# The Content of Organochlorine Pesticides in Surface Waters of the Kurgan Region

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The content of organochlorine pesticides in water has a negative impact on human health and the environment. The aim of this study was to determine the content of organochlorine pesticides DDT (dichlorodiphenyltrichloroethane), DDE (dichlorodiphenyldichloroethylene), 2,4-dichlorophenoxyacetic acid (2,4–D) and hexachlorocyclohexane (α–HCCH, γ–HCCH) in the surface waters of the Kurgan Region (Oblast). This article discusses the content of 2,4-dichlorophenoxyacetic acid (2,4 –D) and organochlorine pesticides (OCP) in surface waters (rivers). The following types of pesticides were determined in water: 2,4–D, α–HCCH (hexachlorocyclohexane), γ–HCCH, DDE (dichlorodiphenyldichloroethylene), DDT (dichlorodiphenyltrichloroethane). Water sampling and measurement of the mass concentration of 2,4-D were carried out in accordance with GOST 31861. The equipment used for water sampling always complied with GOST 31861. In our study, the sample was transferred unfiltered into glass bottles with a capacity of 0.5 - 1 $dm^3$ using a sampler and sealed with ground glass or wrapped with Teflon foil (or aluminum foil), cork or polypropylene stoppers. The use of rubber stoppers and plastic utensils was not permitted. Water samples were taken for the study from April to September. The surface water of the Tobol River and the Uy River was examined in different parts of the region. Sampling in the rivers took place in spring and autumn, at a depth of 0.3 m. A total of 238 water samples were taken during the study period (2015-2022) (34 samples per year). In the Tobol and Uy rivers (Belozerskoye, Kostousovo, Arbinka, Ust-Uyskoye, Zverinogolovskoye villages), no detectable concentrations of pesticides were found at a depth of 0.3 m. The measurements are based on the extraction of herbicides from acidified water samples by extraction with diethyl ether. 2,4-D, α-HCCH (hexachlorocyclohexane), γ-HCCH, DDE (dichlorodiphenyldichloroethylene), DDT (dichlorodiphenyltrichloroethane) were determined using gas-liquid chromatography; a Color-800 gas chromatograph was used to determine these pesticides. The analyzes for organochlorine pesticides were carried out at the Kurgan Center for Hydrometeorology and Environmental Monitoring of the Federal State Budgetary Institution "Ural Department of Hydrometeorology and Environmental Monitoring". No concentrations of the organochlorine pesticides dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), 2,4 – D, hexachlorocyclohexane α – HCCH, γ – HCCH were detected during the study of surface waters of the Kurgan region in 2015-2022. The problem of water pollution by organochlorine pesticides in the Kurgan region is not of global significance. The content of organochlorine pesticides in water has a negative impact on human health and the environment.

**KEYWORDS**

~ Water
~ Dichlorodiphenyltrichloroethane
~ Concentration
~ Reservoir
~ River station
~ Gas chromatographic method

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## 1. INTRODUCTION

Water is one of the most important substances for human life due to various processes and phenomena in living and dead nature (Ohay, Nuriddinnov & Zharkynbek, 2022).

Due to the content of residues, DDT and HCG in the aquatic environment, which are extremely resistant under natural conditions, as well as the possibility that they enter reservoirs and watercourses by various routes from the localization sites, monitoring should be carried out (Galiulin & Galiulina, 2008).

Sources of DDT in the studied marine area can be leaching of the pesticide by rainwater from the soil of the nearest areas, removal of bottom sediments in which previously used DDT has accumulated with river runoff, atmospheric precipitation, as well as the use of a banned pesticide as part of other preparations (Korpakova et al., 2014).

The identification of point and multiple sources of river pollution with residues of the pesticides DDT and HCCH is of great aquatic ecological importance, as river water is used for fishing, domestic and drinking water purposes. If river water is eutrophicated with these substances, there is a risk that they will enter the human body via the food chain and accumulate in individual organs and tissues (Galiulin et al., 2021).

The entry of pesticides into groundwater and mineral water used for domestic, drinking and medical purposes has a particular impact on human health and life expectancy. The problem of drinking water quality is and remains urgent and extremely acute (Dahlberg et al., 2020). Therefore, it is still important to investigate the quantitative and qualitative composition of pesticides in groundwater and mineral waters and the way they enter groundwater and to minimize the negative effects of pesticides on the human body (Osokina, 2012).

