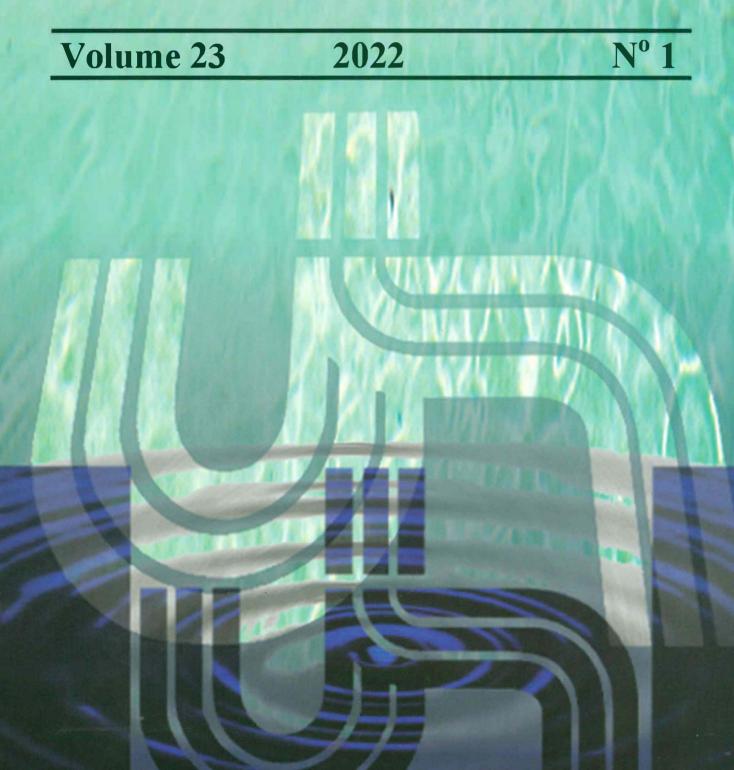
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Hydrochemical regime and water quality of the Danubian lake Katlabukh

Valeriya OVCHARUK^{*}, Natalia KICHUK, Dmytro LUTAI, Lilia KUSHCHENKO, Maria MYROSHNYCHENKO

One of the main sources of water supply in the Ukrainian part of the Danube delta is the Danube lakes, one of which is Katlabukh. The main revenue part in the water balance of the adjacent delta Lake Katlabukh is the inflow of Danube water through canals with offtakes. The water levels in the lake are determined with the rules of the use of the reservoir, as well as with the hydrological regime of the Danube. Water exchange is carried out by off takes Hromadsky and Zhelyavsky. The reduction of water exchange processes with the Danube in combination with anthropogenic impact on the catchment area of small rivers flowing into Lake Katlabukh, as well as the negative phenomena associated with climate change; create many environmental, water, and social problems for the lake. One of the main problems is the unsatisfactory state of water quality in terms of hydrochemical parameters, in particular high mineralization, which limits the use of the lake waters will allow to development of scientifically based recommendations for improving water quality and rational use

KEY WORDS: hydrochemical regime, pollution, lakes of the Danube delta

Introduction

The Danube lakes existed mainly due to the hydrology of the Danube. At the same time, their geographical location along the banks of the Danube had little effect on their historically established hydrochemical regime (Gopchenko et al, 2011; Romanova et al, 2019). With the intensification of agriculture in the 1970s, the additional use of the floodplains of the Danube began, and to protect them, embankment dams were built along the Danube, which radically changed the hydrological and historical water regime of the Danube lakes. It is for this reason that the geographical location of Lake Katlabukh relative to other upstream lakes has created the conditions under which it has become hostage to the level regime of the Danube. Therefore, in recent decades, the filling of Lake Katlabukh in terms of its damping without forced water supply has significantly affected the deterioration of both the level regime of the lake and its hydrochemical condition. It is the reduction of water exchange processes with the Danube in combination with an anthropogenic load on the catchment area of small rivers flowing into lake Katlabukh, as well as the negative phenomena associated with climate change, create many environmental, water, and social problems for the lake. The hydrochemical state of the lake water has deteriorated, and water salinity has increased 4–5 times, i.e. from 800 mg dm⁻³ to 4.7 g dm⁻³. Therefore, it is necessary to analyze carefully

the hydrological and hydrochemical regime of the lake and the rivers flowing into it, to develop both scientific recommendations and operational measures to improve the condition of Lake Katlabukh and optimal conditions for its operation following the Water Framework Directive 2000/60 / EU (Directive 2000/60/EC, 2000).

