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The Impact of the Russian Armed Aggression on the Condition of the Water Area of the Dnipro-Buh Estuary System

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ABSTRACT

The Russian armed aggression is claiming lives of thousands of people, exerting disastrous pressure on the environment of Ukraine, destroying natural landscapes, flora and fauna species, polluting water bodies, damaging a fertile soil layer, poisoning the environment with oil products and heavy metals. Combat zones, frontline areas and occupied territories are suffering most. The purpose of the research was to establish spatio-temporal patterns of the formation of surface water quality in 2018–2023 and determine the impact of the Russian armed aggression on the functioning of the water area of the Dnipro-Buh estuary system. The research was carried out using hydrological, biological and physical-chemical indicators. The negative consequences of the hostilities causing the destruction of the Kakhovka hydroelectric power station dam in 2023 and the drainage of the water reservoir, discharge of pollutants with a concentration of 1.1–51.8 MPC and pollution in the water area of 6800 km^2 of the estuary system and the Black Sea were identified. The dam destruction has a number of negative environmental and socioeconomic consequences. Seasonal indicators of the hydrological regime of the Dnipro-Buh estuary system testified to deterioration of the system condition by 1.42–1.82 time. In particular, there was stagnation of water masses, an increase in the saturation of water sources with biogenic elements by 2.1 times, a rise in the density of algae distribution, an increase in chlorophyll concentration by 2.9 times. Deterioration of the condition of surface waters to the Polytrophic state and deterioration of physical-chemical properties of water by 4.0 times was also identified. The research findings prove that the damage to the environment can be regarded as ecocide that is an important informational base for developing the measures and implementing technologies of post-war restoration of the ecological condition of water bodies and ensuring their zonal sustainability.

Keywords: Dnipro-Buh estuary, Kakhovka Dam, Black Sea, water quality, impact of war, Ukraine.

INTRODUCTION

Water quality is a basis for safety and sustainability of water resources and contains indicators of the health of aquatic ecosystems. Freshwater sources are the main factor of the existence of human communities, aquatic animals and food security of the country. Rapid population growth, urban expansion in river catchment areas and extensive economic activity have become the main causes of degradation and transformation of water bodies. The Dnipro is one of the largest transboundary rivers of Europe, its basin area being 511 thousand км^2 (57.3% of the area is in Ukraine). The river basin covers over 48% of Ukraine's territory, accumulates about 80% of its water resources which satisfy food and drinking needs of more than 70% of Ukraine's population. In the territory of the Dnipro basin, there are large industrial complexes (over 60% of the domestic industrial production), farmlands (agrogenic transformation in the Ukrainian territory of the basin is over 70%), and the largest urban agglomerations of the country (Pichura et al., 2017).

Deterioration of the ecological situation in the Dnipro basin is related to deforestation, "chemicalization" of agriculture, the construction and functioning of the Dnipro reservoir cascade, discharge of large volumes of polluted water, etc. (Pichura et al., 2018; Breus et al., 2018; Boiko et al., 2018). At present, the ecological situation is complicated due to the Russian armed aggression. The hostilities cause catastrophic losses of the environment, including destruction of natural landscapes, flora and fauna species, pollution of water bodies, and damage to a fertile soil layer.

The environmental consequences of the hostilities reduce the level of ecological security of Ukraine, mainly, in the frontline regions, the areas of hostilities and occupied territories. The situation in the Dnipro-Buh estuary system became more complicated after 06/06/2023, when the Kakhovka HPS dam was destroyed (Vyshnevskyi et al., 2023; Romanova et al., 2024; Hartmane et al., 2024; Hapich et al., 2024). The dam explosion caused the transfer of substantial volumes of pollutants through the Dnipro-Buh estuary to the Black Sea, the drainage and transformation of the reservoir water area. The dam explosion has led to a man-made disaster which has environmental, economic and social consequences. According to the UNO data, Ukraine's losses caused by the dam destruction amount to more than USD 14.0 billion. Regarding the impact of the consequences of the dam explosion on the environment, it is noteworthy that the volumes of environmental losses manifesting themselves in deterioration of hydrological, biological and physical-chemical conditions, intensification of eutrophication process and signs of environmental problems in the Dnipro-Buh estuary system and the Black Sea allow regarding the above mentioned actions as ecocide.

Currently, the Ukrainian and international communities are actively discussing the issue of feasibility of reconstructing the hydroelectric station dam and filling the Kakhovka Reservoir. It should be noted that the environmental conditions were unsatisfactory in terms of the indicators of surface water quality in the period of the functioning of the reservoir water area; however, the reservoir was of great socioeconomic importance for water-deficient regions of the Steppe zone of Ukraine (Pichura et al., 2018, 2020a). In particular, the reservoir water discharges to the Lower Dnipro were important for maintaining the necessary ecological flow and water content of the estuary system functioning. In turn, the Dnipro-Buh estuary system is an important water area of sustainable natural existence of aquatic flora and fauna, a source of providing fisheries with water resources, of satisfying drinking, cultural, household and recreational needs of the population (Kutishchev et al., 2021, 2022). In this context, the estuary system has become a sensitive indicator of the impact of the Russian armed aggression which manifests itself through degradation and transformation of the environment. Hence, when making a decision on the feasibility of the post-war reconstruction of the Kakhovka Reservoir, it is necessary to take into account changes in the functioning of the water area and surface water quality of the Dnipro-Buh estuary system. Therefore, the purpose of the research was to establish the spatio-temporal patterns of the formation of surface water quality in 2018–2023 and determine the impact of the Russian armed aggression on the functioning of the Dnipro-Buh estuary system and pollution of the Black Sea.

MATERIAL AND METHODS

Research scheme and materials

The scheme of the research on spatio-temporal patterns of the formation of surface water quality and migration of pollutants in the Dnipro-Buh estuary system and the Black Sea includes four logical-successive blocks (Figure 1).

Actual data of the authors' field observations and the data of the State Environmental Inspectorate of the Southern Region (SEISR) of Ukraine were used for analyzing the state of surface water quality in 2018–2023. The places of collecting water samples are presented in Figure 2.

The source of actual satellite imagery for decoding and calculating the necessary indices are the data of the spacecrafts Sentinel 2 L2A, Sentinel-3 OLCI L1B from the Copernicus Browser website.

Characteristics of the research territory

The Dnipro-Buh estuary system is a hyperecosystem consisting of the Dnipro-Buh estuarine region which stretches from the dam of the Kakhovka hydroelectric power station (HPS) and the estuary of the Southern Buh river to the Kinburn spit connecting the Dnipro-Buh estuary with the Black Sea and including the united coastal areas of the two rivers (the Dnipro and the Southern Buh). The coastal area of the Dnipro consists of the near-estuary and estuary (delta) areas. The near-estuary area is located between the Kakhovka HPS dam and the city of Kherson. The Dnipro estuary area

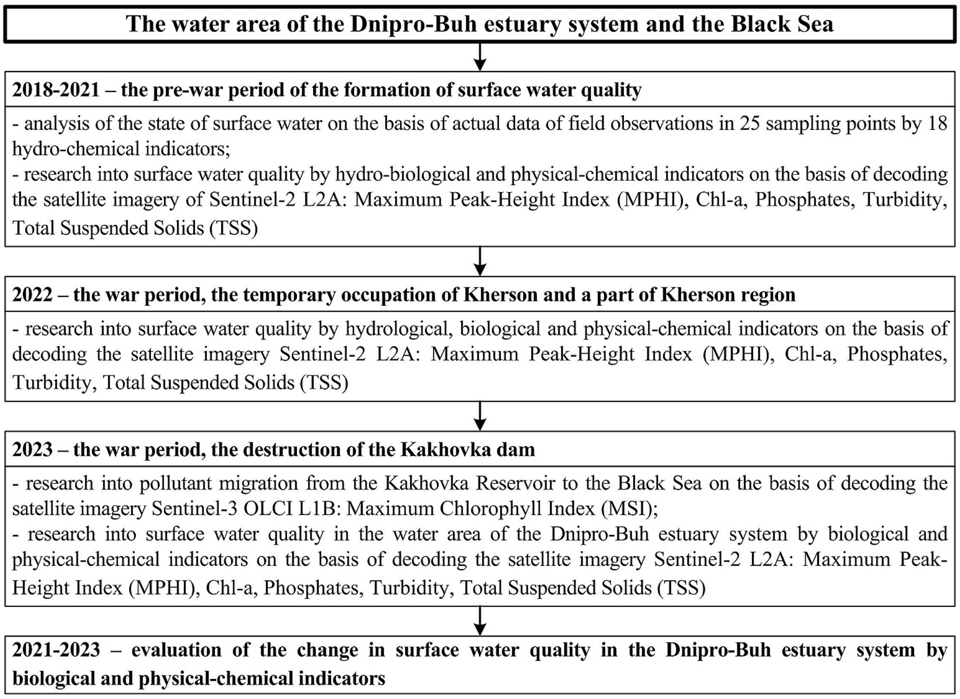

Figure 1. Structural-logical methodological scheme of the research

is a developed delta divided into large and small arms, numerous channels and floodplain lakes. The reserached water area (Figure 2) amounted to 810 km^2, with a total length of 150.8 km.

The Lower Dnipro includes water mosaic-heterogenous areas of the stream and delta-lake systems from the destroyed Kakhovka hydroelectric power station dam to the river estuary, with a length of about 94.4 km. The total area of the Lower Dnipro catchment amounts to 492 km^2. The hydrological, biological and physical-chemical condition of the Lower Dnipro until 06/06/2023 depended on the working regime of the Kakhovka HPS and water flow through its dam. At present, the state of the Lower Dnipro depends on the working regime of the Dnipro HPS at a distance of 230 km upstream from the destroyed Kakhovka HPS dam. The mosaic heterogeneity of the lower part of the river is characterized by three sections of the water area determined by different factors of the formation of surface water quality.

The first section, from the Kakhovka hydroelectric power station dam to the Antonivka railway bridge, with a length of 48.7 km, is characterized by the inflow of surface water within the reservoir, relatively good conditions of the formation of the hydrological regime and surface water quality which are similar to the zonal background characteristics of the Lower Dnipro.

The second section, from the Antonivka railway bridge to the beginning of the Dnipro delta system, with a length of 19.6 km, is characterized by an increased negative impact of highly mineralized surface water of the right tributary of the Inhulets river and the inflow of untreated surface runoff from Kherson. Pollution of the surface water of the Inhulets river occurs as a result of discharges of mine waters and industrial wastewater of Kryvyi Rih and Inhulets mine process plants, that determines the income of dry residues from 21500 to 3900 mg/dm^3, including chlorides (Cl^-) in the amount of 425–1365 mg/dm^3, sulfates (SO_4^{2}) – 670–842 mg/dm^3 (State Agency of Water Resources of Ukraine, 2021). In particular, the surface runoffs from Kherson have an increased negative impact on the Dnipro river. The surface water of this section corresponds to the “dirty” – “very dirty” classes according to the norms of water suitability for fishery purposes. The main pollutant causing deterioration of the Dnipro water quality is a considerable excess of oil products entering the suburban river area with untreated municipal wastewater.