An important factor that has a negative impact on the health of the population and its habitat is water pollution, which can not only be a medium for the spread of harmful pollutants, but also a direct source of pollutants that enter the human body. In the reservoir, pesticides are chemically and biologically transformed, which in turn depends on many factors (solubility, volatility, sorption properties, lipophilicity, temperature of the aqueous phase, etc.). The primary task of state policy should be to preserve the health of the nation, which is why monitoring, environmental protection and the development of sanitary standards are a promising and priority area (Pivneva, 2017; Donets et al, 2020).

Organochlorine compounds entering the aquatic ecosystem are contained in various types of bottom sediments, which can become the main source of water pollution and hydrobionts for a long time (Kozlova & Gordienko, 2021; Pechenyuk, 2019; Moshchenko, Lishavskaya & Chernova, 2008).

The problem of water pollution is a global concern. The content of organochlorine pesticides in water has a negative impact on human health and the environment.

The aim of this study was to comprehensively investigate the content of organochlorine pesticides such as dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), 2,4-dichlorophenoxyacetic acid (2,4-D) and hexachlorocyclohexane isomers (α-HCH, γ-HCH) in surface waters of the Kurgan region. The study covered the Tobol and Uy rivers and was conducted from 2015 to 2022, providing a fairly complete picture of the state of water bodies in the region.

During the study, several important sampling sites were selected to ensure the representativeness of the data. The water samples were analyzed for the presence of the aforementioned pesticides using modern analytical methods such as gas chromatography. With this method, pesticides can not only be detected, but their concentrations can also be determined with a high degree of accuracy.

In addition, the results of the study confirm the need for regular monitoring of the condition of water bodies, as organochlorine pesticides can have negative effects on the aquatic ecosystem and also pose a risk to human health.

## 2. MATERIALS AND METHODS

The subject of the studies carried out in 2015-2022 was the surface water in the Kurgan region: the Tobol River and the Uy River in various districts of the region.

Water samples were taken in accordance with Regulatory Document (RD) 52.24.412.–2009 “Mass concentration of hexachlorobenzene, alpha-, beta- and gamma-HCCH, dicofol, dihydroheptachlor, 4,4'-DDT, 4,4'-DDE, 4,4'-DDD, trifluralin in water bodies". Methodology for performing measurements by the gas chromatographic method” and Regulatory

Document (RD) 52.24.438-2011 “Mass concentration of MCPA and 2,4-D in waters. Technique of measurements by the gas chromatographic method”.

The preparation for the measurement includes the following phases: sampling and storage, preparation of solutions and reagents, preparation of an air purification filter, preparation of a packed column and preparation of a chromatograph.

Water sampling and determination of the mass concentration of 2,4-dichlorophenoxyacetic acid (2,4-D), a widely used herbicide, were carried out strictly in accordance with the requirements of GOST 31861-2012. This standard regulates not only the sampling procedure, but also the requirements for the equipment used to ensure the reproducibility and reliability of the analysis results. All work steps, from the selection of the sampling point to the preservation of the sample, were carried out in compliance with the rules prescribed in GOST. Failure to observe even small details can significantly affect the final result and lead to an underestimation or overestimation of the 2,4-D concentration.

A special sampler was used for sampling, the design of which complied with GOST 31861-2012, excluding contamination of the sample. The choice of the type of sampler depends on the specifics of the reservoir: for surface water bodies, a simple bathometer can be used, for deep water bodies, more complex devices with a remote control mechanism can be used. It is important that the sampler has been thoroughly washed with distilled water before each sampling and then with a small amount of the analyzed water to avoid cross-contamination.

After collection, the unfiltered water sample was immediately transferred to clean glass bottles with a capacity of 0.5-1 dm Glass containers were chosen due to their chemical inertness, which excludes any interaction with the analyzed substance. The use of polyethylene containers is strictly prohibited, as polyethylene can adsorb 2,4-D, which leads to an underestimation of the analysis results. Rubber stoppers are also unacceptable as they may release volatile organic compounds that can distort the results of gas chromatography. The bottles were hermetically sealed with ground glass stoppers or cork stoppers wrapped in Teflon foil or aluminum foil. Teflon and aluminum foil prevent the penetration of impurities from the air and provide additional tightness.