Material and methods

According to physical and geographical zoning, the studied area is located in the steppe zone of Ukraine. Heights vary from north and northwest from 300 m to 0.0 m and -2.0 m – in the Danube floodplain.

Lake Katlabukh is located 10 km northeast of the city of Izmail. It has an area of 68 km², the average width is 2 km, and the maximum width reaches 6 km (Fig. 1).

The shores are steep with the exposure of native rocks. In the south they are waterlogged and merge with the floodplains. The studied lake belongs to the western group of Danube reservoirs located on the left bank of the Danube, and is a continuation of the valleys of the rivers Big and Small Katlabukh, Enika, Tashbunar (Fig. 1), which are shallow and dry in summer.

This area is located in the temperate continental climate. The Black Sea, as well as large reservoirs and a large area up to the floodplains have a mitigating effect on the climate. Winter is short and mild with an unstable frosty period, summer is long and hot, autumn is warm. The low frequency of cyclones in this area is one of the main reasons for the relatively small amount of precipitation -380-410 mm per year. Evaporation exceeds 800 mm. Droughts of varying duration (up to 30-40 days a year) affect the area every 3-4 years, but in the last 15 years the droughts are more frequent. The greatest amount of precipitation (65-45% of the annual norm) falls in the warm period of the year in the form of showers. Precipitation is extremely uneven both in territory and in time. For the cold period of the year the prolonged precipitation of low intensity is typical. In terms of climate, the area is characterized by very high heat resources and significant humidity deficit, which affects significantly the natural conditions, biodiversity and socio-economic development of

the region.

The research aims to study the hydrochemical regime andassess the quality of surface waters by hydrochemical parameters in Lake Katlabukh for many years and per fisheries standards as the most sensitive to changes in the ecological status of reservoirs and rivers using modern calculation methods.

The main revenue part in the water balance of the estuary lake Katlabukh is the inflow of Danube water through canals with regulator sluice Gromadsky and Zhelyavsky (Table 1).

The channels work (the sluices are opened) only during the period of filling the lakes in spring and discharging water into the Danube or its tributaries in autumn.

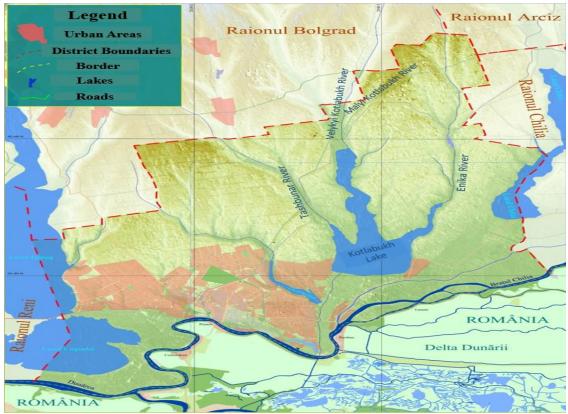


Fig. 1. The Lake Katlabukh location in territory of Ukraine.

Table 1.	Information on channels and sluices-regulators of the lake Katlabukh
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Sluice	Distance from the		ls length m]	Water- carrying		Mark [m BS]		Year of construc-	Regulated water body
	estuary to the tributary of Prorva [km]	Bringing water	Transporting water	capacity [m ³ s ⁻¹]	Of the sluice threshold	Carriageway	Water level $P = 1\%$	tion	
Hromadsky	78.0	0.150	4.650	55	-0.70	3.60	4.60	1964	Lake Katlabukh
Zhelyavsky	73.2	0.050	3.350	70	-0.70	3.60	4.45	1967	Lake Katlabukh

At other times, the sluices are closed. These channels are self-flowing, so the water exchange depends on the mark differences between the levels in the Danube and the lakes. The operating rules of adjacent lakes admit that the regulatory water exchange processes correspond to natural conditions, ie in spring the lake is filled to the normal headwater level (NHL), in summer they are triggered by water intake and evaporation, and in autumn water from the lake is discharged to the dead storage level (DSL). The water level marks are following: normal headwater level (NHL) = 1.70 m BES, dead storage level (DSL) = 0.70 m BS, active reservoir level (ARL) = 3.00 m BS.

