

Original article

Organochlorine Xenobiotics in the Salgir River Ecosystem: Content, Distribution, Ecological Risk

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Abstract

The content and distribution of organochlorine pesticides of the DDT group and polychlorinated biphenyls (PCBs) in water, amphipods, fish and sediments of the Salgir River, as well as in bottom sediments of the Biyuk-Karasu River, were determined. Samples were collected in May and July 2023. An analysis of organochlorine xenobiotics was performed using a GC Chromatec-Crystal 5000 (Russia), equipped with an electron capture microdetector. The Σ DDT concentration in water ranged from 0.53 in the area of the village of Dobroye up to 14.91 ng/L in the village of Molochnoye, whereas Σ 6PCB changed from 0.50 to 37.87 ng/L, respectively. The lowest Σ DDT content (9.06 ng/g) in sediments was detected in the village of Dobroye, the highest one was registered in the village of Molochnoye (71.69 ng/g). The minimum Σ 6PCB concentration (3.41 ng/g) was determined in the area of the village of Beloglinka, the maximum one was in the village of Molochnoye (61.88 ng/g). The pollutants distribution in water and bottom sediments indicates the presence of local DDTs and PCBs sources along the river between the villages of Beloglinka and Molochnoye. The lowest pollutants concentrations in hydrobionts were determined in muscles of schneider caught near the village of Dobroye. The highest ones were registered in the spined loaches caught near the village of Novogrigoryevka and in the bleak caught near the village of Molochnoye. In these fish, the maximum permissible concentration Σ DDT (300 ng/g wet weight) was exceeded. The obtained results were compared with water and sediments pollution in other Crimean, European and Asian rivers. An environmental risk assessment showed that pollution levels are not of concern in the area above Simferopol. In other sampling sites, high environmental risk was noted. The results showed that the environmental risk of PCBs pollution near the village of Molochnoye was higher than that of DDTs pollution.

Keywords: DDT, PCBs, water, bottom sediments, hydrobionts, environmental risk, Salgir River

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Acknowledgments: This work was supported by the state contracts with the RC FBH “Study of peculiarities structure and dynamics of freshwater ecosystems of the Northern Black Sea coast” (no. 123101900019-5) and partially within the state contracts of IBSS of RAS “Molismological and biogeochemical foundations of homeostasis of marine ecosystems” (no. 121031500515-8), “Regularities of formation and anthropogenic transformation of biodiversity and bioresources of the Azov-Black Sea basin and other areas of the World Ocean” (no. 121030100028-0) and “Fundamental studies of population biology of marine animals, their morphological and genetic diversity” (no. 121040500247-0).

For citation: Malakhova, L.V., Karpova, E.P., Belogurova, R.E., Gubanov, V.V., Prokopov, G.A., Chesnokova, I.I., Kurshakov, S.V., Statkevich, S.V., Shavriev, D.G. and Ovechko, S.V., 2023. Organochlorine Xenobiotics in the Salgir River Ecosystem: Content, Distribution, Ecological Risk. *Ecological Safety of Coastal and Shelf Zones of Sea*, (4), pp. 116–133.

Хлорорганические ксенобиотики в экосистеме реки Салгир: содержание, распределение, экологический риск

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Аннотация

Определено содержание и распределение хлорорганических пестицидов группы ДДТ и полихлорированных бифенилов (ПХБ) в воде, амфиподах, рыбах и донных осадках р. Салгир, а также в донных отложениях ее притока Биюк-Карасу, отобранных в мае и июле 2023 г. Анализ хлорорганических ксенобиотиков проводили на газовом хроматографе «Хроматэк-Кристалл 5000», оснащенном микродетектором электронного захвата. Концентрация Σ ДДТ в воде изменялась в широком диапазоне: от 0.53 в районе с. Доброго до 14.91 нг/л в с. Молочном, Σ 6ПХБ – от 0.50 до 37.87 нг/л соответственно. Наименьшее содержание Σ ДДТ (9.06 нг/г) в донных отложениях обнаружено в с. Добром, наибольшее – в с. Молочном (71.69 нг/г). Минимальная концентрация Σ 6ПХБ (3.41 нг/г) определена в районе с. Белоглинка, максимальная – в с. Молочном (61.88 нг/г). Распределение загрязнителей в воде и донных отложениях свидетельствует о том, что по течению реки между селами Белоглинка и Молочным расположены локальные источники поступления ДДТ и ПХБ. В пробах гидробионтов наиболее низкие концентрации ДДТ и ПХБ определены в мышцах быстринок у с. Доброго. Максимальное содержание загрязнителей обнаружено в тканях щиповок у с. Новогригорьевка и уклеи у с. Молочного, у которых было отмечено превышение ПДК Σ ДДТ, составляющей 300 нг/г сырой массы. Полученные результаты были сопоставлены с загрязнением воды и донных отложений в других реках Крыма,

Европы и Азии. Оценка экологического риска показала, что уровень загрязнения Салгира выше Симферополя не вызывает беспокойства. На остальных территориях отмечен высокий экологический риск. Результаты показали, что экологический риск, связанный с загрязнением ПХБ в районе с. Молочного был выше, чем связанный с загрязнением ДДТ.

Ключевые слова: ДДТ, ПХБ, вода, донные отложения, гидробионты, экологический риск, река Салгир

Благодарности: работа выполнена по теме ФГБНУ «НИЦ ПСГ» 123101900019-5 «Изучение особенностей структуры и динамики пресноводных экосистем Северного Причерноморья» и частично в рамках тем ФИЦ ИнБЮМ 121031500515-8 «Молисмологические и биогеохимические основы гомеостаза морских экосистем», 121030100028-0 «Закономерности формирования и антропогенная трансформация биоразнообразия и биоресурсов Азово-Черноморского бассейна и других районов Мирового океана» и 121040500247-0 «Фундаментальные исследования популяционной биологии морских животных, их морфологического и генетического разнообразия».