The third section, from the beginning of the river delta system to the Dnipro mouth, with a length of 26.1 km, is characterized by the inflow of sewage from Kherson and the formation of stagnant lake waters with a low or medium flow capacity in the Dnipro delta. The municipal

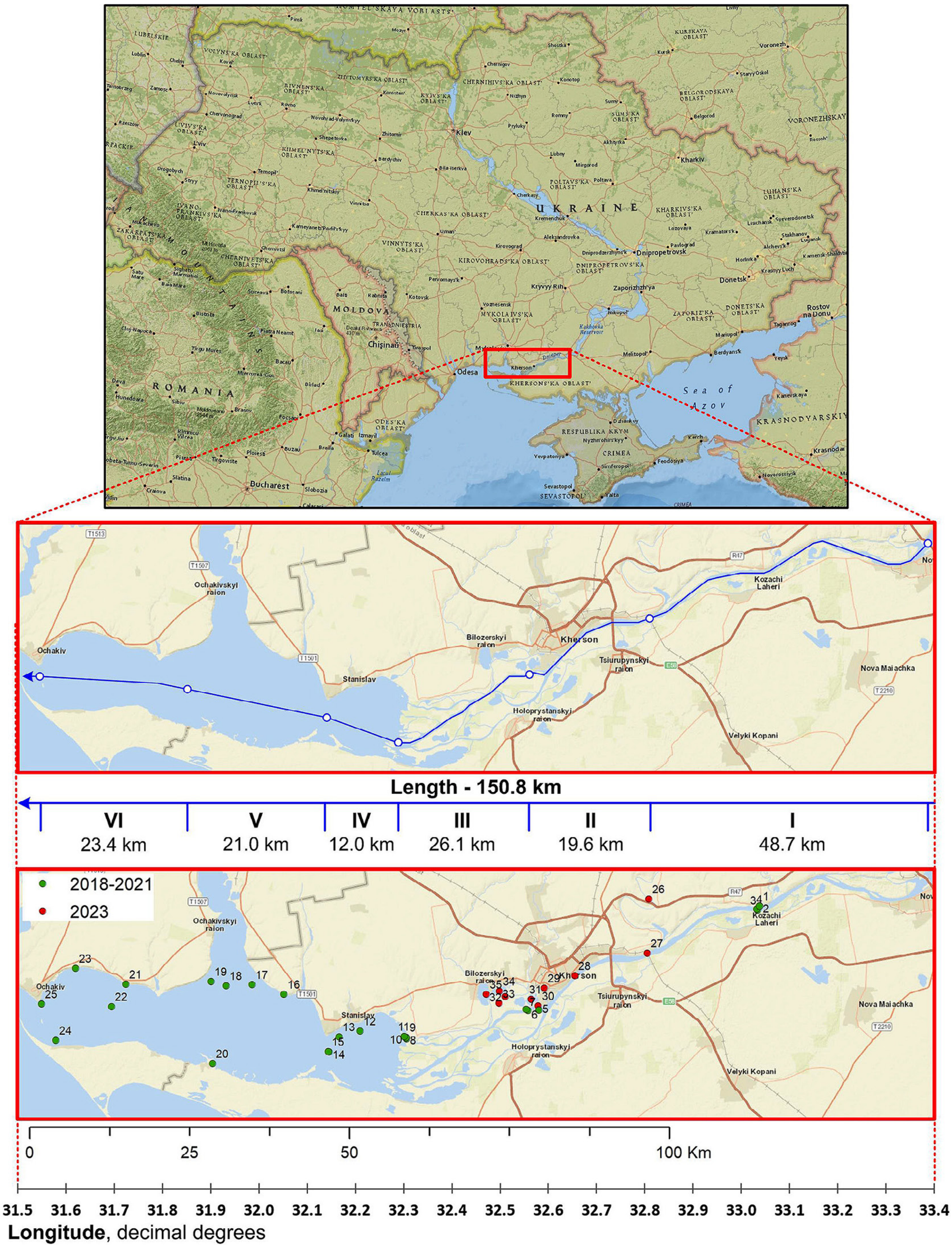

Figure 2. The water area of the Dnipro-Buh estuary system; the water area of the Lower Dnipro – the length of the river course is 94.4 km: I – from the Kakhovka hydroelectric power station dam to the Antonivka railway bridge, within the mouth of the Inhulets river; II – from the Antonivka railway bridge to the beginning of the Dnipro delta system, within the city of Kherson; III – from the beginning of the river delta system to the Dnipro mouth. The Dnipro-Buh estuary – with a length of 56.4 km: IV – eastern section; V – central section; VI – western section

treatment plants with a total area of 85.2 ha have a treatment capacity of 45–50 thousand m^3 of wastewater per day. The total length of the sewage network is 297 km. The municipal treatment plants were built in 1975, they have a two-stage scheme of wastewater treatment: mechanical treatment – screens, sand traps and primary settling tanks, retaining heavy pollution and treating sewage by 35–40%; biological treatment – wastewater treatment by bio-organisms, supported by oxygen supply (aero-tanks), which allows treating wastewater up to 90% and more (Pichura et al., 2020b).

Over the period of 2016–2021, the average value of certain indicators of hydro-chemical characteristics of sewage discharge which immediately entered the Virovchyna river and were redistributed to the Koshova river and the Dnipro, was characterized by an excess of maximum permissible concentrations (MPC) in accordance with the criteria of fishery purposes, in particular: the content of suspended solids – by 4.2 times, phosphates – by 3.6 times; dry residue – by 1.3 times; sulfates – by 1.7 times; chlorides – by 1.2 times; sodium+potassium – by 2.6 times; ammonium nitrogen – by 3.8 times; oil products – by 2.0 times. This level of pollution had a negative impact on the functioning of the hydro-ecosystem of the Lower Dnipro. First of all, untimely treatment of biological ponds caused discharges of substantial volumes of polluted sediments resulting in the inflow of 400 tons of surface active agents, nitrogen oxides, sulfur, phosphorous, oil products, etc. to the Dnipro river (Pichura et al., 2020b).

The Dnipro delta is the second largest delta in Ukraine after the Danube delta. Its area is about 350 km², including channels, floodplain lakes, backwaters, wetlands, river arms, tributaries and a number of small alluvial islands in the estuary itself. Veykyi Potomkin island stands out for its size. Other large islands are as follows: Bakaiskyi, Bilohrudyi, Borshchovy, Velykyi, Velykyi Sokolyn, Hapskyi, Zabych, Karantynnyi, Kruhlyk, and Toloka. The main delta arms: Rvach (a shipping canal), Konka, Koshova, Staryi Dnipro, Perebiina, Chaika, Kanava, Nova Konka, Seredynka, Lytvynka, Svyniachka, and Korabela. The Dnipro delta is a part of the Lower Dnipro the water of which flows to the Dnipro-Buh estuary.

The Dnipro-Buh estuary is an open oligohaline estuary in the northern part of the Black Sea, located within Kherson and Mykolaiv regions of Ukraine. The estuary is shallow, its average depth being 3.5–4 m, its maximum depth being 12 m. It is connected to the Black Sea by a 3.6 km wide strait (between the Ochakiv Cape and the Kinburn Spit). The southern shoreline has low sandy banks; the northern shoreline largely has high (up to 20–35 m) steep banks, composed of clay-sandy rocks, with sand and shell spits in some areas. The bottom near the spits is sandy, covered with loamy and sandy silt at a depth. The surface flow in the estuary consists of 94.3% of the Dnipro flow and of 5.7% of the Southern Buh. The research territory of the estuary is divided into three parts: IV – eastern section, V – central section, and VI – western section. The eastern section of the estuary is immediately under the influence of the Dnipro flow. The flow rate in this area is mainly seasonal, since it immediately depends on the Dnipro output throughout the year. The central section of the estuary is under the influence of river and sea waters. The area is located in the zone of transformation of river waters into brackish waters. The water masses are stratified vertically that slows down the process of their mixing and leads to the formation of anaerobic zones in hot seasons. The western section is mainly under the influence of river waters. The average salinity of the estuary water is 3.6‰. In particular, it varies between 1.0 and 3.3‰ in the eastern section, between 1.0 and 6.0‰ in the central section, and between 1.0 and 11.0‰ in the western section.

RESEARCH METHODS

The research into the trophic state of the surface water in the water area of the Dnipro-Buh estuary system was carried out calculating the intensity of saturation of floating algae with a chlorophyll pigment (Chl-a, μg/dm³) by maximum peak-height index (MPHI) (Peppa et al., 2020):

$$MPHI = B5 - B4 - \left.\frac{(B8\text{-}B4)\times(705\text{-}665)}{842\text{-}665}\right\} \rightarrow \text{Chl-a} = 2223.18MPHI + 24.03 \quad (1)$$

where: B4, B5, and B8 are the reflectance and λB4 = 665 nm, λB5 = 705 nm, and λB8 = 842 nm are the central wavelengths of the corresponding bands of Sentinel-2 L2A. The MPHI value ranges from -1.0 to 1.0. The value higher than MPHI = 0.004 indicates presence of Chl-a in the algae of the surface water.

The content of phosphates (mgP/dm³) was calculated on the basis of the established dependence (author's research):

$$P = 0.0102\text{Chl-a}^{0.6995},\ r^2 = 0.984 \quad (2)$$

The turbidity of the surface water (Turb, NTU) was determined by the following formula (Zhan et al, 2022):

$$\text{Turb} = 194.79\left(B5\times\left(\frac{B5}{B2}\right)\right) + 0.9061 \quad (3)$$

where: B4, B5, and B8 are the reflectance bands of Sentinel-2 L2A.

Total suspended solids (TSS, mg/dm³) was calculated on the basis of the established dependence (Nurjaya et al., 2019):

$$TSS = 3.4216\text{Turb},\ r^2 = 0.987 \quad (4)$$

The surface water quality was determined using the classification presented in Table 1 (Romanenko et al., 1998). Class I includes waters which are the least affected by anthropogenic loads. The values of their hydro-chemical and hydro-biological indicators are close to the natural values of a certain region. The waters of Class II are characterized by changes in comparison with the natural values, but these changes do not disrupt the ecological balance. Class III includes the waters which are subject to considerable anthropogenic impact the level of which is close to the limit of ecosystem sustainability. The waters of Classes IV–V have impaired ecological parameters, and their ecological condition is regarded as ecological regression (Urasov et al., 2009).

Maximum permissible concentrations of substances in the water area of the Dnipro-Buh estuary system were determined by the most stringent standards of surface water quality and water bodies for drinking needs, cultural, household, recreational and fishing purposes in Ukraine and the European Union (Table 2) (Klymenko et al., 2012).

Table 1. Classes and categories of surface water quality by ecological classification

Water quality classes	I	II		III		IV	V
Water quality categories	1	2	3	4	5	6	7
Chl-a, µg/dm^3	<2	2– 4	5–10	11–30	31–50	51–150	>150
Phosphate, mgP/dm^3	<0.015	0.015–0.030	0.031–0.050	0.051–0.100	0.101–0.200	0.201– 0.300	>0.300
Total suspended solids, mg/dm^3	<5	5–10	11–20	21– 30	31–50	51–100	>100
Water quality according to cleanliness (pollution)	Very clean	Clean		Polluted		Dirty	Very dirty
	Very clean	Clean	Clean enough	Slightly polluted	Moderately polluted	Dirty	Very dirty
Trophic class	Oligotrophic	Mesotrophic		Eutrophic		Polytrophic	Hypertrophic
Turbidity, NTU							

Permissible turbidity	Low turbid	Fairly turbid	Rather turbid	Turbid	Very turbid
< 5	5– 15	15– 25	25–35	35– 50	> 50

Table 2. Standards of surface water quality for different purposes

Indicator		Standards of water quality		
		for fishing	for drinking	for cultural, household and recreational purposes
Total suspended solids, mg/dm^3	TSS	≤25	≤25	≤30
Turbidity, NTU	Turb	≤3.5	≤3.5	≤5
Hydrogen indicator	pH	6.5–8.5	6.5–8.5	6.5–8.5
Dissolved oxygen, mgO$_2$/dm^3	DO	>6	4	>4
Biochemical oxygen demand for 5 days, mgO$_2$dm^3	BOD	≤2	≤3	≤3
Permanganate oxidation, mgO$_2$/dm^3	PO	≤5	≤5	≤5
Chemical oxygen demand, mgO$_2$/dm^3	COD	≤20	≤15	≤15
Dry residue, mg/dm^3	DR	≤1000	≤1000	≤1000
Iron, mg/dm^3	Fe	≤0.1	≤0.1	≤0.1
Chlorides, mg/dm^3	Cl^-	≤300	≤200	≤200
Sulfates, mg/dm^3	SO_4^{2}	≤100	≤150	≤150
Nitrite nitrogen, mg/dm^3	NO_2^-	≤0.02	≤0.1	≤0.1
Nitrate nitrogen, mg/dm^3	NO_3^-	≤9.1	≤25	≤25
Phosphates, mgP/dm^3	PO_4^{3-}	≤0.2	≤0.2	≤1.14
Petroleum products, mg/dm^3	PP	≤0.05	≤0.05	≤0.05
Copper, mg/dm^3	Cu	≤0.001	≤0.02	≤0.02
Lead, mg/dm^3	Pb	≤0.10	≤0.01	≤0.01
Zinc, mg/dm^3	Zn	≤0.01	≤0.5	≤0.5

The transfer of pollutant concentrations in the Black Sea after the destruction of the Kakhovka HPS dam was calculated using maximum chlorophyll index (*MCI*) (Gower et al., 2005):

$$MCI = B11 - \left[B10 + (B12 - B10) \times \frac{709-681}{754-681}\right] \quad (5)$$

where: B10, B11, and B12 are the reflectance and λB10 = 681 nm, λB11 = 709 nm, and λB12 = 754 nm are the central wavelengths of the corresponding bands of Sentinel-3 OLCI L1B.

Correlation and regression analysis was used to establish the relationships between concentrations of substances in the water area of the Dnipro-Buh estuary system.