Hydrological features of the estuary area of the Danube are such that the amplitude of fluctuations in water levels decreases from 5–6 m (Reni) to 1.5–2.0 m (Vilkove). The geographical position of Lake Katlabukh, in relation to other upstream lakes, created the conditions under which it became hostage to the level regime of the Danube. Therefore, in recent decades, the filling of Lake Katlabukh in the conditions of dams construction without forced water supply has significantly affected the deterioration of both the level regime of the lake and its hydrochemical state. The water quality in these lakes is largely determined by the water quality of the Danube and small rivers that flow directly into the lakes.

To analyze the hydrochemical regime of Katlabukh Lake for a long period of observations (2000–2018), data from the monitoring gauges of the Danube Regional Water Resources Monitoring Laboratory (which existed until June 2019) were accepted, and state water monitoring was carried out according to the approved monitoring program of the State Agency Water Resources of Ukraine. Currently, all materials of observations on the lake and its tributaries are transferred to the Basin Department of Water Resources of the Black Sea and Lower Danube, and regular hydrological and hydrochemical observations are conducted by the Izmail Department of Water Management. This paper uses information on 4 items of the monitoring network according to the above program, which is shown in Fig. 2, namely:

- Lake Katlabukh PS-2 is on the Suvorov irrigation system, Izmail district;
- small river Tashbunar. The total length of the river is 40.0 km. Located in the Izmail and Bolgrad districts, the river flows into the Katlabukh reservoir. The river flow is regulated; observation point is 1.4 km from the estuary, on the road bridge;
- small river Velykyi Katlabukh. The total length of the river is 49.0 km. Located in the Izmail, Bolgrad, Artsyz districts, the river flows into the Katlabukh reservoir. The river flow is regulated; the observation point is on the road bridge on the route Izmail – Odessa;
- the small river Yenika. The total length of the river is 40.0 km. Located in the Izmail and Artsyz districts, the river flows into the reservoir Katlabukh. The river flow is regulated; the observation point is 0.1 km from the estuary, within village Pershotravneve, Izmail district.

Existing modern methods of water quality assessment are considered as the analysis of compliance of actual values of water parameters with the maximum permissible limits. But the number of regulated parameters is quite large, so there is a need to generalize information about the ecological status of surface waters based on the use of complex indicators that average and smooth the source information (Osadchyy et al, 2013; Kichuk et al 2016; Snizhko 2001).

To assess the water quality of the studied objects, the hydrochemical water pollution index (WPI) was used, which is calculated according to six indicators. Using this index, you can compare the quality of water in different water bodies, even in the presence of different pollutants. Calculations are made according to the formula:

$$WPI = \frac{1}{6} \sum_{i=1}^{6} \frac{C_i}{MPC_i},$$
(1)

where

- *MPCi* the maximum permissible concentration of the chemical component;
- *Ci* the actual concentration of the chemical component;
- 6 -the number of ingredients.

To compare the quality of water in different areas, to determine their dynamics, the classes of water quality are used as criteria (Snizhko 2001; Yurasov et al., 2012), in particular the criterion for assessing the quality of water by WPI (Table 2).

Estimation of water quality according to WPI was performed using 6 chemical indicators for the lake Katlabukh, V. Katlabukh, Yenika, and Tashbunar: oxygen, phenols, oil products, ammonium nitrogen, nitrate-nitrogen, and BOC_5 .

To generalize the status of surface waters and to identify possible trends in changes in their quality, in addition to determining the WPI, the assessment of the level of surface water pollution In the first citation, according to the current methodology in Ukraine (KND 211.1.1.106– 2003) with the water pollution coefficient (WPC).