Для цитирования: Хлорорганические ксенобиотики в экосистеме реки Салгир: содержание, распределение, экологический риск / Л. В. Малахова [и др.] // Экологическая безопасность прибрежной и шельфовой зон моря. 2023. № 4. С. 116–133. EDN LZDHFHFW.

Introduction

Organochlorine pesticides of the dichlorodiphenyltrichloroethane (DDT) group and polychlorobiphenyls (PCBs) are among the most common and dangerous persistent organochlorine compounds (OCs) synthesized by humans. In this regard, the content, distribution and influence of OCs on environmental components became the subject of study all over the world in the 1970s. It was determined that OCs have a toxic effect on aerobic organisms, leading to various pathologies of the reproductive, nervous, immune and endocrine systems [1–4].

In May 2001, the United Nations Environment Programme adopted the Stockholm Convention on Persistent Organic Pollutants, which prohibits the production and use of twelve hazardous chemicals, including DDT and PCBs ¹⁾. However, OCs are still found in significant concentrations in the environment [5], including freshwater and marine coastal waters of the Crimea [6, 7].

The largest Crimean river system is the Salgir River with its side streams. The study of pollution in the Crimean rivers is carried out by the Crimean Department of Hydrometeorology and Environmental Monitoring, which conducts observations including analysis of water quality in accordance with sanitary and hygienic standards. In general, according to reports from government agencies, the water of the Salgir River is characterized as “dirty” ²⁾, and according to the indicators of biological and chemical oxygen consumption, the water of the Salgir River in the area of the village of Dvurechye was characterized as

¹⁾ UNEP, 2023. *History of the Negotiations of the Stockholm Convention; Nations Environment Programme*. Available at: <https://chm.pops.int/TheConvention/Overview/History/Overview/tabid/3549/Default.aspx> [Accessed: 19 November 2023].

²⁾ Council of Ministers of the Republic of Crimea, 2023. *[Report on State and Protection of Environment of Republic of Crimea]*. Simferopol: OOO Print, 448 p. (in Russian).

“very polluted”³⁾ in 2020. However, data on the content of persistent organic pollutants DDT and PCBs in the Salgir River ecosystem are not provided either in reports or in any other open sources.

The paper aims to study the current pollution of the Salgir and Biyuk-Karasu Rivers ecosystem with DDT and PCBs. To achieve this purpose, the following tasks were solved: determination of the OCs concentration in the water and soils of the Salgir River and the soils of the Biyuk-Karasu River; assessment of the OCs accumulation in hydrobionts; determination of the components of the Salgir middle course ecosystem that accumulate OCs as much as possible; assessment of the environmental risk from the OCs effects.

Materials and methods

To achieve this goal, in May and July 2023, samples of water, sediments, crustaceans and fish fauna were taken in four districts of Salgir above (in the area of the village of Dobroye – Stations 1 and 2) and below the city of Simferopol (the village of Beloglinka – Stations 3 and 4), near the village of Molochnoye (Station 5), near the village of Novogrigoryevka (Station 6). In three districts of the Biyuk-Karasu River near Belaya Skala (Station 7), the villages of Zybiny (Station 8) and Uvarovka (Station 9), samples of bottom sediments only were taken.

Water samples were taken in glass jars with a volume of 6 liters. The OCs in the water were determined with the help of gas chromatography in accordance with the environmental requirements PND F 14.1:2:3:4.204-04 (2014). Sediments (0–5 cm layer) were also taken directly into glass containers. In a stationary laboratory, the soils were thoroughly homogenized and dried in air. The natural humidity as a percentage of the wet weight was calculated from the difference between the wet and dry weight. The OCs in sediments were determined in accordance with the standard procedure GOST R 53217-2008 (ISO 10382:2002).

The fish were selected with a dragnet, gill and hand nets with a mesh from 3 to 18 mm. The fish were identified using determinants⁴⁾. Bottom invertebrates were collected manually with tweezers from rocks and also with a hydrobiological scraper and sieve. The collected material was not fixed, but cooled for further processing. The determination of the material was carried out using profile determinants⁵⁾.

The OCs content was determined in the tissues of amphipods (Amphipoda) *Dikerogammarus villosus* (Sowinsky, 1894), in the gonads, muscles and internal organs of the following male and female fish (Teleostei): schneiders *Alburnoides maculatus* (Kessler, 1859), chubs *Squalius cephalus* (Linnaeus, 1758), juvenile bleaks *Alburnus alburnus* (Linnaeus, 1758) and zopes *Ballerus ballerus* (Linnaeus, 1758). The whole bodies of juvenile specimens of round gobies *Neogobius melanostomus* (Pallas, 1814) and spined loaches *Cobitis taenia* (Linnaeus, 1758) were analyzed.

³⁾ Trofimchuk, M.M., ed., 2021. [Quality of Surface Waters of the Russian Federation. Information on the Most Polluted Water Bodies of the Russian Federation (Annex to Year-Book for 2020)]. Rostov-on-Don, 160 p. (in Russian).

⁴⁾ Movchan, Yu.V. and Smirnov, A.I., 1981. [Fauna of Ukraine, Vol. 8. Fishes, Issue 2 Cyprinidae, Part 2]. Kiev: Naukova Dumka, 360 p. (in Ukrainian).

⁵⁾ Tsalolikhin, S.Ya., ed., 1995. [Keys to Freshwater Invertebrates of Russia and Adjacent Lands. Vol. 2.] St. Petersburg, 629 p. (in Russian).

In the samples of hydrobionts, the OCs concentrations were determined in accordance with the method MVI.MN 2352-2005, and the content of total lipids was determined gravimetrically [8]. The sum of total extracted lipids is expressed in fractions (%) per wet weight.