The samples were analyzed for 2,4-D content using a Tsvet-800 gas chromatograph. This device has a high sensitivity and enables the determination of trace 2,4-D impurities in a wide concentration range: from $10^{-4}$ to $10^{-6}$ vol.% without preliminary concentration and from $10^{-6}$ to $10^{-10}$ vol.% with concentration methods. The choice of concentration method, e.g. liquid extraction or solid phase microextraction, depends on the expected concentration of 2,4-D in the sample. Prior to analysis, samples can undergo additional preparation, including extraction with an organic solvent and cleaning of interfering substances. To ensure the accuracy of the analysis, 2,4-D standard solutions of known concentration were used to create a calibration curve. The calibration curve should be linear in the range of the working concentration.

It is important to emphasise that all stages of the analysis, from sampling to the processing of the results, were carried out in accordance with the requirements of the analytical methodology, which guarantees the reliability and reproducibility of the data obtained. The analysis results were processed taking into account all possible sources of error, and the conclusions were based on statistically significant data. In addition, regular calibration and maintenance of the "Tsvet-800" gas chromatograph are an essential part of the process to ensure the accuracy of the measurements. Sampling in the rivers took place in spring and autumn at a depth of 0.3 m. A total of 238 water samples were taken during the study period (2015-2022) (Fig. 1, Fig. 2).

During the study, the following locations were identified for surface water sampling in the Kurgan region:

- Tobol River, Arbinka settlement, 20.6 km upstream of the dam of the Kurgan reservoir;
- Tobol River, Zverinogolovskoye village, 0.4 km downstream of the highway bridge, within the cross-section of the water level gauge (898 km);
- River Uy, village Ust-Uyskoye, 0.3 km above the highway bridge (8 km);
- Tobol, village Kostousovo, 16 km below Kurgan, 5 km below the confluence of the river Chernaya, 22 km below the water level;
- Tobol, Belozerskoye village, 2.2 km upstream of the source of the Tobolchik, 0.1 km upstream of the highway bridge (626 km).

The geographical coordinates were not determined using a GPS receiver.

The measurements were carried out using gas-liquid chromatography; a Tsvet-800 gas chromatograph was used to determine these pesticides.

The analyses for organochlorine pesticides were carried out at the Kurgan Centre for Hydrometeorology and Environmental Monitoring of the Federal State Budgetary Institution "Ural Department of Hydrometeorology and Environmental Monitoring".

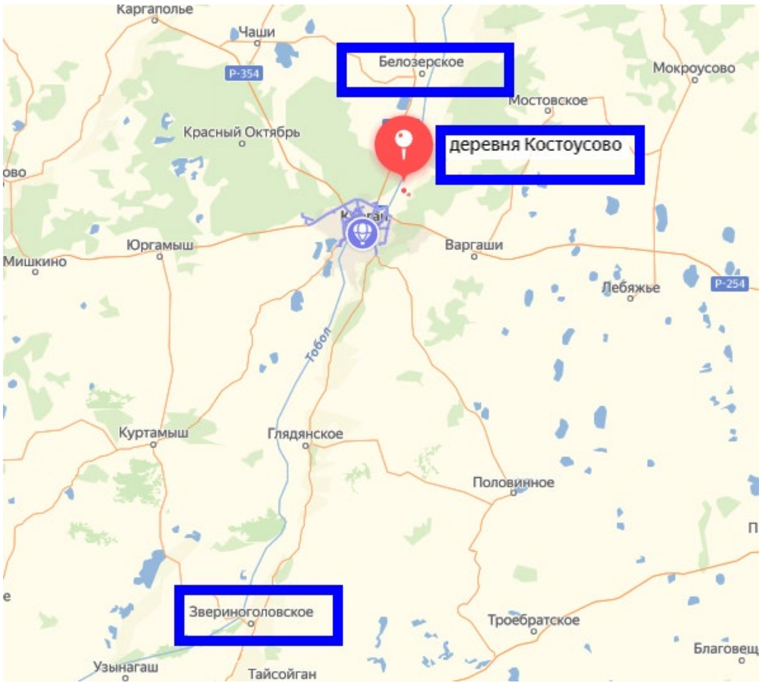


Figure 1. Schematic map of the location of the research objects (sampling of the surface water of the Tobol River)


Figure 2. Schematic map of the sampling of the surface water of the river Uy

## 3. RESULTS

The river network of the Kurgan region is part of the Ob-Irtysh and Kara Sea basins. It is formed by the Tobol, Iset and Miass rivers, their tributaries and lakes.