Water pollution coefficient (WPC) is a generalized indicator that characterizes the level of pollution and shows the multiplicity of exceeding water quality standards in the parts of MPL. The value of the water pollution coefficient is calculated for ten indicators only. These indicators include indicators exceeding the maximum permissible limits.

The obtained numerical values of the water pollution coefficient allow us to assess the state of water by pollution levels. Indicators of water pollution with the water pollution coefficient are given in Table 3.

The following indicators were used for calculations: BOC₅, ammonium nitrogen, nitrate nitrogen, nitrite nitrogen, copper, zinc; total iron, chlorides, petroleum products, phenols.

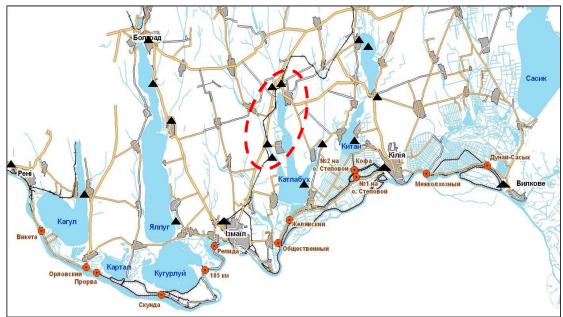


Fig. 2. Water quality monitoring points in the area of activity of the Danube BDWR.

Table 2.	Criteria for	assessing the	anality of	water using	the WPI
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Water quality class	Text description	Value of WPI
Ι	Very clean	≤ 0.3
II	Pure	> 0.3 - 1.0
III	Moderately polluted	> 1.0 - 2.5
IV	Polluted	> 2.5 - 4.0
V	Dirty	> 4.0 - 6.0
VI	Very dirty	> 6.0 - 10.0
VII	Extremely dirty	> 10.0

 Table 3.
 Indicators of water pollution with the water pollution coefficient

The value of pollution	1	1.01-2.50	2.51-5.00	5.01-10.0	More than 10
Pollution level	Unpolluted (clean)	Slightly polluted	Moderately polluted	Dirty	Very dirty

Results and discussion

The hydrochemical regime and water quality of lake Katlabukh are influenced by several factors: the volume of runoff of small rivers and its mineralization; the volume of water intake for irrigation and water supply; the amount of precipitation and evaporation from the water surface of lakes; the volume of filling from the Danube and discharge of water into the river (Romanova et al, 2019). Determination of water carried mineralization out according was to the laboratory of the Danube BDWR in such facilities as Lake Katlabukh, Velykyi Katlabukh, Yenika, and Tashbunar.

The dynamics of the average annual mineralization of water bodies for the period 2000–2018 are shown in Fig. 3. The highest mineralization is observed in

the Velykyi Katlabukh and Yenika Rivers, which are associated with both natural conditions and anthropogenic pollution.

Lake Katlabukh and the rivers flowing into it are characterized by high water salinity. A significant contribution to such indicators is made, first of all, by sulfate ions, as well as chloride ions, sodium, and potassium ions. To identify the anthropogenic impact on the hydrochemical regime of the studied objects, studies of pollution with nutrients, organic substances, and heavy metals were conducted. To quantify the content of organic matter in the water of Lake Katlabukh and its rivers, the indicators of chemical oxygen consumption (COC) and 5-day biochemical oxygen consumption (BOC₅) were used. In surface waters, the values of BOC₅ vary from 0.5 to 4.0 mg dm⁻³ relative to O₂ and there are seasonal and daily fluctuations (Fig. 4). The highest rates

of organic pollution are characteristics of the Yenika River and Lake Katlabukh, which is associated with water pollution in the Danube.

The significant pollution by heavy metals (manganese, iron), as well as phenols and, to a lesser extent, petroleum products, is also observed in all studied water bodies. Such a significant degree of pollution, in our opinion, is due primarily to the anthropogenic impact on the catchment area of small rivers. The hydrochemical index of water pollution (HIWP) was also used to assess the water quality of the studied objects (Snizhko, 2001). Estimation of water quality according to WPI was performed on 6 chemical indicators for the lake Katlabukh, V. Katlabukh River, Yenika River, Tashbunar River: oxygen, phenols, oil products, ammonium nitrogen, nitrate-nitrogen, and BOC5 based on the data of the Danube BDWR laboratory for 2000-2018. Analysis of the dynamics of the average annual values of HIWP at the observation points for the study period showed that the level of pollutants remains the same, fluctuating up or down depending on the anthropogenic impact. The dynamics of the average annual values of WPI for the studied period are presented in Fig. 5.