Qualitative and quantitative analysis of OCs was carried out with the help of the gas chromatographic method in the Shared Use REC “Spectrometry and Chromatography” of IBSS of RAS using a CG Chromatec-Crystal 5000 (Russia), equipped with an electron capture microdetector. The content of p,p'-DDT, its metabolites p,p'-DDE and p,p'-DDD, as well as six congeners of polychlorinated biphenyls (according to IUPAC: 28, 52, 101, 138, 153 and 180), were determined. Quantitative determination of the OCs was performed by absolute calibration within the linear range of the detector. The detection limit for the OCs varied from 0.05 to 0.1 ng/L in water samples, from 0.01 to 0.05 ng/g in sediments and hydrobionts. The OCs concentration in sediments is calculated for the dry weight of samples, in hydrobionts – for the wet weight.

According to the OCs data in water, sediments and hydrobionts of the Salgir, the accumulation factor (AF) in sediments and bioaccumulation factor in hydrobionts (BAF) were calculated using the following formula: $AF(BAF) = C_s(h),g/C_w \cdot 1000$, where C_s,h – concentration of OCs in sediments or in tissues of hydrobionts (ng/g);

C_w – concentration of OCs in water (ng/L).

T a b l e 1. Organochlorine compound (OC) toxicity data for fish and crustacea in freshwater ecosystems

OC	EC50, mg/L ⁶⁾	
	Fish	Crustacea
p,p'-DDE	0.0960	0.0535
p,p'-DDD	0.1100	0.0090
p,p'-DDT	0.0800	0.0090
PCB 28	0.1600	0.1600
PCB 52	0.0030	0.0030
PCB 101	0.0100	0.0100
PCB 138	0.0026	0.0010
PCB 153	0.0013	0.0013
PCB 180	0.0250	0.0010

To assess the environmental risk from the effects of OCs on the Salgir hydrobionts, the internationally accepted risk coefficient RQ was used, which was calculated using equation [9]: $RQ = MEC/PNEC$, where MEC – measured concentration of OCs in hydrobionts; $PNEC$ – concentration of OCs, below which no harmful effects on organisms will occur with prolonged or short-term exposure. $PNEC$ is usually calculated by dividing toxicological dose descriptors ($LC50$ or $EC50$) by assessment factor [9]:

⁶⁾ EPA. *ECOTOX Knowledgebase*. 2023. [online] Available at: <https://cfpub.epa.gov/ecotox/search.cfm> [Accessed: 19 November 2023].

$PNEC = (LC50 \text{ or } EC50)/\text{Assessment Factor}$. Most commonly used mortality indicator $LC50$ and $AF = 1000$ factor were taken for calculating $PNEC$ during the study. Toxicological parameters $EC50$ were taken from the open *ECOTOX* database⁶⁾ (Table 1).

An RQ value greater than one means high environmental risk, in the range from 0.1 to 1 – average environmental risk, from 0.01 to 0.1 – low environmental risk, and below 0.01 – insignificant environmental risk [9].

Results

At Stations 1–4, the DDT and PCBs concentration in the water was low in May and July. On average, the sum of the concentration of DDT and its metabolites (Σ DDT) was 1.30, the sum of the concentration of PCB congeners (Σ 6PCB) was 1.85 ng/L (see Fig. 1, *a*). The composition and the same content of DDT and metabolites at these stations indicate a single source of pesticide intake in the Simferopol Region. Among PCB congeners at Stations 1–4, only PCBs 138 and 153 were found in all samples. The low content of Σ 6PCBs indicates the absence of significant sources of PCBs in the areas of these stations.

Downstream of the Salgir, at Stations 5 and 6, a significant increase in the OCs concentration was observed (Fig. 1, *a*). The highest Σ DDT content was determined at Station 5 in the area of the village of Molochnoye (Table 2). At this site, the content of the initial DDT was 72% of the total concentration of DDT and metabolites, which means its recent entry into the river area. Downstream,

Table 2. Concentrations (ng/L) of DDT, its metabolites, and indicator PCB congeners in the Salgir River water in May and July 2023

Station no.	Sampling date	p,p'-DDE	p,p'-DDD	p,p'-DDT	PCB 28	PCB 52	PCB 101	PCB 153	PCB 138	PCB 180
1	23.05	0.23	0.27	BDL	0.12	1.64	0.20	0.41	0.29	BDL
2	06.07	1.02	0.20	1.04	N/D	N/D	N/D	0.09	0.41	N/D
3	23.05	0.83	0.47	0.22	0.41	2.36	N/D	0.32	0.48	N/D
4	06.07	0.35	0.24	0.30	0.13	N/D	N/D	0.28	0.14	N/D
5	18.07	5.36	5.21	27.29	1.30	2.81	6.24	1.59	2.98	N/D
6	18.07	2.02	1.15	N/D	1.29	2.54	7.46	1.04	1.32	N/D

Note: BDL – below detection limit; N/D – not detected.

at Station 6, the initial DDT pesticide was not detected in the water, and the sum of the concentrations of its metabolites DDE and DDD turned out to be an order of magnitude lower than at Station 5, but three times higher on average than in the Simferopol Region.

The content of $\Sigma 6\text{PCB}$ at Stations 5 and 6 turned out to be almost the same and amounted to 14.91 and 13.65 ng/L (Fig. 1, *a*), respectively. In the areas of Stations 5 and 6, the sum of the concentrations of OCs in water exceeded on average 11 times their total content at Stations 1–4.

No DDT and PCBs should be recorded in the water of fishery reservoirs, and the approximate permissible level (APL) is 10 ng/L⁷⁾. In the Salgir water above and below Simferopol, both in May and in July, the OCs APL was not exceeded. At Station 5, an excess of the ΣDDT APL was detected by 4 times, and that of the $\Sigma 6\text{PCB}$ APL by 1.5 times. At Station 6, the ΣDDT APL was exceeded 1.3 times.

