waters of the Tatar Strait may be intensive activity of fishing and transport vessels.

In the flounders of the Sea of Japan, DDD and DDE were found of all DDT metabolites, and α-, β- and γ-isomers were found of HCH isomers. Primorye is an agriculturally developed region; in the middle of the XX century, pesticides including organochlorines were widely used there. Being chemically and biologically stable, these compounds could partially or completely remain in the soil, and now they are carried into Sea of Japan waters by surface runoff and river flow. In addition, there are pesticide
According to the Stockholm Convention, developing countries in Asia may use DDT (to protect population from malaria vectors) and HCH (as a remedy for lice and scabies) \[21\]. The Sea of Japan washes the shores of North and South Korea, and through the Korea Strait it is connected to the East China Sea washing the shores of China and the western shores of the Korean Peninsula. Pesticides can enter marine ecosystems through atmospheric transport, river flows, and currents from the East China Sea, carrying pesticide residues from agricultural land, as well as through industrial effluents. The most significant source of DDT and HCH seems to be China as one of the largest producers and consumers of pesticides in the world \[12\]. In the muscles of flounders, DDT is represented mainly by its metabolites DDD and DDE, which indicates that contamination occurred long time ago and initial compound decayed.

Data on the concentration of PCBs in the muscles of fish from the Sea of Japan are very important. The identified levels of PCBs are an order of magnitude higher than those in the flounders from the Sea of Okhotsk and the Tatar Strait (Fig. 6). The Rifovaya Bay is located within the boundaries of the Livadia village, where there are many recreation centers as well as so-called wild beaches. Every year, a huge number of tourists come to the bay coast from both the Far East and other regions of Russia. There are a lot of people at wild beaches, where garbage and waste products are neither cleaned nor taken away. In addition, the city of Nakhodka is located not far from the village, with its operating oil and coal ports, the impact of which can also affect coastal ecosystems. Moreover, the Sea of Japan is an area of intensive navigation and commercial fishing, which can result in PCBs entering the environment and organisms.

Comparison of the average concentrations of OCPs in the flounders studied by us with data for different regions of the World Ocean showed that DDT levels in all regions of the Far Eastern seas of Russia are significantly lower than those in the Atlantic Ocean (141 ng·g\(^{-1}\) of lipids), the Baltic Sea (579 ng·g\(^{-1}\) of lipids in the Gdansk Bay; 732 ng·g\(^{-1}\) of lipids at the mouth of the Visla River), and the Yellow Sea (122 ng·g\(^{-1}\) of lipids) \[10, 14, 29\], but an order of magnitude higher than in the Bering Sea (5 ng·g\(^{-1}\) of lipids) \[14\]. The average levels of α- and γ-HCH in fish are comparable with the concentrations given in the publications mentioned (1 to 6 ng·g\(^{-1}\) of lipids). In the data studied, the comparison was made with \[10, 14\],
β-HCH concentrations were not shown. In [29], the amount of β-isomer was below the detection limits (< 0.002 ng·g⁻¹ of wet weight); in [15], the toxicant levels were not given (since it was identified in 24 % of samples). Nevertheless, β-HCH was the dominant isomer in the flounders from all regions of the Far Eastern seas and exceeded the sum of HCH concentrations in the flounder muscles from the Yellow Sea (13 ng·g⁻¹ of lipids) [10].

PCB levels in the fish of the Sea of Okhotsk did not exceed the concentrations found in flounders of the Atlantic Ocean (518 ng·g⁻¹ of lipids) and the Baltic Sea (259 ng·g⁻¹ of lipids in the Gdansk Bay; 373 ng·g⁻¹ of lipids in the mouth of the Visla River) [15, 29], but significantly exceeded those in flounders from the Yellow (8 ng·g⁻¹ of lipids) and Bering seas (15 ng·g⁻¹ of lipids) [10, 14]. The total level of PCBs in the flounders of the Tatar Strait was between the values for fish from the Gdansk Bay and the mouth of the Visla River (the Baltic Sea). In the Sea of Japan, maximum PCB levels in fish were significantly higher than in the Baltic, Bering, and Yellow seas, as well as in the Atlantic Ocean. Such a big difference in average concentrations of POPs in flounders between the regions indicates a serious anthropogenic pressure on ecosystem of the Rifovaya Bay and the entire area.