The recurrence of pollution classes at the studied water bodies was also calculated. The results of the calculation are given in the table. 4. According to the table, it can be noted that the cleanest water is in Lake Katlabukh, where the values of WPI vary from 0.56 (class II) to 1.87 (class III), but the years with water of the third class for the studied period is only five. The largest value of WPI according to the calculations was observed:

- in V. Katlabukh, in 2012 (WPI 1.83), the high index was affected by nitrogen nitrite and phenols (3.98 mg dm⁻³, 3.9 μg dm⁻³, respectively);
- in Tashbunar, in 2009 (WPI 1.91), the high index was affected by such an indicator as phenols

 $(2.7 \text{ mg dm}^{-3});$

- in Yenika in 2015 (WPI 2.26), the high index was affected by such an indicator as phenols (7.00 mg dm⁻³);
- in the lake Katlabukh PS-2 of the Suvorov irrigation system in 2012 (WPI – 1.7), the high index was affected by phenols (7.60 mg dm⁻³).

The next stage of the study was to assess the quality of water in the studied water bodies and the suitability of these waters for use in fisheries by the water pollution coefficient (WPC).

The results of calculations are shown in Fig. 6.

As can be seen from the graph in Fig. 6, the highest indicators are inherent in the waters of the Yenika River and equal in 2002 -2.88, 2014 - 2.45, 2015 -2.54. These waters are classified as moderately polluted. Also, high values of water pollution coefficient -2.62 in 2009 are characteristics of the waters of the V. Katlabukh River, which allows them to be classified as moderately polluted. This indicates that small river basins are exposed to increasing anthropogenic impact, which is characterized by a fairly high degree of plowing of watersheds, intensification of agricultural production, non-compliance with growing environmental requirements for agricultural production, the presence of powerful sources of pollution in the form of industrial effluents (Kichuk et al 2016; Snizhko 2001).

According to the level of pollution during the studied period of the lake Katlabukh and Tashbunar can be classified as "slightly polluted". The main problem of these water bodies is excessive water pollution with heavy metals, pesticides, phenols, and petroleum products (manganese, iron, sulfates, petroleum products, phenols). The main cause of surface water pollution by these elements is the insufficient level of wastewater treatment coming from municipal, industrial, and

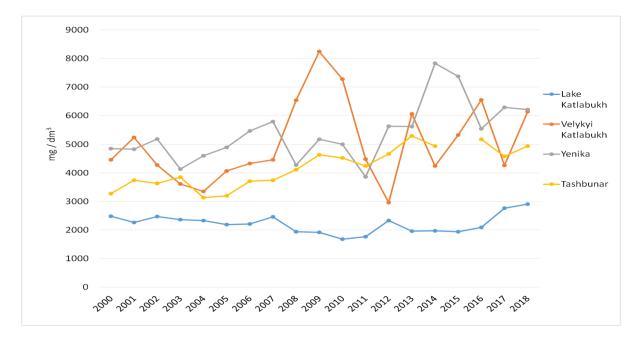


Fig. 3. Average annual values of mineralization of water bodies within the catchment of Lake Katlabukh for the period $2000-2018 \text{ [mg } \text{dm}^{-3}\text{]}$.

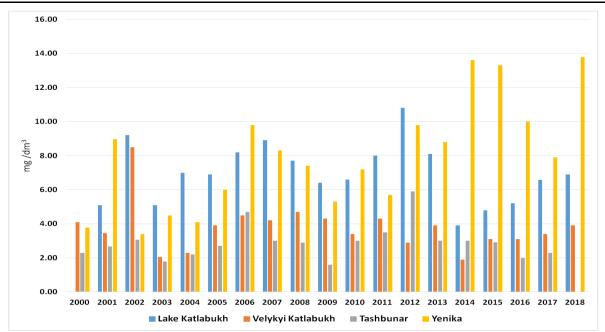


Fig. 4. Average annual values of concentration of BOC_5 of water bodies within the catchment of Lake Katlabukh for the period 2000–2018 [mg dm⁻³].

