#### Monitoring soil, air, and water status

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#### MONITORING INVESTIGATIONS OF SON-KUL LAKE (KYRGYZSTAN) POLLUTED BY PESTICIDES

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**Abstract** – The results of environmental monitoring of Son-Kul Lake (Kyrgyzstan), conducted in 2017–2018 by representatives of environmental non-governmental public organizations with the participation of the Kyrgyz Republic state environmental laboratory and international water quality monitoring experts, are presented, which have been used for giving recommendations for organizing the lake monitoring system. The monitoring was aimed at determining the lake ecological status and further specifying the ways of its sustainable management, including its decontamination from hazardous chemical compounds and solid waste accumulated as a result of pesticide pollution and fishing activities, respectively. The monitoring analyzed the content of a wide range of pesticides in the lake surface water samples, bottom sediments, as well as in fish inhabitants. A series of persistent organic pollutants (POPs), i.e. 4,4'-dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane isomers, polychlorinated biphenyls, and other hazardous chemical compounds were found in collected samples. The observed levels of POPs in the bottom sediments and fish samples were within the limited range, while the analysis of water samples showed an exceeding of the maximum permissible concentrations for DDT and hexachlorocyclohexane for fishery waters. The obtained preliminary results show an urgent need to develop a state monitoring program for Son-Kul Lake and to conduct a continuous monitoring on POPs levels.

*Keywords:* monitoring, Son-Kul lake, pollution, persistent organic pollutants, pesticides, decontamination, 4,4'-dichlorodiphenyltrichloroethane, polychlorinated biphenyls.

### МОНИТОРИНГ СОСТОЯНИЯ ОЗЕРА СОН-КУЛЬ (КЫРГЫЗСТАН), ЗАГРЯЗНЕННОГО ПЕСТИЦИДАМИ

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Аннотация – Представлены результаты экологического мониторинга озера Сон-Куль (Кыргызстан), проведенного в 2017–2018 гг. представителями экологических неправительственных общественных организаций при участии государственной экологической лаборатории и международных экспертов в области мониторинга качества воды, которые позволили дать рекомендации по организации системы мониторинга озера. Мониторинг проводился для определения и экологического статуса озера и дальнейшего определения путей устойчивого управления озером, включая его очистку от загрязнения опасными химическими соединениями и твердыми отходами, накопившимися как следствие применения пестицидов и рыбохозяйственной деятельности, соответственно. В ходе мониторинга анализировалось содержание широкого ряда пестицидов в пробах поверхностных вод озера, донных отложений, а также обитающей в озере рыбы. В пробах обнаружены стойкие органические загрязнители (СОЗ) – ДДТ, изомеры гексахлорциклогексана, полихлорированные бифенилы и другие опасные химические соединения. Содержание СОЗ в донных отложениях и в рыбе находится в пределах нормы, однако анализ проб воды показал превышение ПДК по ДДТ и гексахлорциклогексану для водоемов рыбохозяйственного назначения. Полученные предварительные результаты показали крайнюю необходимость в разработке программы государственного мониторинга для озера Сон-Куль и проведения мониторинга на содержание СОЗ на постоянной основе.

*Ключевые слова:* мониторинг, озеро Сон-Куль, загрязнение, стойкие органические загрязнители, пестициды, очистка, ДДТ, полихлорированные бифенилы.

#### INTRODUCTION

A high-mountain Lake Son-Kul is the largest natural freshwater reservoir of Kyrgyzstan, a unique natural object, a beautiful geographical location of the Kyrgyz Republic and a potential center for ecological tourism in the country<sup>1</sup>. The lake is located in a huge cavity between two internal ridges of Tien Shan on 3016 m high above the sea level in the northwestern part of the Naryn region of the Kyrgyz Republic. The lake area is 36869 hectares (geographical location 41°50'N 75°07'E), the surface area is 278 km<sup>2</sup>, the fresh water volume is 2.4 km<sup>3</sup>, the length is 28 km, the width is 18 km, the maximum depth is about 14 m.

