Ensuring the purity of water resources in the Don River basin

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Abstract. Uncontrolled levels of persistent organic pollutants (POPs), which are prohibited for use under the POPs Convention, are the environmental concerns and, when applied on a large scale, will disrupt entire ecosystems. The identification of their impact on the purity of water resources is relevant and affects the planning of water supply for the population and the economy, the justification of water management measures and the redistribution of water resources within the basin. The aim of the research was to identify the content of hazardous pesticides in the surface waters of water bodies of the river basin Don. The data on the concentrations of α-, γ-hexachlorocyclohexane (HCH), dichlorodiphenyl dichloroethane (DDT), dichlorodiphenyl trichloroethane (DDT), dichlorodiphenyl trichloroethane (DDE), trifluralin, parathion methyl, karbofos, and fosalon were analyzed in surface waters and bottom sediments. It is noted that organochlorine pesticides (OCPs) are found in most places (up to 100%) and in the number of samples in the bottom sediments of the surface waters of the Don River. It is significant that in the water of water bodies of the Don basin, including in the Don River, the detection frequency of the most active γ-HCH is detected more often than α-HCH. In the context of the projected increase in fresh water consumption in the Don River Basin, measures are being discussed to protect water resources from pollution.

1. Introduction

An important modern problem of ecology is the increasing pollution of the environment as a result of anthropogenic influence, especially in connection with the use and penetration of chemicals into the environment, their impact on human health. The most dangerous persistent organic pollutants (POPs) are pesticides used in agriculture, many of which have toxic properties, are resistant to decomposition and are characterized by bioaccumulation [1-3].

Recently, the world has made progress in the development of a policy for the safe management of chemicals, and a number of instruments and programs have been created on this issue, such as the International Conference on Chemicals Management, the Intergovernmental Forum on Chemical Safety, the Intergovernmental Negotiating Committee, the United Nations Environment Programme (UNEP), the International Network for the Elimination of POPs (IPEN), and the UN environmental conventions. In order to solve the problem of POPs, the Stockholm Convention on Persistent Organic Pollutants, which establishes standards for the protection of the environment and public health from the effects of POPs, was opened for signature in Stockholm on 23.05.2001. It was supported by leading chemical industry associations, the European Commission, the Food and Agriculture
Organization of the United Nations (FAO), the Global Environment Facility (GEF), the Council of the United Nations Environment Programme (UNEP), and a number of other international associations and entered into force on 17.05.2004. The Convention adopted a list, currently consisting of 21 chemicals that have the properties of POPs. Countries are allowed to supplement this list. In Russia, the Convention was signed in 2003.

But the problems of the use and elimination of POPs still need to be solved, including in the Russian Federation, where in a number of regions tons of obsolete pesticides are in unacceptable storage conditions, spread through water, air and soil, are deposited at a great distance from the source, accumulating in living organisms, aquatic ecosystems and terrestrial ecosystems. If improperly used and stored, such toxicants of agrochemicals pose a threat to public health, and the environmental impact of their penetration into the environment is more negative than the negative effect of the pests against which they are used. The situation is aggravated by the fact that today there are no environmentally friendly and safe technologies for the destruction of pesticides and their high levels of residual amounts are detected in nature.

2. Materials and methods
The purpose of the work was to consider issues related to the discharge of toxic substances into the water bodies of the Don River basin. Taking into account that one of the possible threats to ecosystems may be uncontrolled levels of POPs prohibited for use in accordance with the Convention on POPs, there is analysis of the assessment of the purity of the water resources of the river basin. Don is relevant. Solving the problems of protecting water resources from pollution also has a practical focus due to the limited volume of water resources against the background of increasing production and increasing demand for fresh water [4].

In this work, we used open-access materials from Roshydromet [5] on the content in surface waters and bottom sediments of water bodies of concentrations of pesticides: α, γ-hexachlorocyclohexan (HCCH), dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethane (DDE), trifluralin (a soil herbicide against weeds), parathion-methyl (an insecticide for insect pest control and ticks), karbofos.