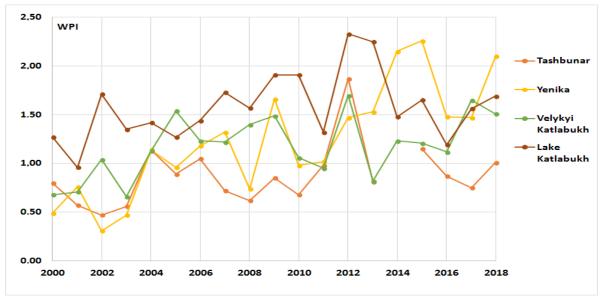


Fig. 5. Dynamics of average annual values of WPI for the studied period.

Name of water bodies	Classification by water pollution index (WPI)				
Name of water bodies	Pollution class	Number of cases [%]			
Tashbunar River	II	5			
Tasiloullar Kivel	III	95			
Valului Katlahuluh Diwan	Ш	79			
Velykyi Katlabukh River	II	21			
Yenika River	II	37			
i ellika kivel	III	63			
Lake Katlabukh	II	72			
	III	28			

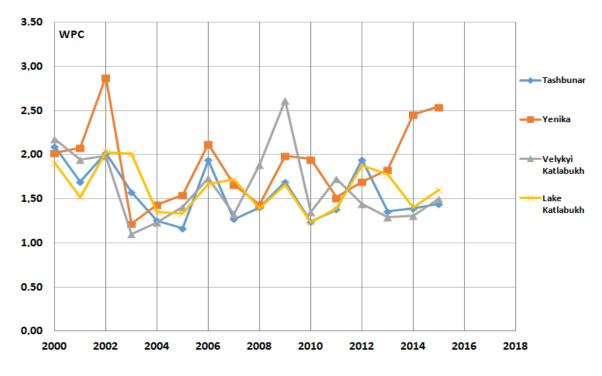


Fig. 6. Dynamics of average annual water pollution coefficient values for the studied period.

agricultural point sources, and with surface runoff. Further study of the water quality of Lake Katlabukh and the rivers flowing into it according to complex indicators of ecological status is envisaged to state with due probability about the possibility of its use for fisheries and to determine the possible use of the water body for other water users.

Conclusion

The main reason for the unsatisfactory condition of the studied objects is the significant anthropogenic impact on the catchment area of small rivers flowing into Lake Katlabukh, deteriorating the quality of its water resources. One of the main factors in the deterioration of water quality is the lack of water exchange in the lake itself due to many negative factors, including geographical location, the impact of climate change, and imperfect management of operational processes.

To improve the condition of surface waters in Lake Katlabukh it is proposed:

- to conduct a detailed analysis of the impact of human activities and natural factors on the water quality of Lake Katlabukh and the rivers flowing into it;
- both for the lake itself and for the territory of its basin to develop a program of specific measures against water pollution by all possible sources of pollution;
- ensure compliance with environmental legislation by all water users, regulate (restrict) or completely prohibit such activities that affect water quality, in particular, fishery water use.

At the moment, a detailed study of natural and anthropogenic factors affecting the water quality of

the lake is being continued in order to create a program of specific measures to improve the current legislation to reduce water pollution not only of the rivers that flow into Lake Katlabukh, but also of the lake itself. In addition, monitoring of compliance with already existing environmental measures of the current legislation is being carried out.

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Valeriya Ovcharuk, Doctor of Geographical Sciences, Associate Professor (*corresponding author, e-mail: valeriya.ovcharuk@gmail.com) Natalia Kichuk, Ph.D. in Geography, Associate Professor Dmytro Lutai, Master of Hydrology Lilia Kushchenko, Ph.D.-student of the Department of Land Hydrology Maria Myroshnychenko, Senior Lecturer of the Department of Ukrainian Studies and Social Sciences Odessa State Environmental University 15 Lvovskaya Str. Odessa, 65016 Ukraine