Conclusions:

1. The accumulation of organochlorine pesticides and polychlorinated biphenyls in the muscles of flounders from the Tatar Strait, the Sea of Japan, and the Sea of Okhotsk of the Far East of Russia was studied. The average concentrations of ∑DDT, ∑HCH, ∑OCP (∑DDT + ∑HCH), and ∑PCB in the muscles of the flounders studied were: in the eastern part of the Sea of Okhotsk – (62 ± 89), (50 ± 52), (100 ± 125), and (92 ± 45) ng·g⁻¹ of lipids; in the southern part of the Sea of Okhotsk – (20 ± 17), (36 ± 37), (54 ± 41), and (99 ± 43) ng·g⁻¹ of lipids; in the Sea of Japan – (40 ± 29), (62 ± 36), (102 ± 50), and (1616 ± 1177) ng·g⁻¹ of lipids, respectively. In the Tatar Strait, the average levels of β-HCH, ∑OCP (∑DDT + β-HCH) and ∑PCB were (221 ± 182), (224 ± 180), and (455 ± 317) ng·g⁻¹ of lipids, respectively.

2. Xenobiotics should not have background concentrations in the environment; however, with the existing global background of POPs, the levels of these compounds in the flounders of the southern part of the Sea of Okhotsk (off the coast of the Kuril Islands), which is characterized by the absence of direct pollution sources and by active hydrodynamics, can be taken as background ones.

3. The Sea of Japan is subject to the greatest anthropogenic pressure, and its PCB concentrations are significantly higher than those in the Far Eastern seas of Russia and in the compared regions of the world as a whole.

*This work was financially supported by the Russian Science Foundation (agreement no. 18-14-00120).*

REFERENCES

1. Amirova Z. K., Speranskaya O. A. *Novye stoikie organicheskie superekotoksikanty i ikh vliyanie na zdrov’ye cheloveka / O. Yu. Tsittser (Ed.).* Moscow : Eko-Soglasie, 2016. 170 p. (in Russ.)

2. Vorozhbit O. Yu., Danilovskikh I. A., Kuzmicheva N. Yu., Titova N. Yu., Shashlo N. V. *Rybnaya promyshlennost’ Dal’nego Vostoka Rossii: sovremennoe sostoyanie, problemy i perspektivy konkurentsospособности / O. Yu. Vorozhbit (Ed.).* Vladivostok : Izd-vo VGUES, 2016, 156 p. (in Russ.)