The results of geochemical analysis showed that at different sampling points, the sediments of the Salgir and the Biyuk-Karasu differed in natural moisture (NM) and, as a result, in granulometric composition. The sediments of the Salgir River were represented by multigrained sands with varying degrees of siltation. Thus, at Stations 1 and 3, it was silted coarse odorless sand with an NM content of 33 and 38%, respectively, at Station 5 – sandy silt (NM – 40%) with putrid odor, at Station 6 – pelitic silt (NM – 54%). In the area of Station 7, the soils of the Biyuk-Karasu River contained 95% of coarse cobbled gravel (from 0.5 to 3 cm) and 5% of aleuritic silt (NM – 19%) with putrid odor, at Station 8 – yellow-gray silt with 27% of NM with inclusions of gravelly fractions, at Station 9 – black silt with algae residues and with 55% of NM.

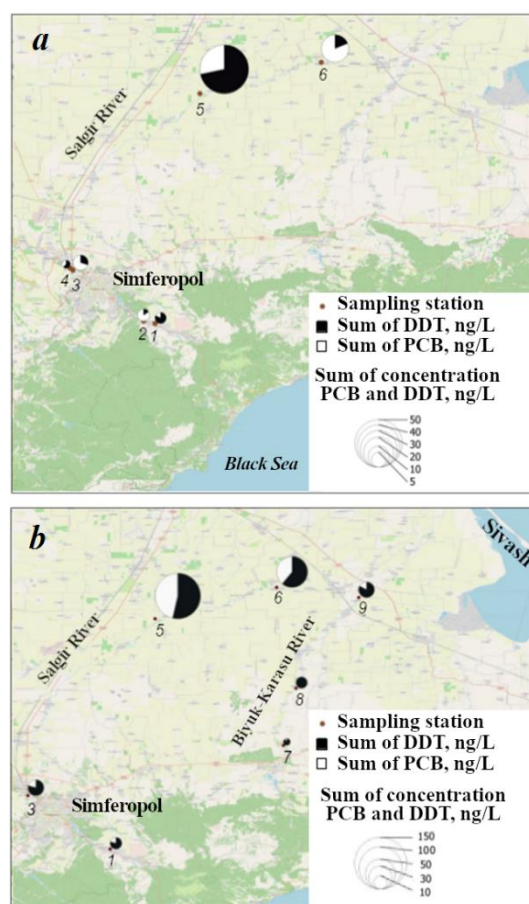


Fig. 1. ΣDDT and $\Sigma 6\text{PCB}$ concentrations in the Salgir River water (*a*) and sediments of the Salgir River (Stations 1–6) and the Biyuk-Karasu River (Stations 7–9) (*b*)

⁷⁾ On the Approval of Water Quality Standards for Water Bodies of Commercial Fishing Importance, Including Standards for Maximum Permissible Concentrations of Harmful Substances in the Waters of Water Bodies of Commercial Fishing Importance: Order of the Ministry of Agriculture of Russia dated December 13, 2016, No. 552 (in Russian).

The amount of OCs concentration in sediments varied in a wide range from 3.03 to 133.57 ng/g (Fig. 1, *b*). The lowest concentrations of Σ DDT and Σ 6PCB were 2.73 and 0.30 ng/g at Station 7, the maximum was 71.69 and 61.88 ng/g at Station 5, respectively.

In the Russian Federation, there are only regional permissible levels (PLs) of the OCs content in sediments⁸⁾, where a safe level of 2.5 ng/g is set for Σ DDT. With the Σ DDT concentrations from 2.5 to 10 ng/g, precipitation is considered slightly polluted, at higher concentrations – polluted. The regional Σ DDT PLs coincide with the norms accepted in international practice in the Dutch Sheets⁹⁾, where there is also Σ PCB PL, which is less than 20 ng/g of wet weight. According to the above standards, sediments in terms of the level of PCB contamination in the area of Stations 7–9 can be classified as clean, at Stations 1 and 4 – slightly polluted, at Stations 5 and 6 – polluted, according to the level of Σ DDT pollution at Stations 1, 7 and 9 – slightly polluted, at Stations 4–6, 8 – polluted.

Fig. 2 shows the results of the determination of lipids and OCs in samples of hydrobionts. The content of total lipids varied from 1.3% in the muscles of female chub to 29.8% in the internal organs of bleak (Fig. 2, *a*). The concentration of OCs in fish tissue samples varied in a wide range: for Σ DDT – from 0.94 to 1153, for Σ 6PCB – from “not detected” to 739 ng/g. The lowest concentration of OCs was determined in the muscles of male and female schneider at Station 1, the highest – in the internal organs of bleak at Station 5 (Fig. 2, *b*). The DDT metabolites, DDE and DDD, were found in all samples of hydrobionts, and in 80 % of samples – the initial DDT. At Station 1, PCBs were not detected in the muscles of male schneider, as well as in the muscles and gonads of female schneider. At more polluted Stations 5 and 6, the concentration of Σ DDT in the bodies of juvenile individuals of bleak, goby and spined loach exceeded the content of Σ 6PCB by 1.5 times on average.

A comparison of the OCs concentration with the MPC, which in freshwater fish for Σ DDT is 300, for Σ PCB – 2000 (in the liver – 5000) ng/g of wet weight, showed that the MPC of OCs was not achieved in muscles, which are a food product. It is obvious that there is no health risk for people when eating fish caught in the studied areas.

In such benthophages as spined loach and round goby, the Σ DDT and Σ 6PCB concentration exceeded on average 4 and 7 times the concentration in potential food items – amphipods (Fig. 2, *b*). This can indicate the process of biomagnification – an increase in the level of OCs content in living organisms of the river trophic chain.

⁸⁾ LenmorNIIproekt, 1996. [Standards and Assessment Criteria of Bottom Sediment Pollution in Water Bodies of St.Petersburg, Regional Standard]. St. Petersburg: LenmorNIIproekt, 20 p. (in Russian).

⁹⁾ AMAP, 2004. PTS Limits and Levels of Concern in the Environment, Food and Human Tissues. In: AMAP, 2004. *Persistent Toxic Substances, Food Security and Indigenous Peoples of the Russian North*. Final Report. Oslo, 2004. Ch. 3, pp. 29–32. Available at: <https://www.amap.no/documents/download/1069/inline> [Accessed: 6 December 2023].

