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*PERSISTENT ORGANIC POLLUTANTS IN THE BENTHAL DEPOSITS OF THE ESTUARIAL ZONES OF THREE RIVERS IN PETER THE GREAT BAY (SEA OF JAPAN)**

SUMMARY. Persistent organic pollutant (POP) concentrations are determined by high-resolution gas chromatography-mass spectrometry in the benthal deposits of the estuarial zones of three rivers in Peter the Great Bay (the Sea of Japan): the Razdolnaya River, the Sukhodol River, and the Gladkaya River. The POP content forms the following row: DDT ≥ PCB > HCH > HCB. The greatest POP content is determined in the benthal deposits of the Razdolnaya River — 1.5-27.7 times higher than the environmentally friendly dosage, according to the standards of Canada (there are no such standards in Russia), which amounts to 44.7, 32.6, 2.2, and 0.75 μg/kg of dry matter, respectively. The other rivers demonstrate the POP occurrence close to the background level of the Central-European part of Russia. These values along with the qualitative composition data of each POP group demonstrate that the global transboundary transfer is the main source of the entry of polychlorinated biphenyls (PCB) into the river ecosystem, and the organochlorine pesticides (OCP) can be brought locally.

KEY WORDS. POP, benthal deposits, estuaries, Peter the Great Bay, Sea of Japan.

Coast and estuarial ecosystems are the zones of high productivity and biological diversity, which explains their exclusive ecological and economic significance [1]. At the same time, these zones are prone to anthropogenic load through large amounts of various pollutants. As a rule, coast and estuarial zones are highly developed water areas with dense population, agricultural and industrial activities.

All these features are typical of Peter the Great Bay located in the north-western part of the Sea of Japan. Among the Far East seas, the Bay is one of the richest in the context of biodiversity; it is the place of development and reproduction of various commercially valuable fish. Its coast is the location of large port cities — Vladivostok and Nakhodka. The population density is the highest in the Far East Federal District. Industry, agriculture, sea and land transportation cause serious pollution in the coastal area of the Bay, affecting its biological, technical, and recreational resources. Wastewaters that are dumped into the Bay bring high

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amounts of pollutants [2]. Considerable amounts of pollutants are delivered via rivers that flow into the Bay [3], [4].

Several large and minor rivers which differ in the level of anthropogenic load flow into the Bay. The largest river in the Primorye Territory, the Razdolnaya River, flows from China and runs along flatlands through the agricultural areas of the Primorye Territory, eventually flowing into the Bay at its northern part. It is the main source of pollutants for the coastal area. The Sukhodol River flows into the Bay at its western part; it is a torrential river with mountain-type flow, being less domestically utilized. The Gladkaya River flows along the southern parts of the Primorye Territory. It is a sluggish river with flatland-type flow. It is the summer recreational area for the people living in the Far East. The water-producing areas of all the three rivers are exposed to intensive motor transportation.

As a rule, the pollutants delivered by the rivers settle in the benthal deposits (BD) of the estuaries within the area of bio-geochemical barrier, where the sea and fresh waters blend [5]. About 90-95% of the suspended matter and 30-40% of the dissolved run-off matter settle here [6]. Hence, the estuary BD pollution can be higher than that of the nearby river and sea ecosystems. Environmentally persistent pollutants present the major hazard.

Persistent organic pollutants (POPs) belong to one of such groups. These are chlororganic compounds with high toxicity, extraordinary biological activity, unusual resistance to environmental changes, and the ability to accumulate in various links of the foodchain. POPs affect all ecosystems including the human one. The most common POPs include polychlorinated biphenyls (PCB) and organochlorine pesticides (OCP) — hexachlorobenzene (HCB), hexachlorocyclohexane (HCH) isomeric mixture and dichloro-diphenyl-trichloroethane (DDT) with its metabolites. Despite the decrease in the POP domestic usage, they still affect the environment, currently remaining in all environmental objects including living organisms. According to the World Health Organization (WHO), the main POP sources include DDT, HCH and HCB being used as pesticides in agriculture and communal services; the industries using POPs in technological processes and producing them as by-products; the plasticizer vaporization; burning domestic and industrial wastes; the industrial equipment with POP content (transformers, condensers, etc.); air and water pollution with POPs being part of industrial waste; other uncontrolled ways [7], [8]. The data on the POP contents in BD of the southern Pacific coast of Russia are limited; they mainly concern DDT and HCH in the open areas of the inner bays. [9], [10].

The purpose of the research is to determine the POP contents in the benthal deposits of the estuarial zones of Peter the Great Bay as the most affected territory.