There are three large rivers (over 500 km): Tobol, Iset and Miass; seven medium-sized rivers (between 100 and 500 km): Uy, Ubagan, Kurtamysh, Yurgamysh, Suyer, Sinara, Tech; small rivers (10-100 km) – 116; small watercourses (less than 10 km) – 333.

There are 449 watercourses in the region with a total length of 5175.5 km. The water resources of the Kurgan Oblast are extremely limited. In terms of surface water resources, the region is one of the last in Russia and one of the last in the Urals. The springs are drying up and stagnating.

The water regime is characterized by pronounced spring floods and stable summer and winter low water (Zavyalova & Koval, 2008).

From 2015 to 2022, comprehensive monitoring of the quality of surface waters in the Kurgan Oblsat was carried out, focusing on two rivers, Tobol and Uy. The aim of this monitoring, the results of which are shown in Table 1, was to determine the content of pesticides. This is an extremely important aspect, as the pesticides used in agriculture in the region pose a significant threat to the river ecosystem. When they enter the water, they can have toxic effects on aquatic flora and fauna, including phytoplankton, zooplankton, fish and other inhabitants. The accumulation of pesticides in the food chain can have negative consequences for human health when fish or water from contaminated sources is consumed.

The study included water samples from various locations of the Tobol and Uy rivers (2015-2022).

As part of the study, which was carried out between 2015 and 2022, 238 water samples were taken from rivers. The samples were taken in spring and autumn at a depth of 0.3 meters below the water surface, which is standard practice for surface waters. The choice of time periods (spring and autumn) is due to the seasonal fluctuations in the hydrological and biogeochemical parameters of the rivers. In spring, the snow melts and the discharge increases, which can influence the concentration of the analyzed substances. In the autumn, on the other hand, the water level drops and the composition of the water masses changes. The choice of a depth of 0.3 meters was justified by the fact that a representative sample was to be obtained from the surface water layer, which is most sensitive to anthropogenic influences.

The water samples were taken in triplicate. Each sample was collected with an OCP concentration in the water of 0 mg / dm³.

| Name of the reservoir | Item name | The location of the river station | Depth, m | Concentration in water, α-HCCH, γ-HCCH, DDE, DDT, 2,4-D, mg/dm3 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| The Tobol River | Arbinka | Within Arbinka village, 20.6 km above the Kurgan Reservoir dam | 0,3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| The Tobol River | Zverinogolovskoye | Within Zverinogolovskoye village, 0.4 km below the road bridge, in the river station of the gauging station (898 km) | 0,3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| The Uy River | Ust'-Uyskoye | Within the village of Ust-Uyskoye, 0.3 km above the road bridge (8 km) | 0,3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| The Tobol River | Kostousovo | 16 km below Kurgan, 5 km below the confluence of the Chernaya River, 22 km below the gauging station | 0,3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| The Tobol River | Belozerskoye | Within the village of Belozerskoye, 2.2 km above the source of the Tobolchik river, 0.1 km above the road bridge (626 km) | 0,3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Table 1. The content of organochlorine pesticides in the surface waters of the Kurgan region 2015-2022.

A study of the water quality of the Tobol and Uy rivers near the settlements of Belozerskoye, Kostousovo, Arbinka, Ust-Uyskoye and Zverinogolovskoye at a depth of 0.3 meters found no pesticides in detectable concentrations. This is an unexpected result considering that potential sources of pollution such as agricultural land are located in the catchment areas of these rivers. The low pesticide concentrations can be explained by several factors. Firstly, the effectiveness of modern tillage methods, including the selective use of fertilizers and pesticides, can significantly reduce their runoff into water bodies. Secondly, the natural self-purification processes of the river, such as the biodegradation of pesticides by microorganisms, play an important role. Thirdly, the hydrological characteristics of the Tobol and Uy rivers, such as flow velocity and terrain characteristics, can influence the spread of pollutants.

## 4. DISCUSSION

According to our investigations, no detectable concentrations of pesticides were found at a depth of 0.3 m in the Tobol and Uy rivers (Belozerskoye, Kostousovo, Arbinka, Ust-Uyskoye, Zverinogolovskoye).