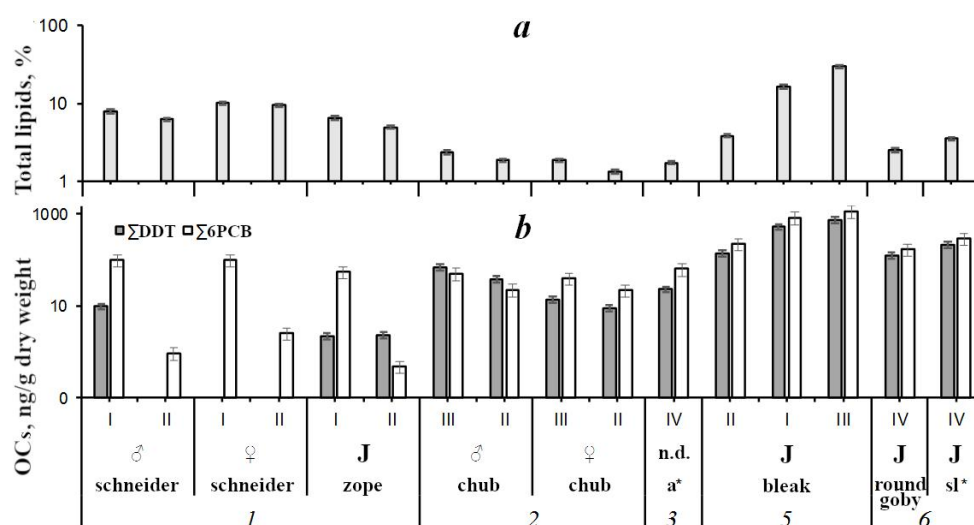


Fig. 2. Total lipids (a) and OCs concentrations (b) in Salgir hydrobionts: I – gonads; II – muscles; III – internal organs; IV – whole body; n.d. – not determined; J – juveniles, a* – amphipods, sl* – spined loach. Digits indicate station numbers

Discussion

Reasons for uneven distribution of OCs in the abiotic components of the Salgir ecosystem

The unequal contamination of the abiotic components of the Salgir ecosystem with the OCs indicates that between Stations 4 and 5, there are sources of OCs intake, which influenced a significant increase in the concentration of pollutants at Stations 5 and 6. At this stage of study, it is impossible to determine the exact source of OCs in this area. Potentially, pollutants can come with wastewater from municipal facilities [1]. It is known that in the Crimea, treated and untreated wastewater is discharged in the Salgir River, the Black Sea and Lake Sivash ²⁾. DDT can appear in residential wastewater from pharmaceuticals. Despite the fact that DDT has been prohibited by the Russian government for several decades, pharmacy chains still offer DDT as an insecticide, as well as insecticidal soap containing DDT, in the 21st century [10]. Drainage waters of more than 80 water consuming enterprises, which take the Salgir water for irrigation of agricultural lands, can also be a source of OCs pollution ¹⁰⁾.

¹⁰⁾ Rodyushkina, N.N., 2017. [Information on Providing Water Bodies for Use on the Basis of Water Use Agreements and Decisions on Providing Water Bodies for Use in the Republic of Crimea as of 11 October 2017] (in Russian).

In the late 1990s, 6.04 kg/ha of pesticides, including DDT, were applied to 1 hectare of farmland to control pests¹¹⁾. The appearance of DDT in the river water can indicate its possible flushing from the drainage area, where warehouses of obsolete pesticides are located. On the territory of the Crimea, 866.9 tons of prohibited and unidentified pesticides are accumulated at 28 solid waste landfills, and the number of unofficial landfills of obsolete pesticides has never been recorded [11]. Filtrates containing dangerous chemical compounds and products of their metabolism enter aquifers from such landfills [1]. In addition, stock-raising facilities (including poultry farms) are the sources of OCs intake to the environment [1]. In the Krasnogvardeyskoye District, at least 11 large stock-raising farms are located in the Salgir drainage area¹⁰⁾. Thus, high local contamination of water and sediments at Stations 5 and 6 can be a consequence of the integral influence of the above-mentioned potential sources. It can be assumed that the main sources of DDT at Stations 5 and 6 were warehouses of obsolete pesticides stored in improper conditions, and the sources of PCBs were atmospheric transport precipitation and residual amounts from previous years of active use of OCs in industry and agriculture. The low concentration of OCs in the water at other stations, which is comparable to the pollution of the Crimean open marine areas [12], can be a consequence of so-called background pollution. Such a background is created by atmospheric transport from southern latitudes, where DDT is still allowed to be used to control insect vectors of malaria, typhus, tick-borne encephalitis, etc. [13, 14].

To identify the factors influencing the accumulation of OCs in sediments, correlation analysis was performed. Close ratio was found between the concentration of DDT, its metabolites and hexachlorobiphenyls 138 and 153 in sediments and their content in water (Fig. 3). For tri-CB 28, such ratio was absent ($R^2_{\text{PCB28}} = -0.09$), and for tetra- and penta-CB 52 ($R^2_{\text{PCB52}} = 0.38$) and 101 ($R^2_{\text{PCB101}} = 0.40$), it was weak. Thus, the concentration of DDT and highly chlorinated PCB congeners in the Salgir soils is closely related to water pollution.

The granulometric composition of sediments can be another factor influencing the accumulation of OCs by them. Indirectly, the granulometric composition can be judged by the NM: the higher the NM, the higher the content of silty fractions. The coefficients of determination (R^2) between the NM and the concentration of ΣDDT and Σ6PCB in the sediments of rivers were 0.36 and 0.25, respectively, which indicates a low correlation between fine fractions and the OCs content. Consequently, the content of pollutants in water was a more significant factor affecting the accumulation of OCs in soils.