The data and methods of the research. The BD samples were taken from three rivers of Peter the Great Bay in September-October, 2008 (Fig. 1): one sample from the Gladkaya estuary, one sample from the Sukhodol estuary, and two samples from the Razdolnaya estuary. The samples were taken by diving in accordance with GOST 17.1.5.01-80 (Russian National State Standard) [11]. Taking into account various abilities of different BD types to accumulate POPs [12], only slime grounds were analyzed, being the most predisposed to their accumulation. After the slime grounds from several stations were mixed, the integrated samples were taken for analyzing.

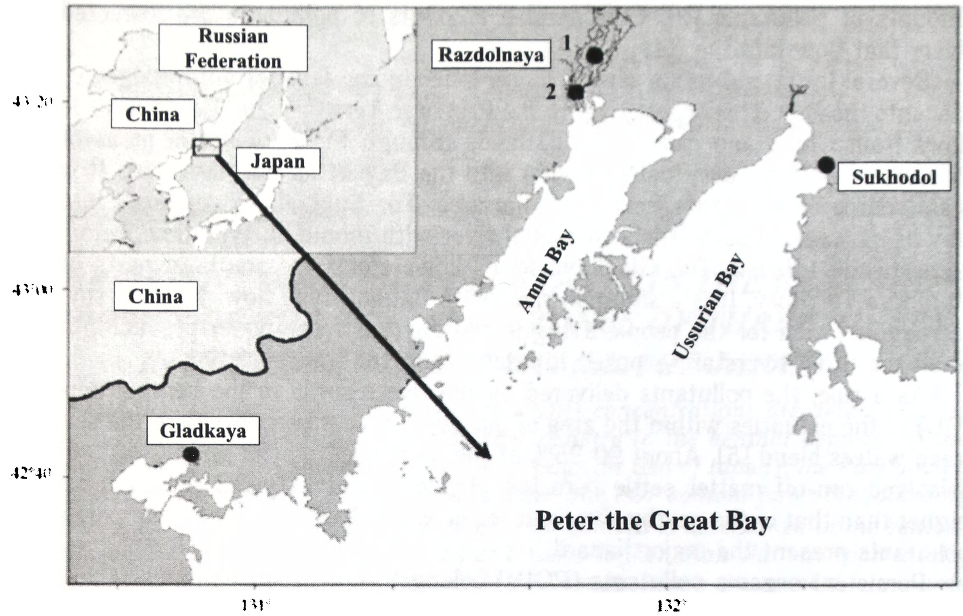

Fig. 1. The benthal deposits sampling locations in the estuarial zones of Peter the Great Bay

The samples were air-dried for further analysis. The dried samples were analyzed for POP content in the Laboratory of Analytical Ecotoxicology of A.N. Severtsov Institute of Ecology and Evolution, Russian Academy of Science, according to the *Measurement Procedure of the Mass Concentrations of Polychlorinated Biphenyls and Chlorinated Pesticides in Soils, Spent Slurries, Solid Wastes, Biological and Plant Materials, Natural and Waste Waters via Chromatography-Mass Spectrometry* (MP LAE-04/05), developed by the Institute of Ecology and Evolution, as described above [13].

The equipment used included the high-resolution (about 10,000) mass-spectrometer, the *HP 6890 Plus* gas chromatograph, the *Finnigan MAT 95XP* mass-spectrometer, and the *SGE HT-8* column (30 m x 0.25 mm i.d x 0.25 μm film thickness). The measurements were carried out at the constant rate of the carrier-gas (helium) flow of 0.75 ml/min. The mass-spectra were obtained by electron impact ionization at the electron energy of 51 eV and the emission current of 0.9 mA. The substances were identified by their retention time and the matching of the isotope ratios of the registered peaks and the theoretical values. The measures were calculated by the correlation of the peak space areas of a certain congener to the corresponding peak of the isotope-marked standard. The POP contents were measured in microgram per 1 kg of dry matter. We determined 27 PCB congeners with different chlorinity, HCB, HCH isomers, and DDT with its metabolites.

Results and discussion. The representatives of various POP groups were traced in all the tested BD samples (Table 1).