The eastern territory of the lake is a part of the Karatal-Zhapyryk National Nature Reserve. Ten species of fish have been recorded in the lake, and from 41 to 69 bird species are native for the lake area, while Son-Kul is an important migration point for waterfowls.

Currently, the Kyrgyz republic has faced an actual problem of cleaning Son-Kul Lake from pollution. An intensive fishing activity on Son-Kul Lake has resulted in accumulation of a large number of old abandoned lead weighted fishing nets at the bottom of the lake. When considering a way for removing the nets from the lake, an additional problem arose – a problem of the lake pollution with pesticides, the most of which are hazardous chemicals belonging to the group of persistent organic pollutants (POPs), whose production and use are currently prohibited by the Stockholm Convention on POPs [1, 2].

The lake was polluted by POPs in 1979 after a large locust breeding had occurred in the surrounding area followed by applying pesticides to find the solution. Subsequently, the pesticides had been washed out by atmospheric precipitation and the waters of small rivers and were gradually transferred into the water space of the lake, which led to the mass fish mortality, and catastrophically disrupted the established biocenosis of the lake.

The goal of the study was as follows. Before taking measures to clean the bottom of the lake by removing the old fishing nets, it was necessary to carry out an environmental monitoring for determining potential level of toxic pollution of water and bottom sediments of the lake, as well as pollution of fish inhabiting the lake. In addition to assessment of general risks to human health and the environment, it was also important to prevent the further spreading hazardous substances resulting from the stirring-up of contaminated sludge during the cleaning process. The results of the investigations are presented here.

### CHEMICAL COMPOUNDS – MONITORING OBJECTS

All pesticides, which were found in the samples collected during monitoring

<sup>&</sup>lt;sup>1</sup> https://www.youtube.com/watch?v=6HW0kkZP9mo

investigations, belong to chlorine-containing organic compounds listed as highly hazardous chemicals in the Stockholm Convention on persistent organic pollutants (POPs). Being stable compounds, these substances can be easily gained by environmental objects and then transmitted through food chains, accumulating in aquatic organisms - hydrobionts, fish, mollusks, crustaceans. It is known that the content of chlorinated hydrocarbons, in particular, polychlorinated biphenyls (PCBs) in meat and fish liver can reach several dozens of mg/kg, thus, they represent a serious threat to human health and environmental safety.

The structures of the chemical compounds found in the collected samples of surface waters, bottom sediments and fish of Son-Kul Lake in the course of the environmental monitoring, are presented in Table 1.

4,4'-Dichlorodiphenyltrichloroethane (DDT)	
α-Hexachlorocyclohexane, (1R,2R,3S,4R,5S,6S)-1,2,3,4,5,6-hexachlorocyclohexane	
β-Hexachlorocyclohexane, (1R,2S,3R,4S,5R,6S)-1,2,3,4,5,6-hexachlorocyclohexane	
γ-Hexachlorocyclohexane, (1R,2R,3S,4R,5R,6S)-1,2,3,4,5,6-hexachlorocyclohexane, lindane	
Hexachlorobenzene	

<i>Table 1.</i> Structures of the main chemical compounds found in Son-Kul Lake
monitoring investigations in 2017

## MONITORING INVESTIGATIONS OF SON-KUL LAKE (KYRGYZSTAN)

	Pentachlorobenzene	
CI CI CI	2,4'-Dichlorobiphenyl	
	2,2',5-Trichlorobiphenyl	
	2,4',5-Trichlorobiphenyl	
	2,4,4'-Trichlorobiphenyl	
	2,2',5,5'-Tetrachlorobiphenyl	
	2,3,3',4',6-Pentachlorobiphenyl	
	2,3,3',4,4'-Pentachlorobiphenyl	
	2,2',4,5,5'-Pentachlorobiphenyl	
	1-exo,2-endo,4,5,6,7,8,8-Octachloro-2,3-exo-epoxy- 2,3,3a,4,7,7a-hexahydro-4,7-methanoindene, oxy-Chlordane	