MS Excel 2016 was used for creating graphs and performing cross-sectional analysis. Image processing, mapping and spatio-temporal analysis were performed using ArcGis 10.6.

RESULTS AND DISCUSSION

Formation of water quality in 2018–2021

Hydro-biological and physical-chemical conditions, the changes of which occur as a result of the impact of many factors, are important indicators of surface water quality. They include the water level and stream velocity, natural-climatic conditions, the intensity of human activity, the impact of hostilities, etc. Application of biological and physical-chemical methods involves determining abiotic factors: activeness of algae development and intensity of chlorophyll accumulation, temperature, water transparency and turbidity, concentration of suspended solids, ionic composition, mineralization, concentration of biogenic elements, organic matter, dissolved oxygen, different toxins, hydrogen indicator (pH), etc.

In the pre-war period (2018–2021), surface water quality in the Dnipro-Buh estuary system was determined by the impact of human activity and climatic conditions. Pollutants systematically migrated to the lower part of the river and the estuary through waters of the middle and lower courses of the Dnipro. This caused accumulation and excess of the MPC values of pollutants. One of the main factors of the Dnipro water quality deterioration was construction in the water protection sanitary zones. It is noteworthy that these zones of the Dnipro basin were also widely used in agriculture. Diffuse pollution of natural sources with surface-erosion runoffs and sewage in warm and hot seasons caused massive algal bloom, intensive eutrophication, a reduction in oxygen content in the water, significant deterioration of physical-chemical and trophic states of the water area, as well as an increase in the number of mass fish deaths.

In the spring flood season, the Dnipro water is characterized by an excess of the content of organic compounds, manganese, indicators of color and turbidity, chemical and biological oxygen demand by water quality standards, which causes additional inflow of substances in the upper and middle courses through the Dnipro tributaries flowing across wetlands (the Prypiat, Teteriv and Irpin rivers) and are fed by waters rich in organic matter (the Desna river), manganese and other compounds. Additional negative pressure on the hydrological network of the Dnipro is exerted either by the war hotspots or local sources of pollution, discharges from treatment plants of large cities occupying the leading place. Over the past decade, the content of biogenic substances in the wastewater entering treatment plants has increased tenfold.

In addition to the changes in the physical-chemical regime of the Dnipro river, microbiological and viral pollution of surface water occurs resulting in the annual closure of beaches in summer seasons. Another cause of water quality deterioration is bank abrasion, occurring as a result of anthropogenic impacts and under the influence of natural factors. Most of the Dnipro banks are destroyed due to illegal construction in the water protection sanitary zone. Deterioration of the Dnipro hydrological regime as a result of the construction of six water reservoirs which do not allow the river to function properly according to its natural conditions is still a serious problem.

Anthropogenic disturbance of the natural state of the water catchment and transformation of the Dnipro riverbed system determined division of the hydrological series into three periods: Period I (1818–1935) – formation of the natural conditions of the flow before the construction of the Dnipro water reservoirs; Period II (1936–1977) – the period of construction of the reservoir cascade, anthropogenic transformation of the flow and the formation of new hydrological conditions; Period III (1978–2022) – the functioning of the reservoir cascade, anthropogenically and climatically determined formation of the flow and stabilization of new hydrological conditions. Period IV of the division of the hydrological series began after the destruction of the Kakhovka Reservoir dam (06/06/2023).

In Period I of the formation of the water regime in the lower course of the Dnipro river, the average annual value of the flow amounted to 1704 m^3/s, in Period II – 1530 m^3/s, in Period III– 1344 m^3/s. The reduced flow in Period III was caused by a decrease in the amount of precipitation by 40%, an increase in the average annual temperature in this period by 2.5°C and acceleration of evapotranspiration by 20%. In order to maintain an appropriate level of water exchange and environmentally stable flow in the Lower Dnipro, it was necessary to ensure releases from the Kakhovka Reservoir in the summer-autumn period at the level of 1350 m^3/s in the pulse mode twice a day. However, over the past years, the seasonal value of the flow has reached 340–640 m^3/s (only 25.2–47.4% of the necessary environmental flow) that has had a negative impact on the water balance, become a cause of a critical reduction in the energy of the hydrological functioning of the Lower Dnipro. Exacerbation of these problems occurred under the conditions of increased anthropogenic pressure on the ecosystem of the Dnipro basin affecting the state of the water area of the Dnipro-Buh estuary.

The regularities of the spatial formation of the surface water quality of the Dnipro-Buh estuary system for July–October 2018–2021 were established. It was found that the water quality is characterized by significant differentiation according to different needs in the area from the Kakhovka Reservoir to the estuary channel (Figure 3). It was determined by accelerated anthropogenic load, that caused changes in the natural state, led to imbalance, increased destruction of self-regulation, self-purification and self-regeneration processes in the estuary system. According to the results of the surface water quality by 18 indicators in 25 sites of sample collection, there were systematic deviations of the MPC (the norms for fisheries and drinking needs) of substances in the riverbed and delta systems of the Lower Dnipro. In particular, in the

25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	MPC	Indicator
for fishing																										
1.74	1.45	2.63	1.97	1.95	2.80	2.19	2.06	1.91	1.98	1.42	1.48	1.70	1.43	0.89	0.87	0.87	0.73	0.62	0.41	0.46	0.46	0.50	0.35	0.35	≤25	TSS
3.63	3.03	5.50	4.11	4.06	5.85	4.57	4.30	3.98	4.14	2.96	3.09	3.55	2.99	1.86	1.81	1.81	1.52	1.29	0.85	0.97	0.97	1.00	0.73	0.73	≤3.5	Turb
1.07	0.98	1.01	1.04	1.06	1.00	0.96	0.93	1.02	1.01	0.85	0.96	0.94	0.94	0.98	0.97	1.01	0.93	0.95	0.86	0.90	1.03	0.88	1.00	1.02	6.5-8.5	pH
0.78	0.61	0.47	0.92	0.56	0.64	0.30	0.12	0.50	0.16	0.50	0.64	0.58	0.08	0.43	0.87	0.82	0.53	0.34	0.48	0.19	0.47	0.28	0.81	0.80	> 6	DO
37.14	16.22	41.73	12.14	16.65	24.43	49.76	44.23	31.08	24.01	26.01	5.00	7.02	1.07	9.09	3.02	7.38	6.21	2.18	1.29	8.85	2.57	2.46	2.54	8.65	≤2	BOD
0.34	0.90	1.09	0.41	0.63	0.31	0.56	0.65	0.18	0.99	0.71	0.71	0.53	0.64	0.67	0.38	0.36	0.34	0.32	0.40	0.83	0.34	0.36	0.33	0.79	≤5	PO
15.15	7.07	16.67	4.21	7.41	10.10	20.21	17.69	12.63	9.60	10.61	2.02	2.78	0.51	3.64	2.27	3.03	2.53	1.00	0.51	3.54	1.00	1.00	1.00	1.00	≤20	COD
3.60	5.57	6.20	4.21	5.05	2.75	8.73	7.91	3.04	1.92	7.45	2.98	1.22	5.60	6.84	1.12	0.30	0.24	0.36	0.29	0.29	0.19	0.20	0.19	0.16	≤1000	DR
1.50	3.20	4.50	2.61	2.90	1.00	3.23	4.20	1.25	1.00	1.33	3.40	1.03	2.50	2.95	1.31	1.40	3.70	1.20	1.20	1.10	0.14	1.30	0.79	1.50	≤0.1	Fe
6.31	6.69	8.67	4.93	6.02	3.39	14.24	14.65	3.34	2.39	11.63	3.81	1.36	3.47	9.37	1.18	0.43	0.35	0.09	0.10	0.10	0.09	0.10	0.10	0.11	≤300	Cl^-
7.28	10.05	9.16	6.13	7.19	5.30	17.82	19.87	2.14	3.90	17.67	4.15	1.90	6.90	12.18	1.50	0.57	0.45	0.51	0.50	0.54	0.15	0.14	0.17	0.28	≤100	SO_4^{2}
0.150	0.150	0.150	0.750	1.000	0.150	2.825	0.150	0.150	0.150	1.925	0.150	0.150	0.150	1.550	0.150	0.150	0.750	0.150	0.150	0.150	0.150	0.150	0.150	0.000	≤0.02	NO_2^-
0.05	0.05	0.05	0.05	0.08	0.05	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.00	≤9.1	NO_3^-
0.83	0.75	1.01	0.90	0.86	1.08	1.00	0.97	0.90	0.91	0.75	0.77	0.81	0.72	0.56	0.56	0.55	0.51	0.47	0.39	0.42	0.41	0.42	0.34	0.34	≤0.2	P
0.48	0.08	0.12	0.64	1.40	1.00	0.66	0.50	0.34	0.40	0.90	0.70	0.66	0.40	0.40	0.50	0.03	0.04	0.30	0.02	0.76	0.30	0.40	0.35	0.00	≤0.05	PP
3.80	6.35	6.50	5.77	19.67	6.85	5.43	6.20	7.85	5.00	5.33	7.10	6.40	4.50	4.80	5.15	4.50	4.20	4.10	2.40	4.50	3.80	2.80	4.70	3.50	≤0.001	Cu
0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	≤0.10	Pb
2.00	2.95	3.45	3.43	3.20	2.55	3.37	1.30	2.60	3.50	4.40	2.65	1.60	3.50	2.10	2.10	1.90	1.30	1.60	1.20	3.50	1.50	3.00	2.00	7.00	≤0.01	Zn
for drinking																										
1.74	1.45	2.63	1.97	1.95	2.80	2.19	2.06	1.91	1.98	1.42	1.48	1.70	1.43	0.89	0.87	0.87	0.73	0.62	0.41	0.46	0.46	0.50	0.35	0.35	≤25	TSS
3.63	3.03	5.50	4.11	4.06	5.85	4.57	4.30	3.98	4.14	2.96	3.09	3.55	2.99	1.86	1.81	1.81	1.52	1.29	0.85	0.97	0.97	1.00	0.73	0.73	≤3.5	Turb
1.07	0.98	1.01	1.04	1.06	0.96	0.93	0.93	1.02	1.01	0.85	0.96	0.94	0.94	0.98	0.97	1.01	0.93	0.95	0.86	0.90	1.03	0.88	1.00	1.02	6.5-8.5	pH
1.17	0.92	0.70	1.39	0.84	0.96	0.45	0.18	0.75	0.24	0.75	0.96	0.88	0.12	0.64	1.31	1.23	0.79	0.51	0.72	0.28	0.70	0.42	1.22	1.20	4	DO
24.76	10.82	27.82	8.10	11.10	16.28	33.17	29.49	20.72	16.01	17.34	3.34	4.68	0.71	6.06	2.02	4.92	4.14	1.45	0.86	5.90	1.71	1.64	1.69	5.77	≤3	BOD
0.34	0.90	1.09	0.41	0.63	0.31	0.56	0.65	0.18	0.99	0.71	0.71	0.53	0.64	0.67	0.38	0.36	0.34	0.32	0.40	0.83	0.34	0.36	0.33	0.79	≤5	PO
20.20	9.43	22.22	5.61	9.88	13.47	26.95	23.59	16.83	12.81	14.15	2.69	3.70	0.67	4.85	3.03	4.04	3.37	1.33	0.67	4.72	1.33	1.33	1.33	1.33	≤15	COD
3.60	5.57	6.20	4.21	5.05	2.75	8.73	7.91	3.04	1.92	7.45	2.98	1.22	5.60	6.84	1.12	0.30	0.24	0.36	0.29	0.29	0.19	0.20	0.19	0.16	≤1000	DR
1.50	3.20	4.50	2.61	2.90	1.00	3.23	4.20	1.25	1.00	1.33	3.40	1.03	2.50	2.95	1.31	1.40	3.70	1.20	1.20	1.10	0.14	1.30	0.79	1.50	≤0.1	Fe
9.47	10.03	13.01	7.39	9.03	5.09	21.36	21.98	5.01	3.58	17.45	5.71	2.04	5.21	14.06	1.78	0.65	0.53	0.14	0.16	0.15	0.13	0.16	0.15	0.16	≤200	Cl^-
4.85	6.70	6.11	4.09	4.79	3.53	11.88	13.24	1.42	2.60	11.78	2.76	1.27	4.60	8.12	1.00	0.38	0.30	0.34	0.33	0.36	0.10	0.09	0.12	0.19	≤150	SO_4^{2}
0.03	0.03	0.03	0.15	0.20	0.03	0.57	0.03	0.03	0.03	0.39	0.03	0.03	0.03	0.31	0.03	0.03	0.15	0.03	0.03	0.03	0.03	0.03	0.03	0.00	≤0.1	NO_2^-
0.018	0.018	0.018	0.018	0.031	0.018	0.021	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.000	≤25	NO_3^-
0.83	0.75	1.01	0.90	0.86	1.08	1.00	0.97	0.90	0.91	0.75	0.77	0.81	0.72	0.56	0.56	0.55	0.51	0.47	0.39	0.42	0.41	0.42	0.34	0.34	≤0.2	P
0.48	0.08	0.12	0.64	1.40	1.00	0.66	0.50	0.34	0.40	0.90	0.70	0.66	0.40	0.40	0.50	0.03	0.04	0.30	0.02	0.76	0.30	0.40	0.35	0.00	≤0.05	PP
0.19	0.32	0.33	0.29	0.98	0.34	0.27	0.31	0.39	0.25	0.27	0.36	0.32	0.23	0.24	0.26	0.23	0.21	0.21	0.12	0.23	0.19	0.14	0.24	0.18	≤0.02	Cu
0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	0.48	≤0.01	Pb
0.04	0.06	0.07	0.07	0.06	0.05	0.07	0.03	0.05	0.07	0.09	0.05	0.03	0.07	0.04	0.04	0.04	0.03	0.03	0.02	0.07	0.03	0.06	0.04	0.14	≤0.5	Zn
for cultural, domestic and recreational purposes																										
1.45	1.21	2.20	1.64	1.62	2.33	1.83	1.72	1.59	1.65	1.18	1.23	1.42	1.19	0.74	0.72	0.72	0.61	0.52	0.34	0.39	0.39	0.42	0.29	0.29	≤30	TSS
2.54	2.12	3.85	2.88	2.84	4.09	3.20	3.01	2.79	2.90	2.07	2.16	2.48	2.09	1.30	1.27	1.27	1.07	0.91	0.59	0.68	0.68	0.70	0.51	0.51	≤5	Turb
1.07	0.98	1.01	1.04	1.06	0.96	0.93	0.93	1.02	1.01	0.85	0.96	0.94	0.94	0.98	0.97	1.01	0.93	0.95	0.86	0.90	1.03	0.88	1.00	1.02	6.5-8.5	pH
1.17	0.92	0.70	1.39	0.84	0.96	0.45	0.18	0.75	0.24	0.75	0.96	0.88	0.12	0.64	1.31	1.23	0.79	0.51	0.72	0.28	0.70	0.42	1.22	1.20	> 4	DO
12.38	5.41	13.91	4.05	5.55	8.14	16.59	14.74	10.36	8.00	8.67	1.67	2.34	0.36	3.03	1.01	2.46	2.07	0.73	0.43	2.95	0.86	0.82	0.85	2.88	≤3	BOD
0.34	0.90	1.09	0.41	0.63	0.31	0.56	0.65	0.18	0.99	0.71	0.71	0.53	0.64	0.67	0.38	0.36	0.34	0.32	0.40	0.83	0.34	0.36	0.33	0.79	≤5	PO
10.10	4.71	11.11	2.80	4.94	6.74	13.48	11.80	8.42	6.40	7.07	1.35	1.85	0.34	2.42	1.52	2.02	1.68	0.67	0.34	2.36	0.67	0.67	0.67	0.67	≤15	COD
3.60	5.57	6.20	4.21	5.05	2.75	8.73	7.91	3.04	1.92	7.45	2.98	1.22	5.60	6.84	1.12	0.30	0.24	0.36	0.29	0.29	0.19	0.20	0.19	0.16	≤1000	DR
0.75	1.60	2.25	1.30	1.45	0.50	1.62	2.10	0.63	0.50	0.67	1.70	0.51	1.25	1.48	0.66	0.70	1.85	0.60	0.60	0.55	0.07	0.65	0.39	0.75	≤0.1	Fe
5.41	5.73	7.43	4.23	5.16	2.91	12.20	12.56	2.86	2.05	9.97	3.26	1.17	2.98	8.03	1.02	0.37	0.30	0.08	0.09	0.09	0.08	0.09	0.09	0.09	≤200	Cl^-
1.46	2.01	1.83	1.23	1.44	1.06	3.56	3.97	0.43	0.78	3.53	0.83	0.38	1.38	2.44	0.30	0.11	0.09	0.10	0.10	0.11	0.03	0.03	0.03	0.06	≤150	SO_4^{2}
0.003	0.003	0.003	0.015	0.020	0.003	0.057	0.003	0.003	0.003	0.039	0.003	0.003	0.003	0.031	0.003	0.003	0.015	0.003	0.003	0.003	0.003	0.003	0.003	0.000	≤0.1	NO_2^-
0.09	0.09	0.09	0.09	0.15	0.09	0.10	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.00	≤25	NO_3^-
0.15	0.13	0.18	0.16	0.15	0.19	0.18	0.17	0.16	0.16	0.13	0.13	0.14	0.13	0.10	0.10	0.10	0.09	0.08	0.07	0.07	0.07	0.07	0.06	0.06	≤1.14	P
0.080	0.013	0.021	0.107	0.233	0.167	0.110	0.083	0.057	0.067	0.150	0.117	0.110	0.067	0.067	0.083	0.006	0.007	0.050	0.004	0.127	0.050	0.067	0.058	0.000	≤0.05	PP
0.004	0.006	0.007	0.006	0.020	0.007	0.005	0.006	0.008	0.005	0.005	0.007	0.006	0.005	0.005	0.005	0.005	0.004	0.004	0.002	0.005	0.004	0.003	0.005	0.004	≤0.02	Cu
0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	≤0.01	Pb
0.020	0.030	0.035	0.034	0.032	0.026	0.034	0.013	0.026	0.035	0.044	0.027	0.016	0.035	0.021	0.021	0.019	0.013	0.016	0.012	0.035	0.015	0.030	0.020	0.070	≤0.5	Zn