3. Results and Discussion
Water resources of the river basin the Don is estimated at 28 km$^3$, decreasing to 14 km$^3$ in low-water years. About 70% of the water resources of the basin are formed on the Upper and Middle Don in the area from the source to the town of Kalach-on-Don [6, 7]. A number of water bodies in the basin are characterized by extremely poor-quality waters [8, 9]. A long period of their pollution leads to depletion, degradation, loss of economic value, and poses a threat to aquatic ecosystems [10]. According to Roshydromet, it is noted that organochlorine pesticides (HOPS) are not present in the surface waters of the Don River, but are found in most points (up to 100%) and the number of samples in bottom sediments (table 1).

It is significant that the water of water objects of the don basin, including the river Don and the incidence of detection of the most active isomer γ-HCCH prevails over the detection frequency of α-HCCH, which may indicate continued during these years unauthorized application of preparations that contain HCCH, or receive them from atmospheric precipitation at global transport of air masses from areas of application and receipt of watersheds of rivers from the dumping of pesticides or pesticide, tables 2, 3.

The maximum number of samples with the pesticides γ-HCCH was detected in water samples in 2015. (3.4 %), α-HCCH (3.9 %) – in 2014 If we compare these indicators by year, we should note their variability: the average content of all identified pesticides in 2014 compared to 2013 increased slightly, in 2015 compared to 2014 – decreased by 2.4 times, in 2016 compared to 2015 – increased by 2.4 times. In 2017, there was an improvement in the situation, since no traces of the concentrations of the declared POPs included in the list of substances prohibited for use in accordance with the Convention on POPs were found, table 3.
Table 1. The frequency of detection of organochlorine pesticides in water and bottom sediments of surface waters Don, % [5]

|                | Water                          | Bottom sediments           |
|----------------|-------------------------------|-----------------------------|
|                | α-HCCH | γ-HCCH | DDT | DDE | α-HCCH | γ-HCCH | DDT | DDE |
| 2013           | 0(5)   | 0(5)   | 0(5) | 0(5) | 100(5) | 100(5) | 100(5) | 100(5) |
|                | 0(15)  | 0(15)  | 0(15) | 0(15) | 100(15) | 100(15) | 100(15) | 100(15) |
| 2014           | 0(5)   | 0(5)   | 0(5) | 0(5) | 100(5) | 100(5) | 100(5) | 100(5) |
|                | 0(20)  | 0(20)  | 0(20) | 0(20) | 100(20) | 100(20) | 100(20) | 100(20) |
| 2015           | 0(5)   | 0(5)   | 0(5) | 0(5) | 100(5) | 100(5) | 100(5) | 100(5) |
|                | 0(23)  | 0(23)  | 0(23) | 0(23) | 43(23) | 65(23) | 73(23) | 82(23) |
| 2016           | 0(2)   | 0(2)   | 0(2) | 0(2) | 100(2) | 100(2) | 100(2) | 100(2) |
|                | 0(12)  | 0(12)  | 0(12) | 0(12) | 100(12) | 100(12) | 100(12) | 100(12) |
| 2017           | 0(2)   | 0(2)   | 0(2) | 0(2) | 100(2) | 100(2) | 100(2) | 100(2) |
|                | 0(9)   | 0(9)   | 0(9) | 0(9) | 78(9)  | 78(9)  | 89(9)  | 56(9)  |

Note: In parentheses are the number of points (numerator) and the number of samples (denominator) in which organochlorine pesticides (OCPs) were determined.

Table 2. Limits of change (numerator) and average content (denominator) of OCPs in bottom sediments of surface waters Don, mcg / kg [5]

|                | α-HCCH | γ-HCCH | DDT | DDE |
|----------------|--------|--------|-----|-----|
| 2013           | 1.0-2.0 | 1.0-2.0 | 1.0-3.0 | 1.0-3.0 |
|                | 1.33   | 1.60   | 2.13 | 1.67 |
|                | 1.0-2.0 | 1.0-2.0 | 2.0-3.0 | 1.0-3.0 |
| 2014           | 1.55   | 1.70   | 2.40 | 2.00 |
|                | 0-1.0  | 0-2.0  | 0-3.0 | 0-2.0 |
|                | 0.430  | 0.78   | 1.04 | 1.08 |
| 2015           | 1.0-3.0 | 1.0-3.0 | 2.0-7.0 | 1.0-5.0 |
|                | 1.58   | 1.75   | 3.66 | 2.41 |
|                | 0-1.0  | 0-2.0  | 0-2.0 | 0-1.0 |
|                | 0.780  | 1.00   | 1.22 | 0.560 |