Table 1

The POP contents in the grounds of the estuarial zones, the rivers of Peter the Great Bay basin (μg/kg of dry matter)

POP	River estuarial zones			
	Gladkaya	Sukhodol	Razdolnaya 1	Razdolnaya 2
HCB	0.063	0.026	0.434	0.753
HCH sum	0.508	0.485	2.185	2.006
PCB sum	6.900	11.500	17.311	32.633
DDT sum	6.300	12.900	40.450	44.700

The POP contents in all tested samples formed the following row HCB < HCH < PCB < DDT. The maximum BD levels were registered in the estuary of the Razdolnaya River. The greatest differentiation of various POP groups was from 4.7 times (PCB) to 7.1 times (DDT), which correlates with the data published earlier on different levels of anthropogenic contamination and ground toxicity in these zones [14]. The range of DDT concentrations in the BD of certain inner bays and harbours of Peter the Great Bay registered in the period of 2004-2008 varied from 2 to 10 μg/kg in the Amur and Ussurian bays and from 27 to 130 μg/kg in the Zolotoy Rog Bay, most exposed to anthropogenic load [10]. The HCH sum in the Amur Bay for the period of 2002-2004 varied from 0.1 to 7.4 μg/g at different stations [9]. According to our data, the DDT concentration in the estuary of the Razdolnaya River is much higher than that of the Amur Bay, while HCH remains within the same range. The HCH and DDT sums in the Gladkaya and Sukhodol rivers equal the average concentrations in the Amur and Ussurian bays, cf. in the Azov Sea [15], the OCP sum in the BD ranged from 0.1 to 43.3 μg/kg, the average concentration during summer was 2.37 μg/kg. The average PCB concentration in that area varied from 1.2 to 14.5 μg/kg.

The correlation of the POP contents in the estuarial BD of the Far East region and in the freshwater objects of the European part of Russia revealed significant difference. For example, in the northern part of the Sheksninsk Broad of the Rybinsk Reservoir, exposed to municipal-industrial system of the city of Cherepovets, the contents of PCB, HCB and DDT with metabolites were 425.6, 0.83 and 27.1 μg/kg of dry matter in 2006. The amount of PCB was dozens of times higher than that of the estuaries of the Gladkaya, Sukhodol, and Razdolnaya rivers. The rest of the reservoir showed the following background POP levels: 24.3, 0.34, and 2.3 μg/kg of dry matter, respectively [16]. The revealed differences indicate that in the estuaries of the rivers in Peter the Great Bay the contents of HCB and DDT exceeded the background levels registered in the European part of Russia several times. The content of PCB was either equal to or lower than the background levels. This suggests that the source of the PCB entry into the river ecosystem is the global transboundary transfer, while for OCP, the transfer is local.

The qualitative analysis of HCH in the BDs of the Gladkaya, Sukhodol, and Razdolnaya rivers demonstrates the dominance of the most toxic γ-isomer in its content (Table 2). In aquatic medium, γ-HCH is decomposed by microorganisms and undergoes photochemical isomerization, being transformed into the more stable isomer α-HCH. Consequently, the longer HCH stays in the environment, the higher the content of α-isomer is. The increased level of the latter compared to other isomers denotes sustained HCH presence in the environment. This may be explained either by the large distance between the local source of the OCP entry into the river and the place of its detection, or by its long-term presence in the water object. All tested samples demonstrate the concentrations of α-HCH/γ-HCH <1, which denotes a relatively recent entry of the pesticide in the estuarial zones.

Table 2

The correlation of different HCH isomers and DDT metabolites in the benthal deposits of the estuarial zones, the rivers of Peter the Great Bay basin (μg/kg)

OCP	Gladkaya	Sukhodol	Razdolnaya 1	Razdolnaya 2
α-HCH	0.03	0.06	0.183	0.154
γ-HCH	0.38	0.307	1.570	1.374
β-HCH	0.067	0.050	0.334	0.350
d-HCH	0.031	0.023	0.098	0.128
DDE sum	0.477	0.489	1.620	1.769
DDD sum	2.258	3.696	7.684	9.973
DDT sum	3.561	8.723	31.143	32.990

The p,p' DDT isomer composes up to 77% of most commercial DDT products. As the result of physico-chemical and biological processes in sea water, DDT having entered and having been circulating in the environment for a long time is transformed into the more persistent DDD and DDE, which begin to dominate over metabolites mixtures. The correlation of the sums looks as follows: DDT/DDE < 1 [17]. The same correlation for the estuarial zones of the investigated rivers was >> 1: 7.5 (the Gladkaya River), 18.6 (the Sukhodol River), 19.2 and 18.7 (the Razdolnaya 1 and 2 rivers, respectively) (Table 2). This qualitative composition indicates the ongoing entry of DDT into the water-collecting areas of these rivers. Apparently, these compounds are mainly used in the Razdolnaya River basin. It must be mentioned that the greatest part of its water-collecting area is located in the territory of China. Therefore, the source of the river pollution can be localized outside the Russian borders. Further and detailed investigations are required to clarify that.