Western part
Central part
Eastern part
River delta
River bed
Dnipro-Buzka Estuary
Dnieper River
Flow Direction

Figure 3. Regularities of the formation of water quality in relation to maximum permissible concentrations in the water area of the Dnipro-Buh estuary system, July–October, 2018–2021

riverbed water area (Samples No. 1–7), there was a deficiency in dissolved oxygen (DO) – from 20 to 80% of the norm, an excess of biological oxygen demand (BOD) by 1.29–8.85 times. It was caused by rapid reproduction of aerobic bacteria requiring oxygen for their functioning, the creation of hypertoxic conditions, the formation of stressful conditions, the existence of patches with dead aquatic animals. There was also an excess of chemical oxygen demand (COD) by 1.33–4.72 times that testifies to the entry of untreated wastewater with organic and mineral substances, including humic substances, hydrogen sulfide, sulfites and iron to the water area. The concentration of iron (Fe) exceeds the MPC by 1.1–1.5 times. The was a considerable excess of copper (Cu) by 2.4–4.7 times in comparison with the norms for fishery needs. According to the impact of heavy metals on fish, chlorides, nitrates and copper sulfates are the most toxic substances. A high level of copper in the water environment and food aquatic animals disrupts fish homeostasis and causes toxicosis. Pathological changes of fish liver occur as a result of poisoning with copper salts. A chronic impact of copper sulfate results in a reduction in the amount of mucus on fish skin and the damages of fins, the skin cover becomes pale and rough. Eating such fish is highly dangerous for humans. There were some cases of a slight deviation of the hydrogen indicator (pH) to the alkaline environment of 1.02–1.03 of the MPC.

The waters of the Dnipro delta system (Samples No. 8–11) were characterized by medium and low levels of the retention time and water stagnation in floodplain lakes that considerably worsened its properties. Turbidity is the indicator of water microbiological pollution. The value of turbidity of the surface waters was 1.29–1.86 MPC,that testifies to the presence of fine organic and inorganic impurities in water sources, the formation of silt by phyto- and zooplankton, which adds a yellow-green color and unpleasant smell to water. According to the results of the decoded satellite imagery of Sentinel 2 L2A (Figure 4), in the river delta system there was a high density of algae, their intensive

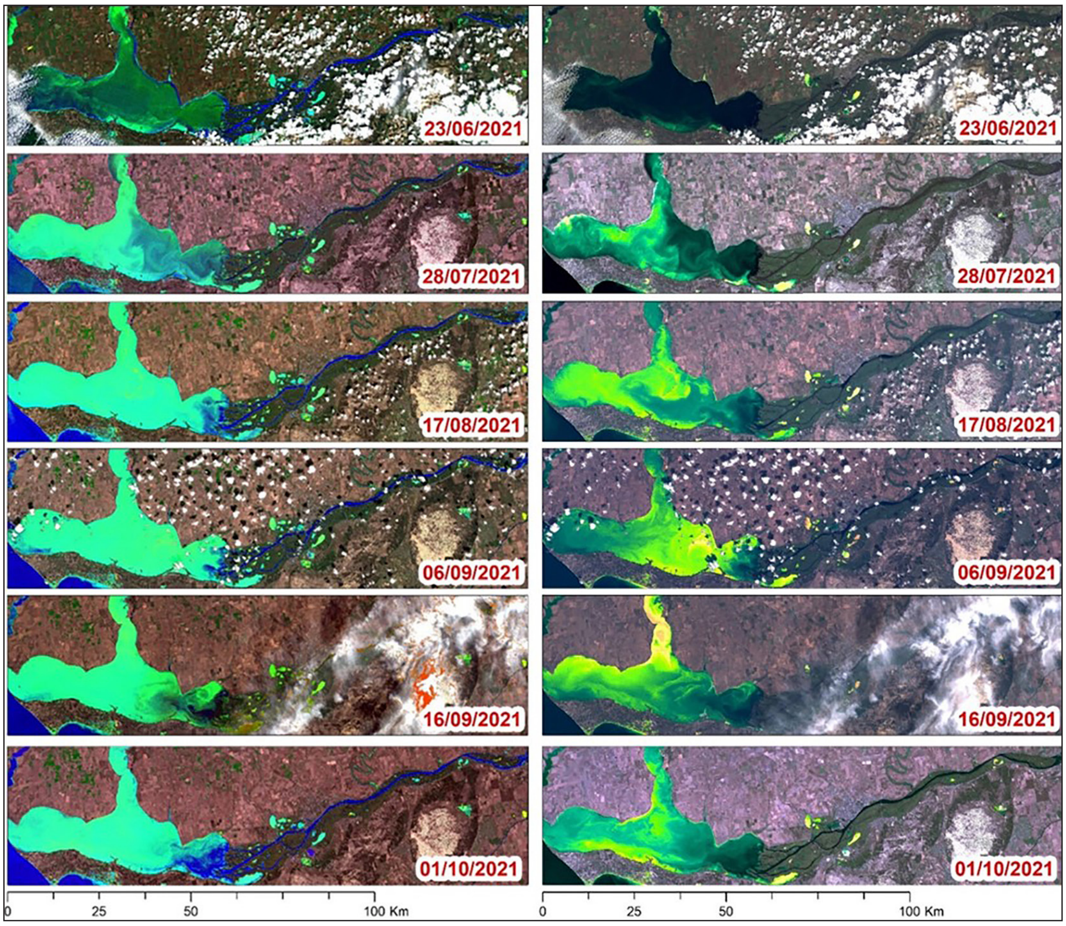

Figure 4. State of the water quality by hydro-biological and physical-chemical indicators in the Dnipro-Buh estuary system, 2021: a – algae density and water turbidity, b – intensity of algal bloom and concentration of suspended solids

bloom, a significant level of turbidity and accumulation of suspended solids in the floodplain lakes.

In July–October 2021, the average value of the surface water turbidity in the floodplain lakes varied from 13.5 to 26.9 NTU – 3.75–7.39 MPC, the maximum value being 52.5–74.1 NTU – 14.58–20.58 MPC. The concentration of Total Suspended Solids (TSS) varied between 46.2 and 92.0 mg/dm^3 – 1.85–3.68 MAC, the maximum values ranged from 180.0 to 253.5 mg/dm^3 – 7.20–10.14 MPC. In turn, there was a significant level of phosphate accumulation (PO_4^{3-}), ranging from 0.12 to 0.19 mgP/dm^3 – 0.60–0.95 MPC, with a critical increase in their concentration to the level of 0.38–0.45 mgP/dm^3 – 1.90–2.25 MPC. A high level of phosphate content is a cause of high algae density and their intensive growth in the floodplain lakes. The lakes overgrown with cyanobacteria have a dense layer of organic matter that prevents sunlight from entering the water depth, which is a reason for a sharp increase in the consumption of dissolved oxygen in the process of destruction and release of toxic substances, causing oxygen deficiency in the water, fish deaths and degradation of the habitat of aquatic animals. Algae die-offs result in accumulation of dead organic matter in the bottom sediments, siltation of water bodies, additional accumulation of organic matter and sulfur, and the formation of the anaerobic layer.