# EXPERIMENTAL

### Monitoring participants

The work was carried out by the Non-Governmental Organization "Independent Environmental Expertise" [3] together with the State Agency for Environmental Protection and Forestry under the Government of the Kyrgyz Republic and the Finnish Environment Institute (SYKE) in the framework of the Programme for Finland's Water Sector Support to Kyrgyzstan and Tajikistan (FinWaterWEI II) [4].

Sampling procedures were performed at Son-Kul Lake in August 2017 and in July 2018. The collected samples were analyzed in the SYKE laboratory and in the laboratories of the Department of Disease Prevention and State Sanitary and Epidemiological Surveillance under the Ministry of Health of the Kyrgyz Republic and Issyk-Kul Department GAOOSLKh by standard methods.

### Procedures for environmental monitoring

### Analysis of surface waters

The location of water and bottom sediment sampling in August 2017 was marked using the global GPS positioning system and mapped (Fig. 1).

Water samples were analyzed in the SYKE laboratory for evaluation of the following substances:  $\alpha$ -hexachlocyclohexane,  $\beta$ -hexachlocyclohexane, and 2,2',5-trichlorobiphenyl (see table 1 for chemical structures).

### Sampling procedure

Water sampling was carried out in accordance with the procedure described in Appendix 1 of the manual for public environmental monitoring: "Guidelines for environmental inspectors on public monitoring of the state of the environment" [5].

Chemically resistant plastic containers with a volume of 1 l were used as sampling vessels. Each container was marked with a serial number of the sample (sampling location), which was also recorded in the sampling log. Samples were taken up from a boat at a depth of 3 and 5.8 m.

Transportation of samples to the analytical laboratory was organized in such a way as to exclude overheating and overcooling of the samples. The collected samples were stored in temperature-controlled containers. Storage and transportation of water samples was carried out in thermocontainers at a temperature of  $4^{\circ}$ C.

### Analysis of soil of bottom sediments

The location of the soil sampling of the bottom sediments of Son-Kul Lake was also mapped (Fig. 1). Samples of bottom sediments were analyzed for the content of the following pesticides: pentachlorobenzene, hexachlorobenzene, a- and  $\beta$ -hexachlorocyclohexane, 2,4',5-trichlorobiphenyl, 2,4,4'-trichlorobiphenyl, 2,2',5,5'-tetrachlorobiphenyl, 2,3,3',4',6-pentachlorobiphenyl, 2,3,3',4,4'pentachlorobiphenyl, 2,2',4,5,5'-pentachlorobiphenyl, oxy-chlordane, dichlorodiphenyldichloroethylenes, DDT-dehydrochloride, and dichlorodiphenyldichloroethane.

#### MONITORING INVESTIGATIONS OF SON-KUL LAKE (KYRGYZSTAN)



*Figure 1.* Sampling map of water and soil sediments of Son-Kul Lake of environmental monitoring in 2017.

## Sampling procedure

Sampling was carried out in accordance with the method described in [5], on a test site by container sampling technique at a distance of not more than 5 m from the coastline (depending on depth). Sampling was performed with the help of nitrile gloves and washed (stainless) steel scoop. The collected material was placed in a plastic bag with an assigned serial number, which was then placed in a storage container, with an internal temperature of 4°C. All samples were recorded in a field log with registered climatic conditions observed during the sampling period, and other necessary information.

# Analysis of pesticide level in fish

In addition to water and bottom sediments sampling, six fish specimens were collected in Son-Kul Lake in August 2017 and analyzed for POPs level. Each sample was assigned a serial number, the samples were placed in a storage container and delivered to the laboratory.