The qualitative analysis of PCB shows that the PCB congener profile in the BD samples from the three rivers is mostly similar to the composition of the commercial mixture Arochlor-1254: pentachlorobiphenyls prevail everywhere, composing 43-59% of the samples (Table 3), while its part in the mixture amounts to 53% of the total [8]. At the same time, unlike Arochlor-1254, the BD of the Sukhodol and Razdolnaya rivers contain the greater part of tetrachlorobiphenyls: 27 and 36%, respectively (15% in Arochlor-1254), and the lower-chlorated congeners (mono-, bi- and trichlorobiphenyls) are registered in all the samples. Their total sum in the sample taken from the Gladkaya River is the greatest, being 15%; it is 1.8% for the Sukhodol River and 6.9-7.5% for the Razdolnaya River (it is <1% in Arochlor-1254). This indicates the possible occurence of another commercial PCB mixture in the BD samples — Arochlor-1248. The samples taken from the Sukhodol River correspond the composition of Arochlor-1254 to the greatest extent. Since Sovol P-53 widely used in Russia is compositionally similar to Arochlor-1254, this indicates the occurrence of quite a recent but minor PCB entry into the river from closely located sources. The samples from the other two rivers are more different from the Arochlor-1254 congener profile, which means the long-term PCB presence in the environment. During this time, PCB transformed, which reduced dechlorination of the formerly highly chlorinated congeners (as the result, the low-chlorinated congeners began to dominate). This process usually takes place in the BD of aquatic ecosystems due to anaerobic microorganism activity, which is quite slow and requires much time [18].

Table 3

Total composition of homologous PCB groups with different chlorinity in the benthal deposits of the estuaries of Peter the Great Bay (ng/kg of dry matter)

PCB group	Estuaries			
	Gladkaya	Sukhodol	Razdolnaya 1	Razdolnaya 2
Monochlorinated	33	< 5	32	83
Bichlorinated	189	< 5	916	1,559
Trichlorinated	839	201	240	800
Tetrachlorinated	2,191	3,066	6,276	11,658
Pentachlorinated	3,002	6,762	7,762	15,425
Hexachlorinated	604	1,400	2,046	3,043
Heptachlorinated	26.9	70.7	34.4	55.9
Octachlorinated	1.0	6.8	4.6	9.1
Nonachlorinated	< 0.1	< 0.7	< 0.3	< 0.3
PCB sum	6,886	11,505	17,311	32,633

In the case with the samples from the Gladkaya and Razdolnaya rivers, this PCB degradation may be due either to its old entry from a local source, or long circulation in the atmosphere, or transfer into the River as a result of the permanent global atmospheric transfer.

In our country, the standards for the POP content in BD have not been developed. Therefore, for the purpose of regulation, it is necessary to use the international standards for the POPs in BD, which are currently applied in the countries of the European Union and North America. For example, in Canada, the environmental regulations for DDT, DDD, DDE, the sum of PCB and γ-HCH in BD for freshwater objects are: 1.19, 3.54, 1.42, 34.1 and 0.94, and for sea waters — 1.19, 1.22, 2.07, 5.21 and 0.32 μg / kg of dry matter, respectively. The content of HCB is not standardized [19].

The comparison between the obtained levels of the POP contents in BD and the standards demonstrates that when we observe the Razdolnaya River alone they are exceeded for almost all the chemicals (DDT and its metabolites, γ-HCH, and PCBs). Thereby, the content of DDT exceeds the standard for the BD in all the three rivers, both for fresh and sea waters by 1.8-27.7 times, reaching the maximum values in the Razdolnaya River.

The data obtained demonstrate that although OCP are no longer produced or utilized in most countries of the Northern hemisphere, they are still used in the countries of South-East Asia. Considerable amounts are used in India annually [20]. Being transported over vast areas with winds, the pesticides form the global background level, which results in their presence in the ecosystem components of different climatic zones. The Primorye Territory is not an exception. There are no local sources of the POP entry; and the presence of the latter in the BD can be considered as the demonstration of their global distribution. The low levels of PCB in estuarial areas, as a whole, indicate the absence of high-tech industries in the basins, where such substances are used. However, the ongoing DDT and HCH entry and their accumulation in the BD is higher than the standard level points to an existing environmental risk of river pollution by these substances and it justifies the need to organize the monitoring of the POP contents on the Pacific coast of Russia.

Thus, the conducted research demonstrates the POP presence in the benthal deposits of the estuarial zones of the three rivers in the Primorye Territory. At the same time, DDT with its metabolites and PCB are registered in the largest amounts everywhere; and HCB is the least detected. The highest POP levels are registered in the Razdolnaya River, where their contents are higher than the international environmental standards. The qualitative composition of POPs indicates their possible ongoing entry into the Primorye Territory.

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