Chlorophyll concentration (Chl-a) is an important biological parameter in terms of monitoring water quality and managing water resources, since it is an indicator of the presence of algae, activeness of their photosynthesis and the formation of biomass in the water environment. Since algal growth is often limited by availability of nutrients, high concentrations of chlorophyll are often a result of surface water pollution with municipal wastewater and agricultural runoffs and riverbank abrasion. In July–October 2021, the average value of Chl-a content in algae was 40.9–67.8 μg/dm^3, with the patches of its maximum concentration at the level of 143.7–192.0 μg/dm^3. This characterized the critically high eutrophication of water bodies at the level of Polytrophic and Hyperotrophic states.

In the research period of 2018–2021, the dry residue (DR) was registered at the level of 1.12–6.84 MAC. The DR value reflects the total amount of mineral inorganic salts of calcium, magnesium, potassium, sodium, heavy metals and organic substances dissolved in water. This indicator is used for determining general mineralization of water. In particular, there was a significant deficiency in DO - 0.43–0.87 MPC, an excess of BOD_5 - 2.02–9.09 MPC, COD - 2.57–4.85 MPC, the concentration of Fe at the level of 1.31–3.70 MPC. In the river mouth (Samples No. 10, 11), the content of chlorides (Cl^-) in the water, in accordance with drinking and fisheries norms, exceeded the value by 1.78–9.37 times, the content of sulfates (SO_4^2) – by 1.50–12.18 times. An excess of Cl^- and SO_4^2 worsens the organoleptic properties of water, disrupts the water-salt metabolism of living beings, suppresses gastric secretions, impedes the process of food digestion and aggravates hypertension. High levels of toxic salts in water cause corrosion of metal pipes and equipment used for transporting and storing water. A considerable increase in the content of SO_4^2 in the water against the backdrop of the deficiency in dissolved oxygen causes steady accumulation of hydrogen sulfide as a result of the recovery of sulfuric salts. In Sample No 11, there was excessive content of nitrites (NO_2^-) by 1.55 MPC that was caused by nitrogen oxidation under the influence of nitrifying microorganisms or recovery of nitrate nitrogen under anaerobic conditions and the sufficient amount of organic matter, which testifies to intensification of the processes of organic matter decomposition under the conditions of slow oxidation of NO_2^- and NO_3^- and causes water pollution. There was an excess of Cu in relation to the norms for fishery purposes by 4.20–5.15 times.

According to the hydro-biological state and the level of physical-chemical indicators, the surface water in the Dnipro-Buh estuary in July–October was characterized by Euplytrophic and Polytrophic states. Throughout the water area of the estuary, there were mosaic heterogeneous processes of systematic accumulation and a considerable excess of pollutants in the water. There was an increase in the volume of pollutants in the direction of water mass movement from the western to the eastern section of the estuary and the entry to the Black Sea. The highest accumulation of pollutants and the formation of substantial phytoplankton biomass with a high concentration of Chl-a was registered at the beginning of September 2021 (the satellite image dated 06/09/2021). The concentration of Chl-a in the western section of the estuary ranged between 2.5 and 140.4 μg/dm^3, the average value was 65.9 μg/dm^3. In the central section of the estuary, the content of Chl-a in the algal biomass was 82.1 μg/dm^3, varying between 51.6 and 110.9 μg/dm^3. The average value of Chl-a in the western section amounted to 58.7 μg/dm^3, ranging from 36.6 to 79.8 μg/dm^3. The minimum value of Chl-a was registered at the beginning of November – this period was characterized by a fall in the temperature of water mass, the end of active algal vegetation, algal die-off and a reduction in the density of cyanobacteria on the water surface of the estuary. In this period (as of 10/11/2021), the concentration of Chl-a in the Dnipro-Buh estuary ranged from 12.8 to 36.4 μg/dm^3.

Algal density and the concentration of Chl-a depend on availability of PO_4^{3-} in water. The value of PO_4^{3-} synchronously changed in accordance with the concentration of Chl-a, in particular, its content was 0.18 mgP/dm^3 (0.90 MPC) in the eastern section of the estuary on 06/09/2021, ranging from 0.03 to 0.35 mgP/dm^3 - 0.15–1.75 MPC. The accumulation of PO_4^{3-} amounted to 0.22 mg/dm^3 (1.1 MAC), ranging between 0.16 and 0.28 mgP/dm^3 - 0.80–1.4 MPC in the central section. The concentration of PO_4^{3-} was 0.17 mgP/dm^3 (0.85 MPC), in the range of 0.14–0.22 mgP/dm^3 – 0.70-1.1 mgP/dm^3 in the western section of the water area. On 10/11/2021, the concentration of PO_4^{3-} in the estuary water varied between 0.09 and 0.15 mgP/dm^3 – 0.45–0.75 MPC.

Maximum turbidity (Turb) and concentration of suspended solids (TSS) were observed in July–September 2021. In a warm season, the Turb value varied between 1.2 and 40.0 NTU - 0.34-11.43 MPC. As a result, concentration of TSS varied between 4.1 and 136.9 mg/dm^3 – 0.16–5.48 MPC. In July–October of the research years 2018–2021, in all the sections of the Dnipro-Buh estuary there were deviations from MPC in most indicators, in particular: pH - 1.01–1.07 MPC, DO - 0.08–0.78 MPC, BOD_5 - 1.07–49.78 MPC, COD - 2.02–20.21 MPC, DR - 1.22–8.73 MPC, Fe - 1.03–4.20 MPC, Cl^- - 1.35-14.65 MPC, SO_4^{2} - 1.90-19.87 MPC, and a sporadic excess of NO_2^- - 1.55–2.83 MPC.

According to the results of correlation and regression analysis of the collected water samples from 25 stations, dependencies between the concentrations of substances in the surface waters of the Dnipro-Buh estuary system were established (Figure 5). Medium and strong correlations were established between the concentration of "TSS↔Turb↔Chl-a↔PO_4^{3-}↔BOD_5↔COD↔Cl^-↔SO_4^{2}↔DR"; "Cl^-↔SO_4^{2}↔Fe"; "NO_3^-↔PP↔Cu"; "PO↔Zn↔NO_3^-".

The established correlations allowed developing regression functions of the impact of Chl-a intensity on the concentration of BOD, DR, Cl^-, SO_4^{2} in water, which makes it possible to perform analysis of the concentration of substances in surface waters on the basis of decoding satellite imagery with a high level of reliability.

The water quality results obtained in 2018–2021 reflect the background level of the concentrations of substances by hydro-biological and

	TSS	Turb	pH	DO	BOD	PO	COD	DR	Fe	Cl^-	SO_4^{2}	NO_2^-	NO_3^-	PO_4^{3-}	Chl-a	PP	Cu	Pb	Zn
TSS	1																		
Turb	1.00	1																	
pH	0.27	0.27	1																
DO	-0.08	-0.08	0.45	1															
BOD	0.75	0.75	0.15	-0.20	1														
PO	0.25	0.25	-0.03	-0.33	0.27	1													
COD	0.76	0.76	0.14	-0.21	1.00	0.24	1												
DR	0.65	0.65	-0.02	-0.28	0.70	0.41	0.70	1											
Fe	0.43	0.43	0.02	-0.16	0.43	0.45	0.42	0.65	1										
Cl^-	0.61	0.61	-0.06	-0.25	0.79	0.36	0.79	0.96	0.63	1									
SO_4^{2}	0.56	0.56	-0.15	-0.30	0.72	0.38	0.73	0.95	0.58	0.98	1								
NO_2^-	0.21	0.21	-0.21	-0.12	0.38	0.07	0.39	0.62	0.29	0.64	0.64	1							
NO_3^-	0.34	0.34	0.03	-0.20	0.14	-0.12	0.22	0.30	0.18	0.25	0.23	0.29	1						
PO_4^{3-}	0.99	0.99	0.24	-0.12	0.77	0.23	0.78	0.68	0.44	0.65	0.61	0.25	0.37	1					
Chl-a	0.99	0.99	0.24	-0.12	0.78	0.23	0.79	0.67	0.43	0.65	0.60	0.24	0.35	1.00	1				
PP	0.45	0.44	0.01	-0.06	0.20	0.02	0.23	0.34	-0.02	0.31	0.32	0.36	0.57	0.45	0.45	1			
Cu	0.46	0.46	0.39	0.07	0.20	0.14	0.23	0.32	0.29	0.25	0.21	0.17	0.62	0.44	0.44	0.67	1		
Pb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	
Zn	0.07	0.07	0.11	0.05	0.13	0.52	0.07	0.16	0.02	0.10	0.12	0.16	-0.51	0.04	0.05	0.09	0.07	-	1

Correlation
r ≥ 0.7 - strong
0.5 ≤ r ≤ 0.7 - average
0.3 ≤ r ≤ 0.5 -moderate
0.2 ≤ r ≤ 0.3 - weak
r < 0.2 - very weak

Indicator	Formula	Parameter range	Number of samples for validation	r^2
BOD	1.4621Chl-a – 23.473	Chl-a (18.54–max, μgO_2/dm^3)	20	0.84
COD	6.0685Chl-a – 101.44	Chl-a (18.54–max, μg O_2/dm^3)	20	0.88
DR	$0.2337Chl\text{-}a^{2.4}$	Chl-a (14.9–80.0, μg/dm^3)	25	0.75
DR	120.83Chl-a – 1776	Chl-a (18.54–max, μg/dm^3)	20	0.60
Cl^-	$0.0041\ Chl\text{-}a^{3.1675}$	Chl-a (14.9–80.0, μg/dm^3)	25	0.78
Cl^-	57.5 Chl-a - 974.61	Chl-a (18.54–max, μg/dm^3)	20	0.58
SO_4^{2}	$0.0165\ Chl\text{-}a^{2.6118}$	Chl-a (14.9–80.0, μg/dm^3)	25	0.72
SO_4^{2}	23.358 Chl-a – 359.52	Chl-a (14.9–max, μg/dm^3)	20	0.49

Figure 5. Correlation of the concentrations of substances in the Dnipro-Buh estuary system

physical-chemical indicators in the Dnipro-Buh estuary system in the pre-war period. The level of accumulation of substances depended on human activities and climatic conditions. Therefore, the value of their concentration in 2018–2021 is used a background value in the studies on the impact of hostilities on water bodies, changes in surface water quality and disruption of the ecological balance of the functioning of the Dnipro-Buh estuary system in 2022–2023.

Formation of water quality in 2022

At the beginning of the Russian aggressors' invasion on February 24th, 2022 and the temporary occupation of Kherson region, the Lower Dnipro was actively used for military logistics of the occupiers, transporting equipment and weapons. At that time, one could observe active military logistics, seizure of hydraulic structures, illegal water discharges from the Kakhovka Reservoir, water withdrawal and transfer of large volumes of surface waters to the temporarily occupied left bank of Kherson and Zaporizhzhia regions with further transfer to the Autonomous Crimean Republic. These actions caused disruption of the hydro-biological and hydro-chemical regimes of the Lower Dnipro, from the lower reach to the river mouth and the Dnipro-Buh estuary. According to the data of the State Environmental Inspectorate of Ukraine, illegal withdrawal of surface waters from the Kakhovka and the North Crimean main canals reached 50 m^3/s, causing USD 860,000 losses per day. In particular, additional periodic water discharges to the Lower Dnipro in 2022–2023 (Figure 6) were the cause of significant fluctuations of the water level in the Kakhovka Reservoir.

From the beginning of the hostilities until the liberation of Kherson (24/02–11/10/2022) there were periods of unauthorized water discharge from the Kakhovka Reservoir: from 01/04 to 25/06/2022. This resulted in a cyclic increase in the water level, impulse flushing of the Lower Dnipro and the Dnipro-Buh estuary. The water level in the Lower Dnipro reached 1.46–1.62 m, whereas the normative WL in 2018–2021 was 0.57 m. Water releases reduced the seasonal background concentrations of pollutants in the river and the estuary, in particular, the content of PO_4^{3-} - 0.10±0.01 mgP/dm^3, Chl-a - 27.0 ±5.0 μg/dm^3, Turb - 11.0 ±9.5 NTU, TSS - 37.5 ±32.6 mg/dm^3 (Figure 7).