Note: OCPs – organochlorine pesticides

Positive situation with regard to the content of pesticides in the surface waters of the water bodies of the river basin. Dawn is still unstable. Therefore, in the future, it is necessary to adhere to the policy of protecting basin water resources from pollution. There is no universal solution to this problem. It is important to use all possible ways and methods to do this. Including carrying out inventories of objects of placement of obsolete pesticides with the identification of substances, as a result of which a decision is made on their intended use in the recommended norms or destruction.
Table 3. The content of pesticides in the surface waters of water bodies of the river basin Don [5]

| Pesticide        | The number of observation points | Number of samples | Repeatability of excess MPC in samples, % | Concentration limits, mcg/l | The difference in average concentrations for the current and previous years |
|------------------|---------------------------------|-------------------|------------------------------------------|----------------------------|-------------------------------------------------|
|                  | total +pesticides               | total +pesticides |                                          |                            |                                                 |
| α-HCCH           | 46                              | 0                 | 264                                      | 0                          | 0-0.002                                         | +H                                              |
| γ-HCCH           | 46                              | 2.2               | 264                                      | 0.8                        | 0.005                                          | +H                                              |
| DDT              | 46                              | 0                 | 264                                      | 0                          | 0                                              | H                                               |
| DDE              | 46                              | 2.2               | 264                                      | 0.4                        | 0.005                                          | +H                                              |
| trifluralin      | 3                               | 0                 | 14                                       | 0                          | 0                                              | H                                               |
| parathion methyl | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| malathion        | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| fosalon          | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| 2013             |                                 |                   |                                          |                            |                                                 |                                                 |
| α-HCCH           | 39                              | 7.7               | 233                                      | 3.9                        | 0.4                                            | 0.014                                          | -H                                              |
| γ-HCCH           | 39                              | 10.3              | 232                                      | 2.6                        | 0                                              | 0.07                                           | -H                                              |
| DDT              | 39                              | 0                 | 233                                      | 0                          | 0                                              | H                                               |
| DDE              | 39                              | 0                 | 233                                      | 0                          | 0                                              | H                                               |
| parathion methyl | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| malathion        | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| fosalon          | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| 2014             |                                 |                   |                                          |                            |                                                 |                                                 |
| α-HCCH           | 39                              | 5.1               | 232                                      | 1.7                        | 0                                              | 0.008                                          | +H                                              |
| γ-HCCH           | 39                              | 10.3              | 232                                      | 3.4                        | 0.4                                            | 0.07                                           | -H                                              |
| DDT              | 39                              | 0                 | 232                                      | 0                          | 0                                              | H                                               |
| DDE              | 39                              | 0                 | 232                                      | 0                          | 0                                              | H                                               |
| parathion methyl | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| malathion        | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| fosalon          | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| 2015             |                                 |                   |                                          |                            |                                                 |                                                 |
| α-HCCH           | 39                              | 7.7               | 224                                      | 2.7                        | 0                                              | 0.004                                          | +H                                              |
| γ-HCCH           | 39                              | 7.7               | 224                                      | 2.2                        | 0                                              | 0.007                                          | +H                                              |
| DDT              | 39                              | 0                 | 224                                      | 0                          | 0                                              | H                                               |
| DDE              | 39                              | 0                 | 224                                      | 0                          | 0                                              | H                                               |
| parathion methyl | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| malathion        | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| fosalon          | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| 2016             |                                 |                   |                                          |                            |                                                 |                                                 |
| α-HCCH           | 39                              | 0                 | 224                                      | 0                          | 0                                              | 0                                              | +H                                              |
| γ-HCCH           | 39                              | 0                 | 224                                      | 0                          | 0                                              | +H                                              |
| DDT              | 39                              | 0                 | 224                                      | 0                          | 0                                              | H                                               |
| DDE              | 39                              | 0                 | 224                                      | 0                          | 0                                              | H                                               |
| parathion methyl | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| malathion        | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| fosalon          | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| 2017             |                                 |                   |                                          |                            |                                                 |                                                 |
| α-HCCH           | 39                              | 0                 | 224                                      | 0                          | 0                                              | 0                                              | +H                                              |
| γ-HCCH           | 39                              | 0                 | 224                                      | 0                          | 0                                              | +H                                              |
| DDT              | 39                              | 0                 | 224                                      | 0                          | 0                                              | H                                               |
| DDE              | 39                              | 0                 | 224                                      | 0                          | 0                                              | H                                               |
| parathion methyl | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| malathion        | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |
| fosalon          | 2                               | 0                 | 20                                       | 0                          | 0                                              | H                                               |