Samples were analyzed in the SYKE laboratory (4 samples) and the laboratories of the Department of Disease Prevention and State Sanitary and Epidemiological Surveillance under the Ministry of Health of the Kyrgyz Republic (two samples), where the levels of supposed POPs were determined. The four samples were evaluated for the following POPs:

- Hexachloro-1,3-butadiene;
- Hexachlorobenzene;
- 2,4'-Dichlorobiphenyl;

- α-Hexachlorocyclohexane;
- γ-Hexachlorocyclohexane;
- 2,4',5-Trichlorobiphenyl;
- β-Hexachlorocyclohexane;
- oxy-Chlordane;
- $\gamma$ -Chlordane, (trans-);
- 4,4'-DDE (Dichlorodiphenyldichloroethylene);
- 4,4'-DDD (Dichlorodiphenyldichloroethane);
- 4,4'-DDT (Dichlorodiphenyltrichloroethane).

The two samples were analyzed for the following POPs' level:

- 4,4'-DDT;
- 4,4'-DDD;
- 4,4'-DDE;
- α-Hexachlorocyclohexane;
- β-Hexachlorocyclohexane;
- γ-Hexachlorocyclohexane.

### MONITORING RESULTS AND DISCUSSION

Preliminary data on the lake condition status were taken from the National Plan on Implementation of Stockholm Convention on Persistent Organic Pollutants by the Kyrgyz Republic approved by the Government Decree No. 371-r of July 3, 2006 [2]. Analysis of water samples, coastal soil and bottom sediments of the lake showed a focal character of pesticides' presence with the pollution focus located in the southern part of the coast. The levels of coastal water pollution with DDT and its decomposition products were observed along the south-west coast (0.55–5.92  $\mu$ g/l), southeast coast (0–1.16  $\mu$ g/l), and near the coast at the lake source (0–0.44  $\mu$ g/l). The presence of DDT and its metabolites in the coastal soil and bottom soil had also a focal character. The maximum levels of pollution were found mainly in the bottom soil at a distance of 1 m from the coast (0.92–35.91 mg/kg).

In 2017, an approbation procedure of mechanisms for public participation in decision-making was carried out through the creation of a network of public monitoring and training representatives of environmental NGOs in sampling techniques using the example of Son-Kul Lake. Sampling at Son-Kul Lake by representatives was performed in August 2017 and then in July 2018.

# Results for surface water analysis

The results of the analysis of water samples evaluating levels of three hazardous pesticides:  $\alpha$ -hexachlorocyclohexane,  $\beta$ -hexachlorocyclohexane, and 2,2',5-trichlorobiphenyl are shown in Fig. 2. The obtained concentration values were compared with the known standards for the tested compounds.



*Figure 2.* Analysis results for pesticide content in water samples obtained in the course of the lake monitoring in 2017.

It is noteworthy that in this study we considered and analyzed two types of maximum permissible concentrations (MPCs):

- $MPC_w$  maximum permissible concentration of a substance in the water of a reservoir intended for drinking and household water use (mg/l). This concentration is supposed to cause no direct or indirect effect on human organs throughout human life time, as well as on the health of subsequent generations, in addition, the value should not deteriorate the hygienic conditions of water use [6];
- $MPC_{wf}$  maximum permissible concentration of a substance in the water of the reservoir used for fishing purposes (mg/l). There are two types of established  $MPC_{wf}$  levels the highest (first) category and the second category [7].

The threshold concentration of 2,2',5-trichlorobiphenyl, which changes the organoleptic properties of water, is 0.13 mg/l for water of water bodies of household drinking and cultural water use (MPC<sub>w</sub>), while MPC<sub>w</sub> for  $\alpha/\beta$ -hexachlorocyclohexane in natural water is 0.004 mg/l (4.0 µg/l) [6].