From July to the second decade of September 2022, there was a synchronous reduction in the water level in the Kakhovka Reservoir and the Lower Dnipro. It was caused by the blocking of water discharges to the lower part of the river and a decrease in the water level in the riverbed from 1.21 to 0.19 m that was a consequence of the illegal diversion of water through the main channel to the left bank of Kherson region and the Autonomous Republic of Crimea. Therefore, a reduction in the flow velocity and stagnation of surface waters were the cause of a considerable increase in the number of pollutants in the Dnipro-Buh estuary system in a warm season. There was a high concentration of PO_4^{3-} in the river delta from 0.18 to 0.22 mgP/dm^3 with a record increase of PO_4^{3-} in the floodplain lakes up to 0.44–0.45 mgP/dm^3 – 2.20–2.25 MPC. The average value of PO_4^{3-} accumulation in different sections of the estuary ranged from 0.16 to 0.25 mgP/dm^3 with the patches of the maximum concentration of PO_4^{3-} ranging from 0.33 to 0.37 mgP/dm^3 – 1.65–1.85 MPC. This caused accelerated growth of cyanobacteria, an increase in their biomass and a rise in the Chl-a content in the Dnipro delta from 65.6 to 83.5 μg/dm^3 with the patches of maximum concentration at the level of 215.0–222.0 μg/dm^3. The content of Chl-a

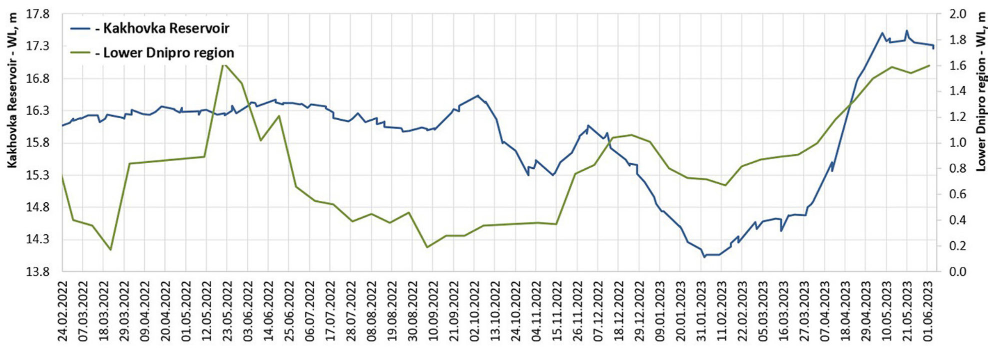

Figure 6. Dynamics of the water level (WL) in the Lower Dnipro, from the beginning of the war on 24/02/2022 to the destruction of the Kakhovka HPS dam on 06/06/2023

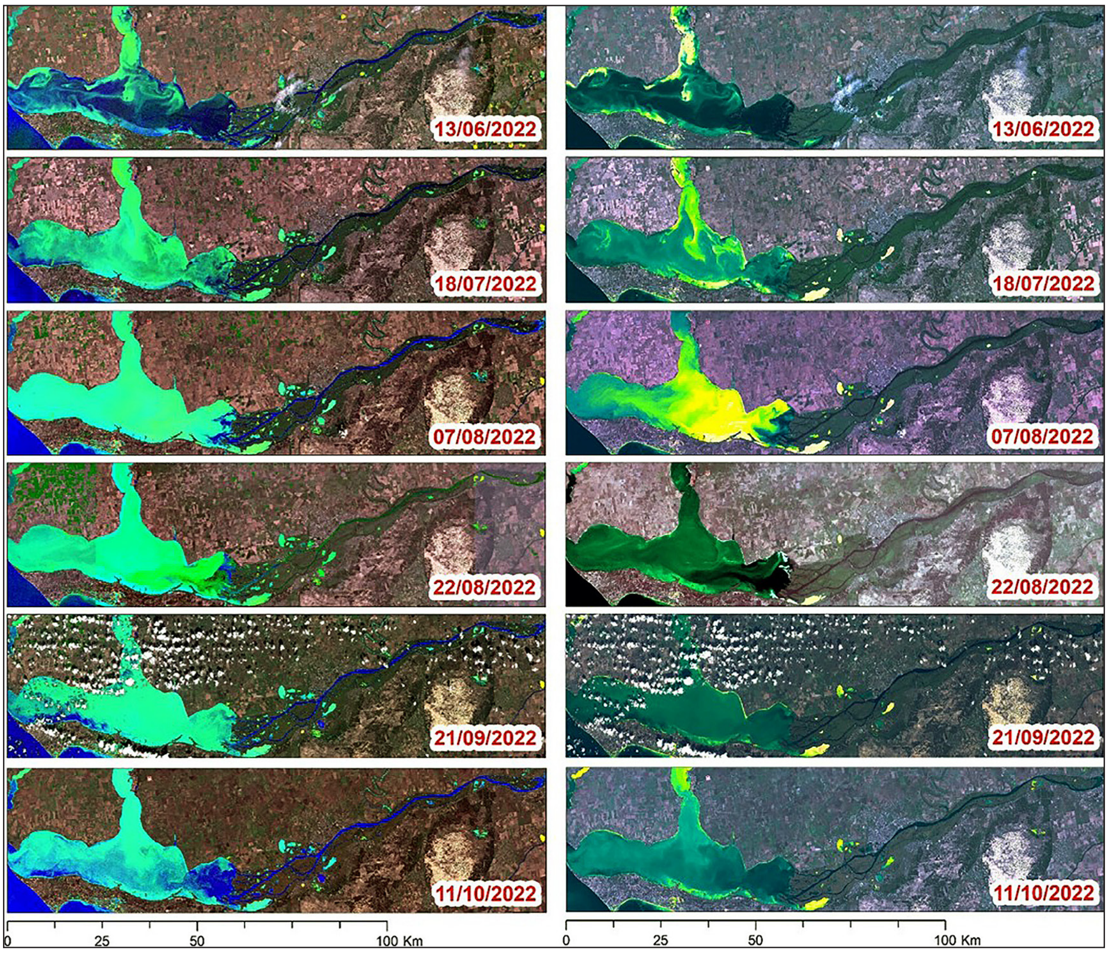

Figure 7. State of the water quality by hydro-biological and physical-chemical indicators in the Dnipro-Buh estuary system, 2022: a – algae density and water turbidity, b – intensity of algal bloom and concentration of suspended solids

in the Dnipro-Buh estuary ranged from 49.1 to 99.2 μg/dm^3, the maximum concentration being 144.0–168.0 μg/dm^3.

According to the physical-chemical indicators of Turbidity and Total Suspended Solids, the environmental situation in the water area was much worse, which was caused by the military water-logistics activity of the occupation forces which led to the shoreline destruction, diffuse pollution of the water sources in Section III of the Dnipro water area (from the Antonivka railway bridge to the beginning of the delta system). In this area, the Turb value in July–August varied between 15.0–18.0 NTU and 71.7–86.3 NTU – 4.3–24.7MPC. The concentration of TSS ranged from 51.3–61.6 mg/dm^3 to 243.3–295.3 mg/dm^3 – 2.05–11.81MPC. The transport of pollutants by the flow and an increase of their concentration were observed in the Dnipro delta, in the western and central sections of the estuary. From 11/09/2022 to 04/10/2022, there was accumulation of water in the reservoir from 16.0 to 16.5 m with small releases to the Lower Dnipro. This caused a slight increase in the flow and transport of pollutants to the estuary. However, these water volumes were not sufficient for flushing the Dnipro riverbed and delta systems. The concentration of pollutants was higher than their background level in 2021.

During the retreat and redeployment of the occupation troops from the right bank of the Kherson region to the left bank of the Dnipro, from 04/10 to 30/10/2022, the enemy considerably unloaded the water to the main canals on the left bank and maintained the necessary water level in the lower part of the river. The water level in the reservoir sharply decreased from 16.51 to 15.30 m, and the volume of water overflow was more than 2.6 km^3.

Active military logistics of the enemy and illegal withdrawal of substantial water volumes through the main canals had a considerable impact on the river hydrological regime that worsened biological and physical-chemical properties of the water in the Lower Dnipro. After the Ukrainian armed forces liberated the right bank of Kherson on 11.10.2022, the occupation forces retained control over the Kakhovka hydroelectric power station and continued unauthorized accumulation, water withdrawal as well as releases from the reservoir. These processes allowed them to control the hydrological regime in the area of accelerated flow in the Lowe Dnipro to prevent the Armed Forces of Ukraine from moving to the left bank. In particular, in the period from 31/10 to 04/11/2022 the aggressor accumulated water in the reservoir and then discharged it in the period from 05/11 to 13/11/2022. It caused an increase in the water level in the lower part of the river, led to larger water surface area and became a reason for accelerated flow preventing the Ukrainian forces from crossing the river. The process of regular water discharge was observed until the end of 2022. From the middle of November to the second decade of December 2022, the enemy accumulated water in the reservoir, and its substantial volumes were transported through the main canals to the temporarily occupied territories. In the period of unloading the surface water by the hydraulic networks, there was a record decrease in the water level in the Kakhovka Reservoir from 16.07 to 14.03 m and a loss of more than 4.5 km^3. The critical minimum water level was registered on 02/02/2023. In the period of winter water accumulation and spring floods, the Russian aggressor purposefully increased the water level in the reservoir to a record high of 17.50 m, which exceeded the average multi-year norm by 1.5 m and raised the water volume in the reservoir from 18.2 to 21.5 km^3. It testifies to clear planning, development and implementation of the measures aimed at deliberately causing a man-made disaster on 06/06/2023. At 2:50 a.m., the criminal military formations of the RF blew up the Kakhovka hydroelectric power station dam.

Formation of water quality in 2023

The dam destruction (Figure 8) caused catastrophic environmental and socioeconomic consequences. At the time of the dam destruction, the water level in the reservoir amounted to 17.26 m, equaling about 20.93 km^3 of water. As of 8:00 a.m on June 9 the water level in the reservoir reduced to 11.74 m, the water losses were 12.0 km^3. As of 12:00 on June 11 the water level was 9.17 m, the losses being 17.53 km^3 or 83.76% of water. The flooded area of the territories of the Lower Dnipro amounted to 600 km^2, there was a rise in the water level of 5.61–6.81 m in different riverbed areas. The disaster caused deaths of people, aquatic animals, terrestrial flora and fauna, bank abrasion, destruction of the main freshwater source for irrigating farmlands of more than 800 thousand ha, deterioration of water supply for settlements and other negative consequences. The emergency zone involved 180 settlements with over 900 thousand people. Water erosion washouts and bank abrasion resulted in diffuse pollution of the Lower Dnipro and transport of large volumes of pollutants by water flows to the Dnipro-Buh estuary and the Black Sea. According to the results of the decoded satellite imagery of Sentinel-2 L2A, as of 08/06/2023, in the water masses of the Dnipro delta and estuary there were high concentrations of biological and physical-chemical substances (Figure 9), which considerably exceeded their background values. The maximum content of PO_4^{3-} reached 0.214–0,232 mgP/dm^3 and more, which exceeded its background value by 1.4–3.1 times. There was an increase in the concentration of Chl-a, its value reached the level of 77.5–86.85 μg/dm^3 and more that corresponded to the Polytrophic state of transported water masses.

The water turbidity was 33.9-50.7 NTU, which exceeded the background level by 3.5–8.7 times. The maximum concentration of TSS varied from 116.0 to 173.5 mg/dm^3, which corresponded to 4.64–6.94 MPC and more. Accumulation and transport of Cl^- was observed at the level 3500–4200 mg/dm^3 – 17.5–21.0 MPC, SO_4^2 ranged from 1420 to 1700 mg/dm^3 – 14.2–-17.0 MPC, the dry residue amounted to 8000–8700 mg/dm^3 – 8.0–8.7 MPC and more. A sharp increase in biological oxygen demand to 90.0–103.5 mgO_2/dm^3 – 45.0–51.8 MPC and a rise in the concentration of chemical oxygen demand to 370.0–425.6 mgO_2/dm^3 – 18.5–21.3 MPC caused a sharp deficiency in oxygen that obviously led to the death of a large number of aquatic animals.