3. Doklad o sostoyanii okruchayushchei sredy v Kamchatskom krae v 2018 godu. Petropavlovsk-Kamchatskii : Ministerstvo prirodnyh resursov i ekologii Kamchatskogo kraia, 2019, 395 p. (in Russ.)
4. Zubtsova I. L. Razmeshchение отходов на территории Сахалинской области. Vologdskie chteniya, 2008, no. S, pp. 109–118. (in Russ.)
5. Informatsionnyi otchet po ob”ektu “Monitoring Kozel’skogo poligona zakhoroneniya yadokhimikatov i pestisidov”. Elizovo : ООО “Nedra”, 2018, 49 p. (in Russ.)
6. Napazakov V. V., Chuchukalo V. I. Pitanie i pishchevye otnosheniya kambal v zapadnoi chasti Beringova morya v letne-osennii period. Izvestiya TINRO, 2002, vol. 130, pp. 595–617. (in Russ.)
7. Postanovlenie Pravitel’stva Sakhalinskoi oblasti. O dolgosrochnoi oblastnoi tselevoi programme “Otkhody proizvodstva i potrebleniya Sakhalinskoi oblasti (2009–2015)”. [Electronic resource]. URL: http://docs.cntd.ru/document/819065590 [accessed: 20.07.2019]. (in Russ.)
8. Fadeev N. S. Spravochnik po biologii i promyslu ryb severnoi chasti Tikhogo okeana. Vladivostok : TINRO-tsentr, 2005, 366 p. (in Russ.)
9. Khristoforova N. K. Dal’nii Vostok Rossii: priродnye usloviya, resursy, ekologicheskie problemy. Moscow: Magistr, 2018, 830 p. (in Russ.)
10. Byun G. H., Moon H. B., Choi J. H., Hwang J., Kang C. K. Biomagnification of persistent chlorinated and brominated contaminants in food web components of the Yellow Sea. Marine Pollution Bulletin, 2013, vol. 73, iss. 1, pp. 210–219. https://doi.org/10.1016/j.marpolbul.2013.05.017
11. Drouillard K. G. Biomagnification. In: Encyclopedia of Ecology : 2nd edition. Vol. 1 / B. Fath (Ed.). [London] : Elsevier, 2008, pp. 353–358. https://doi.org/10.1016/B978-0-444-63768-0.00377-2
12. Grung M., Lin Y., Zhang H., Steen A. O., Huang J., Zhang G., Larssen T. Pesticide levels and environmental risk in aquatic environments in China – A review. Environment International, 2015, vol. 81, pp. 87–97. https://doi.org/10.1016/j.envint.2015.04.013
13. Guerra R., Pasteris A., Righi S., Ok G. Historical record of polychlorinated biphenyls (PCBs) in the continental shelf of the Korea Strait. Chemosphere, 2019, vol. 237, pp. 124438. https://doi.org/10.1016/j.chemosphere.2019.124438
14. Hartwell S. I., Apeti A. D., Pait A. S., Radenbaugh T., Britton R. Benthic habitat contaminant status and sediment toxicity in Bristol Bay, Alaska. Regional Studies in Marine Science, 2018, vol. 24, pp. 343–354. https://doi.org/10.1016/j.rsma.2018.09.009
15. Kopko O., Dabrowska H. Variability of biological indices, biomarkers, and organochlorine contaminants in flounder (Platichthys flesus) in the Gulf of Gdańsk, southern Baltic Sea. Chemosphere, 2018, vol. 194, pp. 701–713. https://doi.org/10.1016/j.chemosphere.2017.12.039
16. Lukyanova O. N., Tsygankov V. Yu., Boyarova M. D. Khristoforova N. K. Bioaccumulation of HCHs and DDTs in organs of Pacific salmon (genus Oncorhynchus) from the Sea of Okhotsk and the Bering Sea. Chemosphere, 2016, vol. 157, pp. 174–180. https://doi.org/10.1016/j.chemosphere.2016.05.039
17. Lukyanova O. N., Tsygankov V. Yu., Boyarova M. D. Organochlorine pesticides and polychlorinated biphenyls in the Bering flounder (Hippoglossoides robustus) from the Sea of Okhotsk. Marine Pollution Bulletin, 2018, vol. 137, pp. 152–156. https://doi.org/10.1016/j.marpolbul.2018.10.017
18. Reddy A. V. B., Moniruzzaman M., Aminabhavi T. M. Polychlorinated biphenyls (PCBs) in the environment: Recent updates on sampling, pretreatment, cleanup technologies and their analysis. Chemical Engineering Journal, 2019, vol. 358, pp. 1186–1207. https://doi.org/10.10134/s0032945215030078
(2021–2030): A call for global action. *Science Total Environment*, 2019, vol. 689, pp. 1304–1315. https://doi.org/10.1016/j.scitotenv.2019.06.444

22. Tsygankov V. Yu. Organochlorine pesticides in marine ecosystems of the Far Eastern seas of Russia (2000–2017). *Water Research*, 2019, vol. 161, pp. 43–53. https://doi.org/10.1016/j.watres.2019.05.103

23. Tsygankov V. Yu., Boyarova M. D. Sample preparation method for the determination of organochlorine pesticides in aquatic organisms by gas chromatography. *Achievements in the Life Sciences*, 2015, vol. 9, no. 1, pp. 65–68. https://doi.org/10.1016/j.als.2015.05.010