The study conducted by V.S. Zybalov and T.G. In the neighboring region - Chelyabinsk Oblast - a Krupnova measurement was carried out due to organochlorine pesticides in the water. At a distance of 500 meters from the warehouse with obsolete pesticides, there is a well whose water is used for watering livestock. In the well, 0.006 mg/kg HCCH was found, which is above the maximum permissible concentration, even taking into account the error in the determination method. It should be noted that the local population feeds their cows with water from the well. Given the high accumulation coefficients of HCCH isomers, they can therefore be present in high concentrations in the milk, posing a serious risk to the health of the local population. In addition, water and sludge samples were taken from the lake, which is located about 700 m from the warehouse. Despite the large distance from the warehouse and the relatively long storage time, high concentrations of both HCCH isomers and DDT and metabolites (1.5 – 45 MPC) were found in the lake and in the bottom sediments (Zybalov & Krupnova, 2014).

However, a comparison with the results of studies from the neighboring region - the Chelyabinsk region, 251 km away - reveals considerable differences. In the Chelyabinsk region, the presence of pesticides was found in similar types of water bodies. This difference may be due to several factors. First of all, the different intensity of agricultural production in the two regions may have a significant influence. Intensive farming methods using large amounts of pesticides are probably more widespread in the Chelyabinsk region. In addition, geological, soil and climatic conditions can affect the migration of pesticides and their accumulation in water bodies. For example, the sandier soils in the Chelyabinsk region may contribute to a more active leaching of pesticides into the rivers than the soils in the Kurgan region (where the studied sections of the Tobol and Uy rivers are located).

River pollution remains one of the most pressing environmental problems, affecting not only the health of ecosystems but also the quality of life of the people who depend on these waters. Examples of pollution can be found in various regions of Russia. For example, the Kuban River, which flows through the Krasnodar region, had a pollution level of 240 maximum allowable concentrations (MAC) in 2002. This indicates serious environmental problems in this region caused by both industrial discharges and agricultural waste.

In the Udmurt Republic, too, the level of river pollution in 2005 was high at 200 MAC, which underlines the need for measures to protect water resources. Another example is the Ob River in Surgut, where the pollution level reached 36 MAC in 2005. These data show that the problem of water pollution is particularly acute in certain regions of Russia.

However, not all regions have such negative indicators. In 2013, studies by A.S. Goryan and L.G. Kolesnikova showed that the water quality in the Amur and Northern water intakes meets the established standards. No pesticide concentrations were detected in their analysis, which is a positive sign for the ecology of this region. This could be due to stricter pollution control measures and sustainable water management (Goryan & Kolesnikova, 2013).

It is important to note that water quality in rivers depends not only on natural factors, but also on human activities. Agriculture, industry and urban development have a significant impact on the condition of water bodies. Therefore, it is necessary to introduce effective wastewater treatment technologies and strengthen emission control to prevent further deterioration of river water quality. Joint efforts by the state, scientific institutions and local communities can significantly improve the situation and ensure the preservation of water resources for future generations.

The pollution of river water with the remnants of the persistent organochlorine pesticides DDT and HCCH continues to this day. This fact is, firstly, a serious warning against the use of poorly researched chemical pesticides in agriculture, which are often extremely persistent in the soil, from where they enter the rivers and have an extremely negative effect on the human body. Secondly, it makes it extremely necessary to monitor the aquatic ecological situation in the pollution areas of the river network (Galiulin, 2010).

The issue of water quality is now a global environmental problem. Water is an important factor for public health. High-quality water should not contain impurities that pose a threat to human health. The main task of the Russian Federation is to provide the population with high-quality drinking water. To achieve this, constant analysis and monitoring of water is essential.

## 5. CONCLUSION

No concentrations of the organochlorine pesticides dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), 2,4 – D, hexachlorocyclohexane α – HCCH, γ – HCCH were detected during the study of surface waters of the Kurgan region in 2015-2022.

The problem of water pollution by organochlorine pesticides was not detected in the Kurgan region. Therefore, the absence of organochlorine pesticides in water does not have a negative impact on human health and the environment. The quality of the surface water of the Tobol and Uy rivers is evidence of the correct use of organochlorine pesticides in the past.

Since the investigated concentrations are contained in the surface waters of the neighboring region, the waters of the Kurgan region must continue to be monitored.

## CONFLICT OF INTEREST

The authors report no conflicts of interest.

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