The calculation of maximum chlorophyll index (MSI) according to the data of satellite imagery of Sentinel-3 OLCI L1B allowed finding that polluted freshwater runoff had been transported to the Black Sea below the mouth of the Dnister river, the area of polluted water resources had reached about 6800 km^2 by June 26, 2023 (Figure 10). At that time (Vyshnevskyi et al., 2023) in the coastal area of Odesa, there was a decrease in

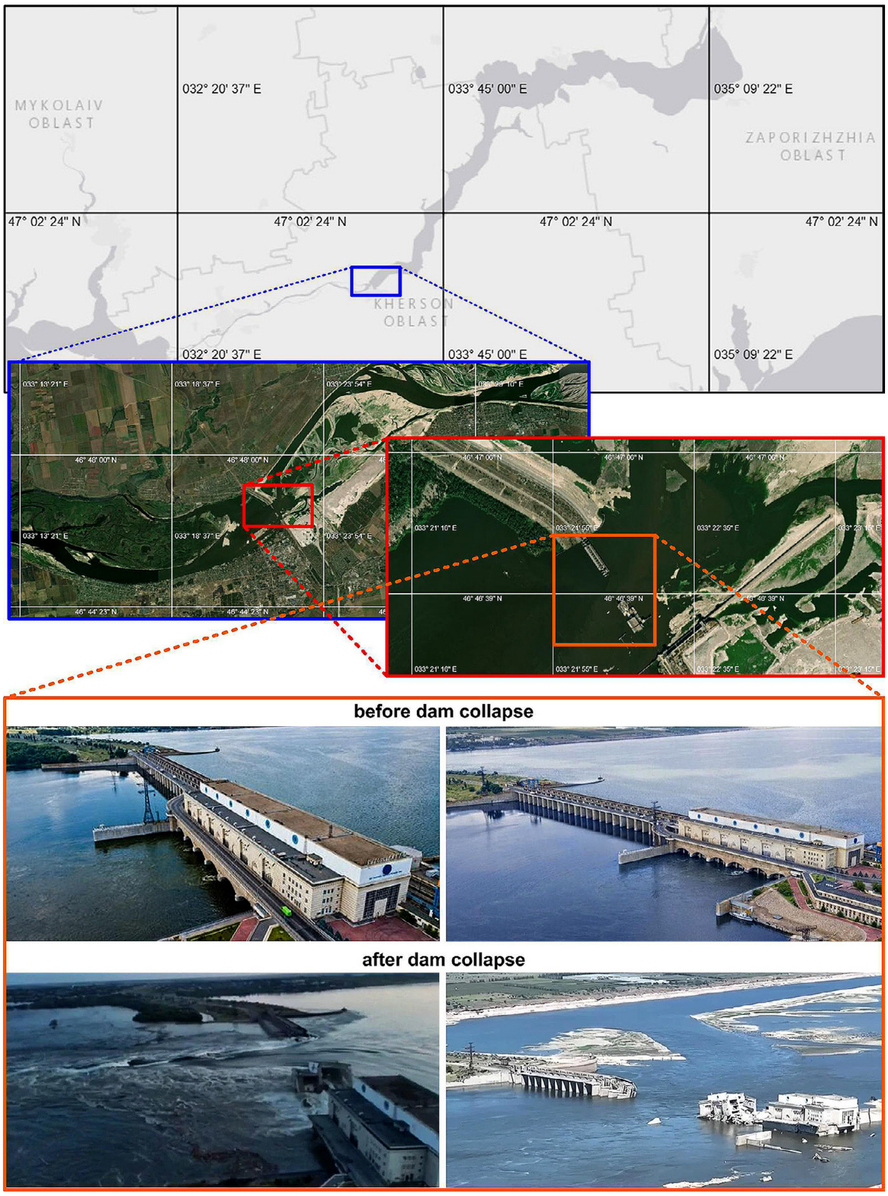

Figure 8. State of the Kakhovka hydroelectric power station dam before and after its destruction

the salinity of the sea water by 2.62 times (from 11.0g/dm^3 to 4.2 g/dm^3), an increase in the concentration of biological substances, the content of phytoplankton, a rise in the maximum permissible concentration (MPC): copper – by 895 times (MPC = 0.02 mcg/dm^3), zinc – by 44.8 times (MPC = 1.0 mcg/dm^3), arsenic – by 3.02 times (MPC = 0,6 mcg/dm^3), oil products – by 2.0 times (MPC = 0.05 mcg/dm^3). According to authors' calculations, it was found that the maximum MSI value in the Black Sea was 0.030. It corresponded to the concentration of Chl-a of about 91.0 μg/dm^3, PO_4^{3-} - 0.24 mgP/dm^3 (1.2 MPC), Turb - 26.0 NTU (7.4 MPC), TSS - 83.4 mg/dm^3 (3.3 MPC), DR - 9220 mg/dm^3 (9.2 MPC), Cl^- - 4260 mg/dm^3 (14.2 MPC), SO_4^{2} - 1770 mg/dm^3 (17.7 MPC), BOD_5 - 110 mgO_2/dm^3 (55.0 MPC), COD - 451 mgO_2/dm^3 (22.6 MPC). The MPC value of substances was calculated for fishery needs. The maximum value of pollutant concentration was taken as 100%, and the areas of the sea water with different levels of pollution were calculated on the basis of the ratio. Differentiation of the concentration of pollutants was calculated in relation to the share of the total area of pollution in the Black Sea - 6800 km^2, including: 29.3% of the water area was characterized by 0–10% of pollutant concentration; 31.8% of the surface water area accumulated 20–30% of pollutants; 22.9% of the water area had a considerable level of pollutant concentration – 30–40%; 16.0% of the territory had a high level of pollutant concentration – >

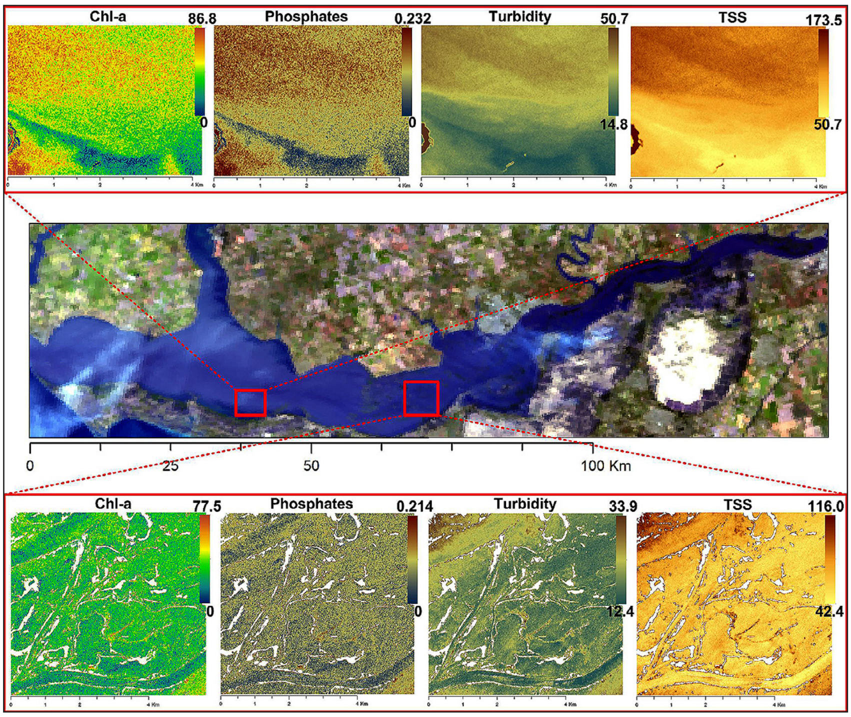

Figure 9. Transport of pollutants by the surface flow in the Dnipro-Buh estuary system as of 08/06/2023

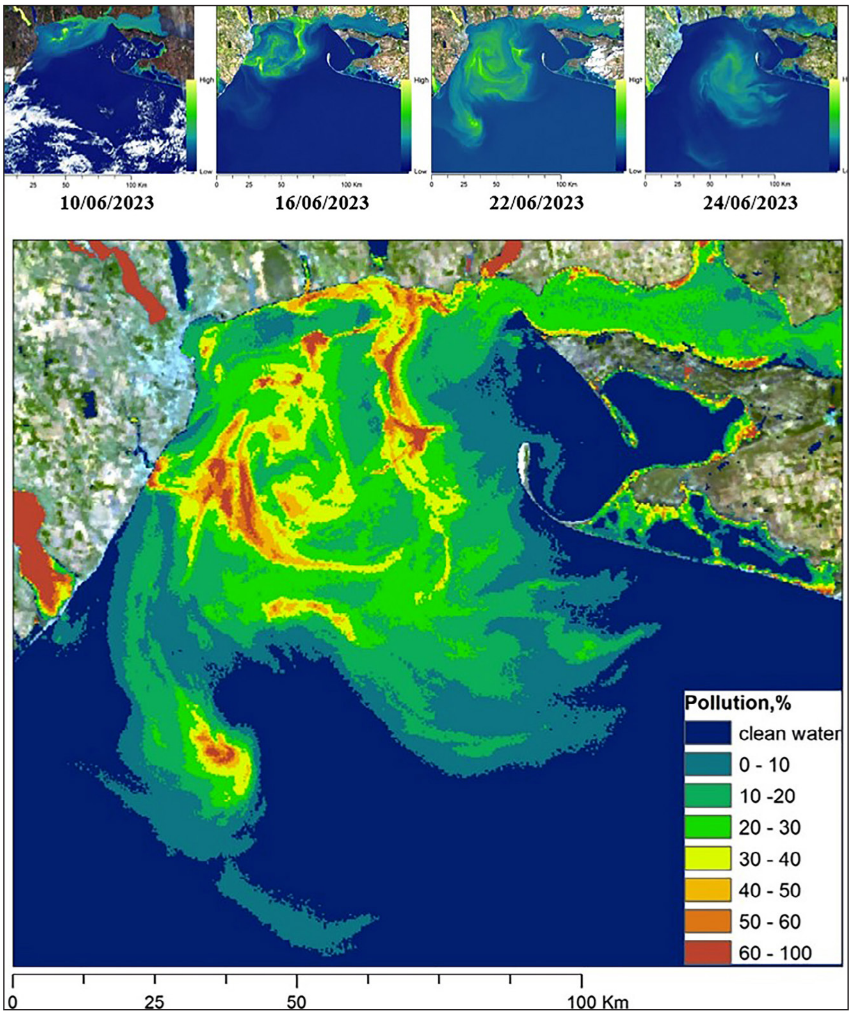

Figure 10. Spread of freshwater masses in the Black Sea, from 10/06 to 26/06/2023

40%. This situation caused deterioration of the living conditions of aquatic animals. There were 150 official cases of dolphin deaths in the Black Sea.

The destruction of the hydroelectric power station dam and the drainage of the Kakhovka Reservoir caused the loss of the territory with artificial freshwater accumulation occupying the area of 2155 km^2 which was important for the South of Ukraine (Pichura et al., 2024). It led to an increase in the length of the required flushing of the Dnipro riverbed in the lower course by 230 km, which needs a rise in the volumes and frequency of peak water discharges from the Dnipro Reservoir which is located higher than the drained Kakhovka Reservoir and occupies the area of 410 km^2. The maximum seasonal fluctuations of the water level in the Lower Dnipro in relation to the values of 2018–2021 decreased by 1.42–1.82 times. The lack of necessary ecological minimal discharges resulted in the disruption of water balance and formation of stagnation zones in the Dnipro-Buh estuary system. It caused sharp deterioration of hydro-biological and physical-chemical properties of the surface waters (Figure 11, 12).

The data of the State Environmental Inspectorate of the Southern Region of Ukraine were used to identify the regularities of a change in dissolved oxygen (DO, mgO_2/dm^3) in the period from 08.06 to 15.11.2023 (Figure 13) in the Lower Dnipro (Samples No. 27–29) and its right tributary – the Inhulets river (Sample No. 26).