24. Tsygankov V. Yu., Boyarova M. D., Lukyanova O. N. Bioaccumulation of organochlorine pesticides (OCPs) in the northern fulmar (*Fulmarus glacialis*) from the Sea of Okhotsk. *Marine Pollution Bulletin*, 2016, vol. 110, iss. 1, pp. 82–85. https://doi.org/10.1016/j.marpolbul.2016.06.084

25. Tsygankov V. Yu., Boyarova M. D., Lukyanova O. N. Bioaccumulation of persistent organochlorine pesticides (OCPs) by gray whale and Pacific walrus from the western part of the Bering Sea. *Marine Pollution Bulletin*, 2015, vol. 99, iss. 1–2, pp. 235–239. https://doi.org/10.1016/j.marpolbul.2015.07.020

26. Tsygankov V. Yu., Boyarova M. D., Lukyanova O. N., Khristoforova N. K. Bioindicators of organochlorine pesticides in the Sea of Okhotsk and the western Bering Sea. *Archives of Environmental Contamination and Toxicology*, 2017, vol. 73, no. 2, pp. 176–184. https://doi.org/10.1007/s00244-017-0380-2

27. Tsygankov V. Yu., Lukyanova O. N., Boyarova M. D. Organochlorine pesticide accumulation in seabirds and marine mammals from the Northwest Pacific. *Marine Pollution Bulletin*, 2018, vol. 128, pp. 208–213. https://doi.org/10.1016/j.marpolbul.2018.01.027

28. Tsygankov V. Yu., Lukyanova O. N., Khristoforova N. K. The Sea of Okhotsk and the Bering Sea as the region of natural aquaculture: Organochlorine pesticides in Pacific salmon. *Marine Pollution Bulletin*, 2016, vol. 113, iss. 1–2, pp. 69–74. https://doi.org/10.1016/j.marpolbul.2016.08.060

29. Waszak I., Dabrowska H., Komar-Szymczak K. Comparison of common persistent organic pollutants (POPs) in flounder (*Platichthys flesus*) from the Vistula (Poland) and Douro (Portugal) River estuaries. *Marine Pollution Bulletin*, 2014, vol. 81, iss. 1, pp. 225–233. https://doi.org/10.1016/j.marpolbul.2014.01.044

**ХЛОРОРГАНИЧЕСКИЕ СОЕДИНЕНИЯ**

**В КАМБАЛАХ РОДА HIPPOGLOSSOIDES GOTTSCHE, 1835**

**ИЗ ДАЛЬНЕВОСТОЧНЫХ МОРЁЙ РОССИИ**

М. М. Донец¹, В. Ю. Цыганков¹,², М. Д. Боярова¹,
А. Н. Гумовский¹, Ю. П. Гумовская¹, Н. К. Христофорова²,³

¹Школа биомедицины, Дальневосточный федеральный университет, Владивосток, Российская Федерация
²Школа естественных наук, Дальневосточный федеральный университет, Владивосток, Российская Федерация
³Тихоокеанский институт географии ДВО РАН, Владивосток, Российская Федерация