¹¹⁾ Goskomgidromet, 1988. [*Yearbook of the Content of Residual Amounts of Pesticides in the Natural Objects of Certain Regions of the Soviet Union. Book II*]. Obninsk: Goskomgidromet, 132 p. (in Russian).

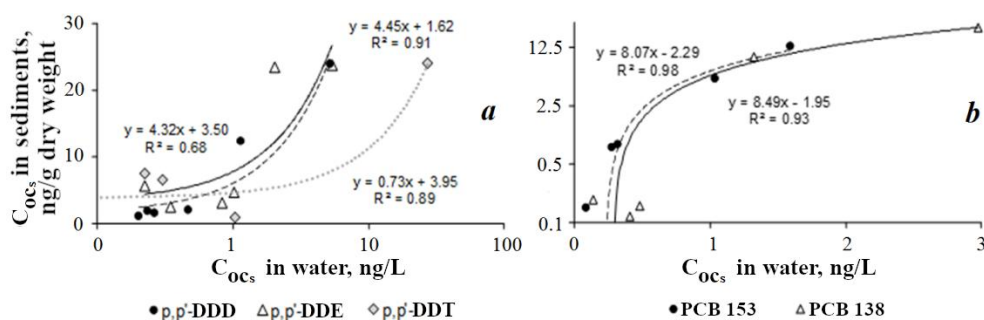


Fig. 3. Ratios of the DDT and its metabolites (a) and PCBs 153 and 138 (b) concentrations in the Salgir River sediments at st.1–6 by the respective values in water

Comparison of the OCs concentration in water and sediments with other rivers

A comparison of the contamination of water and river soils showed that the concentration of Σ PCBs was higher in the Salgir than in the studied Crimean rivers – Chernaya and Uchan-Su [6, 12], as well as Biyuk-Karasu (Table 3), and was comparable to the data obtained in the Czech Republic [15]. At the same time, in such European rivers as the Sele, the Volturno, the Bahlui, the Someşul Mic [16, 17] and the Moscow [18], as well as in the rivers of India [19, 20], this indicator was lower. The content of Σ DDT in the sediments of the Salgir middle course turned out to be one of the highest among the compared areas. The pesticide concentration was three times higher only in the Indian Yamuna River (Table 3).

Mechanisms of removal of OCs from the Salgir waters

The intensive accumulation of OCs from the water by both sediments and biotic components of the Salgir ecosystem is evidenced by the calculated accumulation factor (AF) and bioaccumulation factor (BAF) of OCs (Fig. 4). In different areas of the Salgir, the Σ DDT AF in sediments varied from $2 \cdot 10^3$ at Station 5 to $1 \cdot 10^4$ at Station 6. The AF of Σ 6PCB in sediments was lower and ranged from $9 \cdot 10^2$ at Station 3 to $4 \cdot 10^3$ at Station 5.

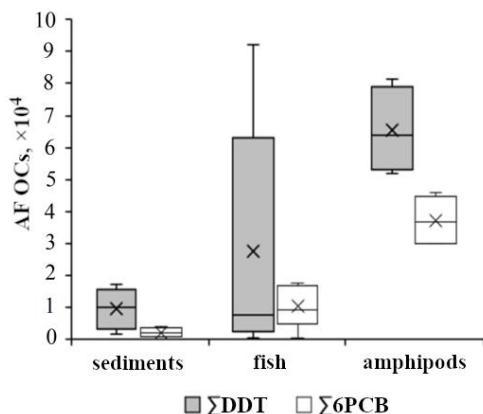


Fig. 4. Accumulation factor (AF) of OCs in sediments and bioaccumulation factor (BAF) of OCs in fish and amphipods of the Salgir River. Horizontal lines show median, crosses are the mean, boxes are interquartile ranges (25 and 75%), whiskers are ranges of AF and BAF values

Table 3. OCs concentration in water and bottom sediments of freshwater ecosystems

Area	Date	Object	Ranges (mean) of $\sum$ DDT	Ranges (mean) of $\sum$ PCB	Work
Bahlui River, Romania	2002	Bottom sediments	(37) ng/g	24–158 (59) ng/g	[16]
Nove Mlyny Reservoir, South Moravia, Czech Republic	2007	Water	N/Dtm	(17.78) ng/L * ¹	[15]
		Bottom sediments	N/Dtm	2.09–38.11 (9.02) ng/g dry weight * ²	
Yamuna River, India	January 2012	Water	0.1–354 (83±26) ng/L	2–779 (99±38) ng/L	[19]
	June 2018	Bottom sediments	0.41–18 ng/g dry weight	553–20 983 ng/g dry weight	[20]
Moscow River	2014	Water	N/Dtm	BDL – 180.7 ng/L * ³	[18]
Someşul Mic River, Romania	May 2017	Bottom sediments	1.00–39.24 ng/g dry weight	2.74–252.72 ng/g dry weight	[21]
Volturno River, South Italy	April – July 2017, April – July 2018	Water	N/Dtm	22.3–24.5 ng/L * ²	[17]
		Bottom sediments	N/Dtm	(64.4) ng/g dryweight	

Continued Table 3

Area	Date	Object	Ranges (mean) of Σ DDT	Ranges (mean) of Σ PCB	Work
Sele River, South Italy	April–February 2020, April – February 2017	Water	ND – 1.96 ng/L * ³	20.8–39.3 ng/L * ³	[5]
		Bottom sediments	0.10–6.12 ng/g dry weight	(79.3) ng/g dry weight	
Chernaya River mouth, south-eastern Crimea	2020–2021	Water	(0.57) ng/L	(3.45) ng/L	[12]
		Bottom sediments	7.3–13.6 (10.0) ng/g dry weight	3.9–27.4 (13.98) ng/g dry weight	[6]
Uchan-Su River (Yalta)	2020–2021	Water	(0.32) ng/L	(1.09) ng/L	[12]
Salgir River	May – July 2023	Water	0.53–37.87 (7.71) ng/L	0.50–14.91 (5.99) ng/L	TW
		Bottom sediments	9.06–71.69 (32.91) ng/g dry weight	3.11–61.88 (23.80) ng/g dry weight	
Biyuk-Karasu River	July 2023	Bottom sediments	2.73–13.08 (8.02) ng/g dry weight	BDL – 2.70 (1.00) ng/g dry weight	TW

Note: N/Dtm– the values were not determined; ND – not detected; BDL – below detection limit, TW – this work.