As can be seen from the figure 2, an exceeding of the MPC was not detected for 2,2',5-trichlorobiphenyl, the observed maximum value for this compound is 0.059 µg/l. However, some water samples showed an exceeding of the MPC value for  $\alpha/\beta$ -hexachlorocyclohexane. It should be noted that the standards discussed above are related to the drinking and household water use. But the regulatory documents of the Kyrgyz Republic contain requirements for *zero content* of DDT

and hexachlorocyclohexane for reservoirs intended for fishery use [8], which can be referred to Son-Kul Lake.

Thus, we have a paradoxical situation – the water of Son-Kul Lake is within the MPC levels for drinking purposes but exceeds the MPC levels for fishery purposes, since small amounts of POPs have been revealed in the lake water (See Fig. 2).

## Results for analysis of bottom sediments

The results for analysis of samples of bottom sediments performed during the monitoring of 2017, are presented in Fig. 3.



*Figure 3.* Pesticide level in bottom sediments samples obtained in the course of the lake monitoring in 2017.

It is worth mentioning that the maximum permissible concentrations of chemical compounds for bottom sediments of water bodies in the Kyrgyz Republic are not regulated. Therefore, we have taken as a basis for comparing the obtained data with the standard ones – the values of maximum permissible concentrations and approximate permissible concentrations of chemicals in soil, which were approved by the Government Decree No. 201 of April 11, 2016. The data are presented in Table 2.

The results of laboratory testing showed that the levels of the majority of the pesticides (hexachlorobenzene, pentachlorobiphenyls, tetrachlorobiphenyls, trichlorobiphenyls,  $\beta$ -hexachlorocyclohexane, DDT and its metabolites (total

amounts),  $\gamma$ -hexachlorocyclohexane (lindane), hexachlorocyclohexane (hexachlorane) did not exceed MPC values for soils when recalculating results in mg/kg. The test results for the remaining compounds cannot be compared with MPCs, since there are no approved standards for these compounds.

*Table 2.* Approximate permissible concentrations (APC) and maximum permissible concentrations (MPC) of pesticides in soil samples

No.	Name	APC	MPC
		(mg/kg) [9]	(mg/kg) [10]
1	Hexachlorobenzene	0.08	0.03
2	Pentachlorobiphenyls	0.10	-
3	Tetrachlorobiphenyls	0.06	-
4	Trichlorobipenyls	0.03	-
5	β-Hexachlorocyclohexane	-	0.1
6	DDT and metabolites	0.1*	
	(total amount)		
7	γ-Hexachlorocyclohexane	0.1*	
	(lindane)		
8	Hexachlorocyclohexane	0.1*	
	(hexachlorane)		

\* Approved by the Government Decree of the Kyrgyz Republic of April 11, 2016, No. 201

Additionally, one sample of bottom sediments was tested. The observed concentrations of six POPs (4,4'-DDT, 4,4'-DDD, 4,4'-DDE,  $\alpha$ -hexachlorocyclohexane,  $\beta$ -hexachlorocyclohexane, and  $\gamma$ -hexachlorocyclohexane) were below the detection limit of the analytical procedure used by the laboratory – 0.005 mg/kg. Thus, basing on these results, it is impossible to make a conclusion on the presence or absence of POPs in the sediment samples in the range from 0.0  $\mu$ g/kg to 5  $\mu$ g/kg.

It should be underlined that almost all the studied samples contained detectable amounts of POPs, at least in small quantities. To this end, we recommend conducting studies of Son-Kul Lake using a more dense sampling grid procedure.

The detection of POPs in the lake bottom sediments in August 2017 required a more detailed study of Son-Kul Lake, which was conducted in July 2018. The data obtained revealed a need to look for safer ways of lifting abandoned fishing nets from the lake bottom so as not to touch the horizons polluted with POPs residues. An action, showing one of the ways of cleaning the lake's bottom from the nets [12], was conducted by a public foundation "Pure Issyk Kul", a voluntary movement. This method is considered to be more time-consuming if compared to the other one when the bottom of the reservoir is firstly purged to clean old fishing nets. The method involves manual lifting the nets from the bottom by divers, thus ensuring the least degree of roiling of potentially contaminated sludge and therefore reducing the risk of water pollution. Professional divers of the voluntary movement have an extensive experience in cleaning the bottom of the Issyk-Kul lake from abandoned fishing nets.