E-mail: maksim.donecz@mail.ru

Хлорорганические пестициды (ХОП) и полихлорированные бифенилы (ПХБ) относятся к группе стойких органических загрязняющих веществ (СОЗ) и являются глобальными суперэкотоксинами. Рыба и морепродукты — важный источник полноценного белка и полиненасыщенных жирных кислот, особенно для жителей приморских районов. До 90% всех поллютантов поступают в организм человека с пищей. Конечным депо СОЗ в окружающей среде являются морские экосистемы, а следовательно, эти вещества могут накапливаться в различных объектах морского промысла. В работе представлены сведения о концентрациях ХОП [изомеры ГХЦГ (α-, β-, γ-),
ДДТ и его метаболиты (ДДД и ДДЕ) и ПХБ в мышцах камбал рода Hippoglossoides Gottsche, 1835, обитающих в дальневосточных морях России (Охотское море, Татарский пролив, Японское море). Липиды экстрагировали из образцов тканей рыб смесью гексана и ацетона с последующим разрушением жировых компонентов концентрированной серной кислотой. ХОП и ПХБ разделяли при помощи колоночной хроматографии полярным и неполярным растворителями. Концентрация ксенобиотиков количественно определяли методом газовой хромато-масс-спектрометрии. Для оценки качества выбранных методик применяли метод стандартных добавок. Средняя воспроизводимость концентраций анализов варьировала от 94,6 до 103,7 %, что говорит о надёжности полученных данных и об эффективности использованных методов. Средние концентрации ∑ДДТ, ∑ГХЦГ, ∑ХОП (∑ДДТ + ∑ГХЦГ) и ∑ПХБ конгенеров составили: в образцах, отобранных в восточной части Охотского моря, — (62 ± 89), (50 ± 52), (100 ± 125) и (92 ± 45) нг·г⁻¹ липидов; в южной части Охотского моря — (20 ± 17), (36 ± 37), (54 ± 41) и (99 ± 43) нг·г⁻¹ липидов; в Японском море — (40 ± 29), (62 ± 36), (102 ± 50) и (1616 ± 1177) нг·г⁻¹ липидов соответственно. Средние концентрации ПХБ в воде южной части Охотского моря — (221 ± 182), (224 ± 180) и (455 ± 317) нг·г⁻¹ липидов соответственно. ДДТ обнаружен в трёх исследованных образцах. В восточной части Охотского моря в камбалах зарегистрированы наибольшие концентрации ДДТ и умеренные — ГХЦГ, что может быть связано с расположением на полуострове Камчатка «могильника» ядохимикатов и пестицидов, в котором захоронены ХОП. Поступление ПХБ в воды южной части Охотского моря может объясниться как активным судоходством, так и наличием стоков с мусорных полигонов, несущих остаточные количества ПХБ в экосистему. Южная часть Охотского моря — самый чистый из исследованных районов, характеризующийся наименьшим содержанием ДДТ, ГХЦГ и ПХБ в организмах. В камбалах из залива Невельского (Татарский пролив) ДДТ практически отсутствовал. В то же время в них выявлен самый высокий уровень содержания ГХЦГ, представленного только β-изомером, что говорит о длительной циркуляции токсиканта в экосистеме. Согласно постановлению Правительства Сахалинской области, на территории о-ва Сахалин есть полигоны размещения пришедших в негодность или запрещённых пестицидов, хранение которых (на момент вступления постановления в силу) осуществлялось с нарушениями, способными привести к серьёзному загрязнению окружающей среды. Скорее всего, источником загрязнения Татарского пролива стали именно они. Другим источником загрязнения ГХЦГ могут быть течения, выносящие воды Японского моря через пролив Невельское в Охотское море. Высокие уровни ПХБ в водах залива могут быть связаны с активным судоходством и, возможно, с влиянием свалок бытовых отходов на о-ве Сахалин. Камбалы из Японского моря характеризуются наибольшим загрязнением СОЗ. Поступление ХОП в акваторию моря может быть связано с поверхностными смыгами, речными стоками, утечками из хранилищ запрещённых к применению пестицидов и атмосферным переносом из стран Азии, где до сих пор разрешено применение некоторых ХОП. Найденные уровни содержания ПХБ на порядок величины превышают таковые в камбалах из Охотского моря и Татарского пролива, что может быть объяснено активным судоходством в водах Японского моря, влиянием действующих нефтепроводов и угольных портов в г. Находке, а также местным загрязнением прибрежной полосы (так называемых диких пляжей). Таким образом, исследована аккумуляция хлорорганических пестицидов (ГХЦГ и ДДТ) и полициклических бифенилов в мышцах камбал из дальневосточных морей России. При существующем глобальном фоне СОЗ, сформировавшемся на планете, уровни этих соединений в камбалах южной части Охотского моря могут быть приняты как фоновые. Наибольшему антропогенному прессу подвержено Японское море, где концентрации ПХБ значительно превышают таковые как в дальневосточных морях России, так и в сравниваемых регионах мира в целом.

Ключевые слова: ДДТ, ГХЦГ, ПХБ, камбы, род Hippoglossoides, дальневосточные моря России.