*¹ Sum of concentrations of six PCB indicator congeners.

*² Sum of the dissolved and weighed forms.

*³ Sum of concentrations of 28, 42, 45, and 49 PCB congeners.

Another mechanism of the aquatic environment purification is the extraction of hydrophobic OCs from water by hydrobionts [22]. According to our data, at a low concentration in the water, Σ DDT BAF and Σ 6PCB BAF in the muscles of the Salgir fish at Station 1 were $9 \cdot 10^2$ and $8 \cdot 10^2$, respectively. At Station 6, where the concentration of OCs was two orders of magnitude higher, BAF was higher than at Station 1, and reached a maximum of $9 \cdot 10^4$ for Σ DDT and $1.5 \cdot 10^4$ for Σ 6PCB (Fig. 4). The highest BAF were determined in crustaceans: the components at Station 3 averaged $7 \cdot 10^4$ for Σ DDT and $4 \cdot 10^4$ for Σ 6PCB.

Assessment of the environmental risk from the effects of OCs on hydrobionts

Depending on the research area, the values of the environmental risk coefficients RQ of individual OCs varied in a wide range from 0.00001 to 25.8 in hydrobionts (Table 4). In general, the RQ of highly chlorinated PCB congeners turned out to be higher than the RQ of DDT group compounds and low-chlorinated PCBs. At Station 1, RQ did not exceed the high risk threshold for all types.

Table 4. Environmental risk coefficient RQ for fish and crustaceans in the Salgir River ecosystem

OC	Schneider and zope (St. 1)	Chub (St. 2)	Amphipods (St. 3)	Bleak (St. 5)	Goby (St. 6)	Spined loach (St. 6)
p,p'-DDE	0.0018	0.21	0.066	1.94	1.0	1.9
p,p'-DDD	0.0002	0.012	1.1	0.38	0.45	0.81
p,p'-DDT	0.0036	0.0014	1.9	0.38	0.17	0.29
PCB 28	0.0003	0.012	0.00001	0.038	0.025	0.045
PCB 52	0.27	2.2	1.4	1.68	1.1	2.2
PCB 101	0.012	4.9	0.47	5.4	4.0	8.4
PCB 138	0.61	4.5	6.1	20.8	21.7	31.9
PCB 153	0.19	1.5	5.8	16.8	16.8	25.8
PCB 180	0.003	0.0053	0.063	0.13	0.18	0.29

Note: RQ values of high environmental risk are given in bold.

Thus, it indicated average environmental risk for PCBs 52, 138 and 153 and no risk for DDT group compounds. At Stations 5 and 6, the DDE RQ exceeded the high risk threshold for fish, and at Station 3, RQ exceeded such a threshold for crustaceans concerning DDD and DDT content. The highest RQ coefficient was determined for hexachlorobiphenyls 138 and 153 for fish at Stations 2, 5 and 6 and amphipods at Station 3.

The results obtained at Stations 5 and 6 suggest that, despite the higher level of DDT pollution, PCB pollution poses a higher environmental risk for these areas of the Salgir ecosystem.

Conclusion

It is difficult to overestimate the economic importance of the Salgir River. The quality of life of people living on the banks of the river and the work of enterprises that are supplied with the Salgir water, depend on the condition of its water. The conducted studies of the levels of pollution of the components of the Salgir and Biyuk-Karasu ecosystems with such organochlorine xenobiotics as DDT and PCBs made it possible to identify the areas of environmental danger for biological objects and, possibly, for people near the villages of Molochnoye and Novogrigoryevka. The results of the study showed that the contamination of the OCs components of the Salgir middle course ecosystem was a serious environmental problem. Therefore, the task is to identify the OCs sources and prevent their intake to the river.

REFERENCES

1. Galiulin, R.V., Galiulina, R.A., Khorobrykh, R.R. and Bashkin, V.N., 2019. Risk of Modern Contamination of River Waters by Pesticide DDT and HCH. *Issues of Risk Analysis*, 16(5), pp. 62–69. doi:10.32686/1812-5220-2019-16-5-62-69 (in Russian).
2. Fedorov, L.A. and Yablokov, A.V., 1999. *Pesticides – The Chemical Weapon That Kills Life (the USSR's Tragic Experience)*. Moscow: Nauka, 462 p. (in Russian).
3. Peivasteh-Roudsari, L., Barzegar-Bafrouei, R., Sharifi, K.A., Azimisalim, S., Karami, M., Abedinzadeh, S., Asadinezhad, S., Tajdar-Oranj, B., Mahdavi, V. [et al.], 2023. Origin, Dietary Exposure, and Toxicity of Endocrine-Disrupting Food Chemical Contaminants: A Comprehensive Review. *Heliyon*, 9(7), e18140. doi:10.1016/j.heliyon.2023.e18140
4. Vasseghian, Y., Hosseinzadeh, S., Khataee, A. and Dragoi, E-N., 2021. The Concentration of Persistent Organic Pollutants in Water Resources: A Global Systematic Review, Meta-Analysis and Probabilistic Risk Assessment. *Science of the Total Environment*, 796, 149000. doi:10.1016/j.scitotenv.2021.149000
5. De Rosa, E., Montuori, P., Triassi, M., Masucci, A. and Nardone, A., 2022. Occurrence and Distribution of Persistent Organic Pollutants (POPs) from Sele River, Southern Italy: Analysis of Polychlorinated Biphenyls and Organochlorine Pesticides in a Water–Sediment System. *Toxics*, 10(11), 662. doi:10.3390/toxics10110662
6. Malakhova, L.V., Lobko, V.V., Malakhova, T.V. and Murashova, A.I., 2022. Comparative Assessment of Organochlorine Pollution of Bottom Sediments in Different Types of Water Bodies in the Sevastopol Region (Crimea). *Chemistry for Sustainable Development*, 30(2), pp. 169–181. doi:10.15372/CSD2022371
7. Malakhova, L., Giragosov, V., Khanaychenko, A., Malakhova, T., Egorov, V. and Smirnov, D., 2014. Partitioning and Level of Organochlorine Compounds in the Tissues