#### Results for fish analysis

To assess the results of testing the POPs content in fish samples, we used the MPCs levels taken from the Technical Regulation on Safety of Fish and Fish Products of the Eurasian Economic Union (EAEU TR 040/2016) [11]. Among the list of the analyzed compounds, only (congeners of) polychlorinated biphenyls are regulated with MPC values for fish and fish products. PCBs are a group of POPs whose monitoring in the air, water and soil is mandatory in developed industrial countries due to their high environmental and public health risks.

The Technical Regulation provides an MPC value for PCBs in all types of fish products of no more than 2 mg/kg. The analysis results showed that the observed concentrations for two types of PCBs (2,4'-dichlorobiphenyl and 2,4',5-trichlorobiphenyl) in all fish samples did not exceed the established MPC level, even for combined results, with the values varied in the range from 0.069 to 0.227 mg/kg.

When analyzing the results for the remaining chemicals, it can be concluded that the concentrations of other POPs, including DDT and its metabolites, are in the range from 9.18 to 9.6  $\mu$ g/kg, which is significantly lower than their levels in the control sample. At the same time, laboratory assistants performing the analysis noted that the fish samples had small size while in their opinion the concentration of POPs in the larger fish samples would be higher.

The results of the analyzes performed in the mentioned domestic laboratory for two fish samples also showed that the concentration of POPs (4,4'-DDT, 4,4'-DDD, 4,4'-DDE,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hexachlorocyclohexane) in fish samples were below the detection limit of the method used by the laboratory – 0.005 mg/kg (5 µg/kg), so, basing on these results, it was impossible to register the presence or absence of concentrations of POPs in samples ranging from 0.0 µg/kg to 5 µg/kg. The results of these analyses are also can't be compared with the standards, since the MPCs for these compounds in fish products have not been approved.

The obtained results make it possible to conclude that the fish samples collected from Son-Kul Lake do not contain any harmful concentrations of POPs. Concurrently, it should be remembered that the analysis of water samples showed an excess of MPCs for DDT and hexachlocyclohehane reservoirs for fishery use as shown above.

#### CONCLUSION

Analysis of monitoring data on the ecological status of Son-Kul Lake, conducted in 2017, showed that the concentrations of POPs found in sediment samples were within the MPC limit values established for soil, while the levels in fish samples complied with the requirements of the Technical Regulation on Safety of Fish and Fish Products of the Eurasian Economic Union (EAEU TR 040/2016).

However, the testing of lake water samples showed an exceeding of the MPCs for DDT and hexachlorocyclohexane for waters of fishery use.

In general, the data obtained revealed the need to look for the safest ways to raise fishing nets from the bottom of the lake, so as not to affect the horizons polluted by POPs residues.

It can therefore be concluded that the preliminary studies conducted in 2017–2018 require the development of a state monitoring program for Son-Kul Lake and performing continuous monitoring of POPs levels.

In addition, in order to ensure safety for the life and health of the population, it is necessary to resume the moratorium on fishing at Son-Kul Lake, since the Law of the Kyrgyz Republic of August 4, 2008, No. 191 "On prohibition of catching, transportation, acquisition, sale and export of especially valuable endemic species of fish inhabiting the lakes Issyk-Kul and Son-Kul" is terminated in accordance with the Law of the Kyrgyz Republic of May 24, 2017, No. 88.

After reexamining the lake condition and obtaining summarized data on the presence of POPs in sediments and fish, it is planned to prepare an analytical note for the Government of the Kyrgyz Republic with recommendations for further Government actions related to cleaning the lake and subsequent using the reservoir for fisheries.

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