Note: 0 - not detected, +H - insignificant decrease, -H - insignificant increase
In irrigation, measures should also be developed to eliminate the sources and causes of pesticide contamination. Proper organization of irrigation and agrotechnically sound application of fertilizers can solve this problem and improve the operation of the entire irrigation and drainage network. Optimal doses of fertilizers should be justified not only by obtaining high yields and profit, but also by minimizing the negative effects on the groundwater and soil of fertilizers during irrigation.

Agroforestry measures are effective for reducing diffuse pollution, especially in agricultural areas, when fertilizers and pesticides are washed out with the runoff. The level of diffuse pollution mainly depends on the amount of runoff from the catchment area. Protective forest stands can reduce diffuse runoff and, consequently, pollution by more than half [11]. Effective and eco-economically justified programs for agroforestry land development contribute to the increase in the level of agricultural production safety, block many negative processes in the centers of degradation and desertification, increase the moisture supply of territories, restore and increase soil fertility, and increase biodiversity [12-14]. The creation of projects and forest reclamation measures to reduce diffuse runoff can be used in the development of a set of measures to improve the Don River basin.

Flow-regulating strips provide intensive water absorption by the soil during heavy rains and snowmelt, retain the maximum possible volume of water in the forest belt, which reduces runoff, and increases the infiltration capacity of the soil. Improving the efficiency of flow-regulating forest strips is carried out by combining them with anti-erosion hydraulic structures (shafts with a height of 0.3-2.0 m at the lower edge, ditches with a depth of 1.0-1.5 m in the lower row spacing and their combinations). Baltic plantings also regulate surface runoff, prevent the increase of ravines and protect them from erosion, shade the slopes, improve their hydrological regime, and promote the rational use of eroded land. A necessary condition for afforestation of the bottom part of ravines and gullies is the completion of anti-erosion works within the catchment area and the channel part of the ravine-beam network. Afforestation of ravines and gullies is carried out by continuous planting of plantings. For volume and high-speed runoff.

4. Conclusion

Water resources of the river basin Don are to varying degrees vulnerable to external influences, especially anthropogenic ones, which exceed all others in mass. The degree of vulnerability depends on the energy potential of the rivers and their ability to slow down their response to changes in conditions. Depletion, degradation, and loss of economic value threaten the aquatic ecosystems of the river basin. Don as a result of long-term pollution of water resources. Absence for a number of years in the water bodies of the river basin. The increase in dangerous concentrations of pesticides prohibited by the Convention on POPs and other defined pesticides can be explained by a sharp reduction or complete cessation of the use of these pesticides in river catchments, replacing them with a new generation of pesticides with high activity at significantly lower doses of the active substance and low environmental resistance.

In order to consolidate the achieved result, it is recommended to conduct inventories of the remaining sites of obsolete pesticides and ensure optimal conditions for their storage, as well as the introduction of safe technologies for the destruction of pesticides containing POPs. Methods of reducing diffuse pollution that forms in the catchment area of the basin, which is one of the causes of pollution of rivers and reservoirs, can be the correct organization of irrigation and the reasonable use of fertilizers during irrigation, as well as protective a forestation. It is important to follow the Convention on POPs, laws and regulations of Federal and regional authorities of the Russian Federation for environmental protection.

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