- of the Black Sea Turbot at the South-Western Shelf of Crimea. *Turkish Journal of Fisheries and Aquatic Sciences*, 14(5), pp. 993–1000. doi:10.4194/1303-2712-v14_4_19
8. Babkina, E.I. and Bobovnikova, Ts.I., 1978. [On Quantitative Extraction of Organochlorine Pesticides and Polychlorinated Biphenyls from Organs and Tissues of Fish]. *Gidrobiologicheskyy Zhurnal*, 14(3), pp. 103–105 (in Russian).
 9. Lin, X., Xu, J., Keller, A.A., He, L., Gu, Y., Zheng, W., Sun, D., Lu, Z., Huang, J. [et al.], 2022. Occurrence and Risk Assessment of Emerging Contaminants in a Water Reclamation and Ecological Reuse Project. *Science of The Total Environment*, 744, 140977. doi:10.1016/j.scitotenv.2020.140977
 10. Yaglova, N.V. and Yaglov, V.V., 2012. Endocrine Disruptors are a Novel Direction of Endocrinologic Scientific Investigation. *Annals of the Russian Academy of Medical Sciences*, 67(3), pp. 56–61. doi:10.15690/vramn.v67i3.186
 11. Dubrovin, I.R. and Dubrovin, E.R., 2017. To a Question about Ecological Safety of the Autonomous Republic of Crimea. *Technico-Tehnologicheskie Problemy Servisa*, (4), pp. 24–28 (in Russian).
 12. Malakhova, L.V. and Lobko, V.V., 2022. Assessment of Pollution of the Yalta Bay Ecosystem Components with Organochlorine Xenobiotics. *Ecological Safety of Coastal and Shelf Zones of Sea*, (3), pp. 104–116. doi:10.22449/2413-5577-2022-3-104-116
 13. Mandavilli, A., 2006. Health Agency Backs Use of DDT Against Malaria. *Nature*, 443, pp. 250–251. doi:10.1038/443250b
 14. Ranson, H., N'Guessan, R., Lines, J., Moiroux, N., Nkuni, Z. and Corbel, V., 2011. Pyrethroid Resistance in African Anopheline Mosquitoes: What are the Implications for Malaria Control? *Trends in Parasitology*, 27(2), pp. 91–98. doi:10.1016/j.pt.2010.08.004
 15. Zelníčková, L., Svobodová, Z., Maršálek, P. and Dobšíková, R., 2015. Persistent Organic Pollutants in Muscle of Fish Collected from the Nové Mlýny Reservoir in Southern Moravia, Czech Republic. *Environmental Monitoring and Assessment*, 187(7), 448. doi:10.1007/s10661-015-4460-3
 16. Dragan, D., Cucu-Man, S., Dirtu, A.C., Mocanu, R., Van Vaeck, L. and Covaci, A., 2006. Occurrence of Organochlorine Pesticides and Polychlorinated Biphenyls in Soils and Sediments from Eastern Romania. *International Journal of Environmental Analytical Chemistry*, 86, pp. 833–842. doi:10.1080/03067310600665571
 17. Montuori, P., De Rosa, E., Sarnacchiaro, P., Di Duca, F., Provisiero, D.P., Nardone, A. and Triassi, M., 2020. Polychlorinated Biphenyls and Organochlorine Pesticides in Water and Sediment from Volturno River, Southern Italy: Occurrence, Distribution and Risk Assessment. *Environmental Sciences Europe*, 32, pp. 1–22. doi:10.1186/s12302-020-00408-4
 18. Eremina, N., Paschke, A., Mazlova, E.A. and Schüürmann, G., 2016. Distribution of Polychlorinated Biphenyls, Phthalic Acid Esters, Polycyclic Aromatic Hydrocarbons and Organochlorine Substances in the Moscow River, Russia. *Environmental Pollution*, 210, pp. 409–418. doi:10.1016/j.envpol.2015.11.034
 19. Kumar, B., Singh, S.K., Mishra, M., Kumar, S. and Sharma, C.S., 2012. Assessment of Polychlorinated Biphenyls and Organochlorine Pesticides in Water Samples from the Yamuna River. *Journal of Xenobiotics*, 2(1), e6. doi:10.4081/xeno.2012.e6
 20. Kumar, B., Verma, V.K., Mishra, M., Piyush, Kakkar, V., Tiwari, A., Kumar, S., Yadav, V.P. and Gargava, P., 2021. Assessment of Persistent Organic Pollutants in Soil and Sediments from an Urbanized Flood Plain Area. *Environmental Geochemistry and Health*, 43(9), pp. 3375–3392. doi:10.1007/s10653-021-00839-9
 21. Barhoumi, B., Beldean-Galea, M.S., Al-Rawabdeh, A.M., Roba, C., Martonos, I.M., Bălc, R., Kahlaoui, M., Touil, S., Tedetti, M. [et al.], 2019. Occurrence, Distribution

and Ecological risk of Trace Metals and Organic Pollutants in Surface Sediments from a Southeastern European River (Someșu Mic River, Romania). *Science of the Total Environment*, 660, pp. 660–676. doi:10.1016/j.scitotenv.2018.12.428

22. Polikarpov, G.G. and Egorov, V.N., 1986. *Marine Dynamic Radiochemoecology*. Moscow: Energoatomizdat, 174 p. (in Russian).

Submitted 21.06.2023; accepted after review 15.08.2023;
revised 11.10.2023; published 20.12.2023

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