In the first days of the destruction of the Kakhovka hydroelectric power station dam, there was transport of polluted water masses that caused flooding of the shoreline territories characterized by a sharp decrease in dissolved oxygen. The value of DO concentration for fishery needs in the period of 08–15/06 reached its critical level in the Inhulets river (Sample No. 26) – 4.8→2.5 mgO_2/dm^3 (0.80→0.42MPC), in the Lower Dnipro, near the Antonivka railway bridge (Sample No. 27), the value of DO fell from 6.9 to 5.8 mgO_2/dm^3 (1.15→0.97MPC). In the period of 15–25/06 when the water gradually receded, the content of DO in the Inhulets river varied between 3.7 and 2.2 mgO_2/dm^3 (0.62→0.37MPC), in the Dnipro river – from 6.3 to 5.3 mgO_2/dm^3 (1.05→0.88

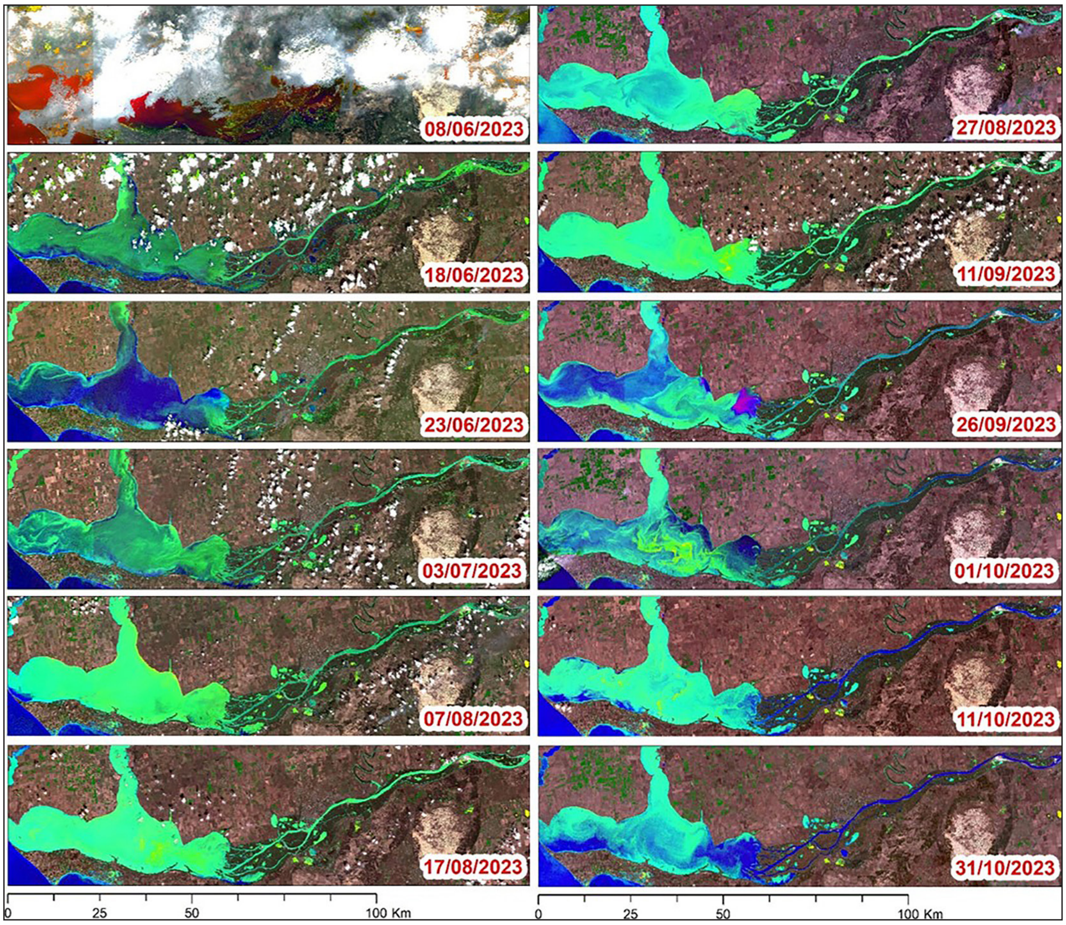

Figure 11. Density of algae distribution and water turbidity in the Dnipro-Buh estuary system, 2023

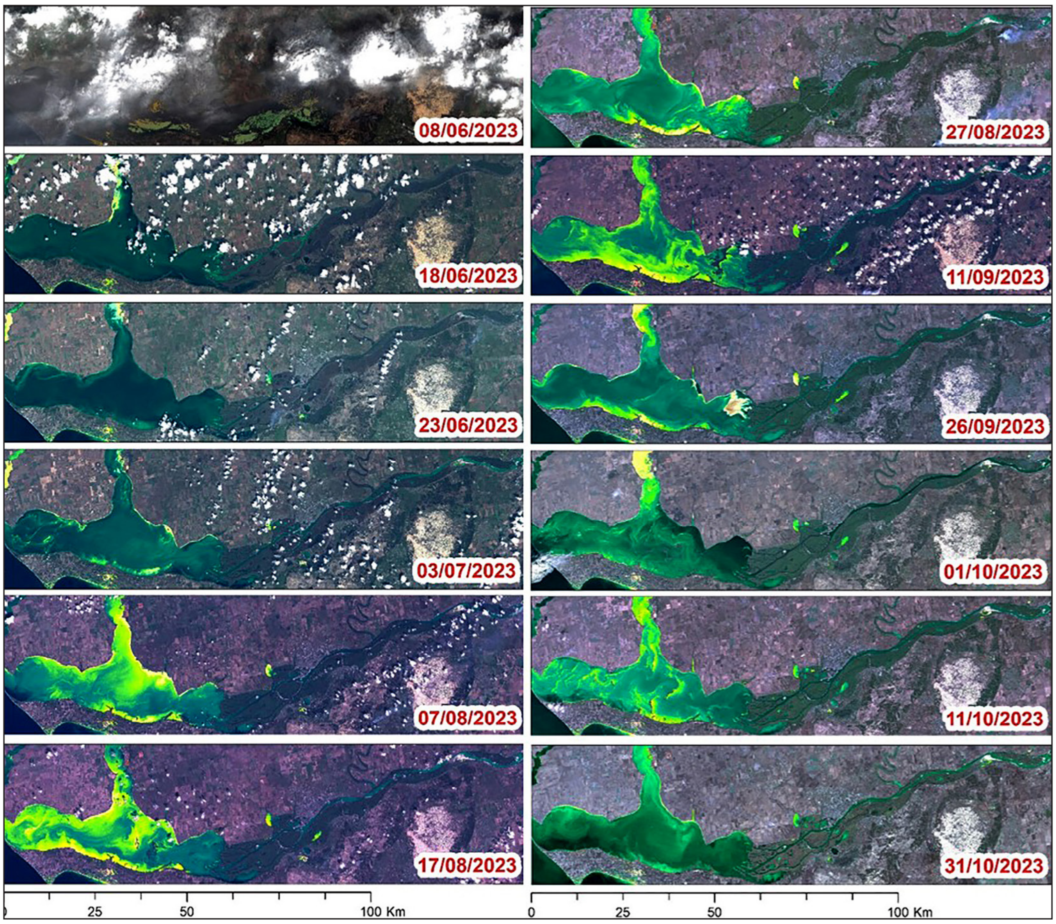

Figure 12. Intensity of algal bloom and concentration of suspended solids in the Dnipro-Buh estuary system, 2023

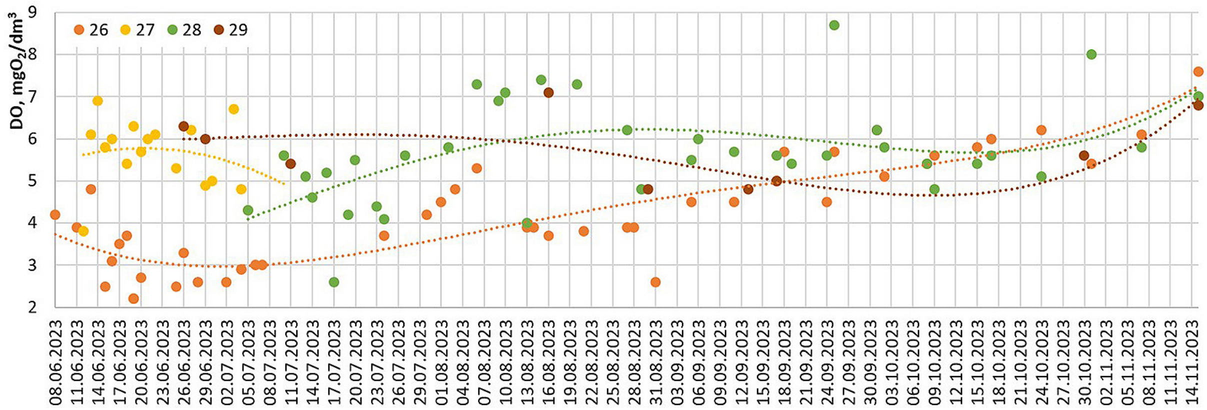

Figure 13. Changes in the content of dissolved oxygen in the water of the Lower Dnipro and the Inhulets river

MPC). As of June 18, 2023 there was a high record level of pollutant concentration in the Lower Dnipro. In Sections I–III, in the direction from the dam to the river mouth, the values of Chl-a varied from 53.3–128.0 μg/dm^3 to 42.0–77.60 μg/dm^3; PO_4^{3-} - from 0.20–0.34 mgP/dm^3 (1.0–1.7 MPC) to 0.16–0.25 mgP/dm^3 (0.80–1.25 MPC); Turb - from 22.1–54.0; NTU (6.3–15.4 MPC) to 16.5–28.3 NTU (4.7–8.1 MPC); TSS - from 75.6–184.8 mg/dm^3 (3.0–7.4 MPC) to 56.5–96.8 mg/dm^3 (2.3–3.9 MPC). From the end of June to the beginning of July 2023 there was a fall in pollutant concentration in some riverbed areas of the Lower Dnipro by 1.4–3.1 times. It was caused by the transport and accumulation of pollutants in the Dnipro-Buh estuary and the Black Sea.

After the water receded, until the beginning of August 2023, there was low concentration of dissolved oxygen with a gradual increase from 2.5 to 5.3 mgO_2/dm^3 (0.42→0.88 MPC) in the Inhulets river, from 4.3 to 5.8 (0.72→0.97 MPC) in the Dnipro river within Kherson (Sample No. 28), from 5.3 to 6.0 (0.88→1.0 MPC) within the river delta (Sample No. 29). The value of Chl-a varied between 46.6 and 67.2 μg/dm^3; PO_4^{3-} - 0.15–0.19 mgP/dm^3 (0.75–0.95 MPC); Turb - 10.5–17.3 NTU (3.0–4.9 MPC); TSS - 35.9–59.2 mg/dm^3 (1.44–2.37 MPC). Low values of pollutant accumulation were observed in the water of the Dnipro-Buh estuary in relation to the background values of 2021, in particular: Chl-a - 27.8–69.8 μg/dm^3; PO_4^{3-} - 0.10–0.20 mgP/dm^3 (0.50–1.0 MPC); Turb - 3.5–18.6 NTU (1.0-5.3MPC); TSS - 12.0–63.6 mg/dm^3 (0.48–2.54 MPC).

The seasonal maximum level of DO concentrations in Samples 28 and 29 was registered at the level of 6.9→7.3 mgO_2/dm^3 (1.15→1.22 MPC) in the period of August 5–25. It was due to precipitation and slight flushing of the Lower Dnipro. In particular, in the lower part of the Inhulets riverbed there was a reverse process of a reduction in the content of DO - 5.3→3.73 mgO_2/dm^3 (0.88→0.62 MPC), which was caused by accumulation of organic matter and seasonal activeness of algal bloom. In this period, there were large concentrations of pollutants at the level of 1.1–5.5 MPC in the surface waters of the Dnipro riverbed and delta, their further transport by the river flow to the estuary and accumulation at the level of 1.9–9.7 MPC.

High air temperatures, systematic accumulation of pollutants and accelerated development of phytoplankton caused eutrophication and negative environmental conditions of the lower part of the river until the third decade of September. Over this period, deficiency in dissolved oxygen at the level of 0.97→0.80 MPC was observed in 80% of water samples. In particular, in the water of the Dnipro riverbed in Sections I and II there was untypically high concentration of pollutants at the level of the Polytrophic state: Chl-a - 54.9–78.7 μg/dm^3; PO_4^{3-} - 0.17–0.22 mgP/dm^3 (0.85–1.10 MPC); Turb - 14.6–25.5 NTU (4.17–7.30 MPC); TSS - 50.0–87.3 mg/dm^3 (2.00–3.50 MPC). The maximum content of pollutants in the water of the estuary in the direction of "eastern→central→western" areas varied at the level "4.3–9.0 MPC→3.0–6.4 MPC→2.2–4.6 MPC".

As of September 25, there was a peak increase in DO concentration to 8.7 mgO_2/dm^3 or 1.45 MPC. That was caused by the water discharges from the Dnipro reservoir and heavy flushing of the Lower Dnipro riverbed. According to the results of the decoded satellite image as of September 26, there was a substantial release of pollutants in the Eastern estuary at the level of 5.0–10.4 MPC and more. In this period, pollutant concentration in the Dnipro riverbed reduced by 40–47%.

A seasonal autumn decrease in surface temperatures and a reduction in the intensity of water temperatures from the second decade of October led to the gradual suppression and cessation of negative hydro-biological and physical-chemical processes in the water at the beginning of November, which affected an increase in the concentration of dissolved oxygen in all the water samples – to 6.8 → 7.6 mgO_2/dm^3 (1.13 → 1.27 MPC). From October 11 to October 31, 2023, the concentration of pollutants in the Lower Dnipro decreased. The content of substances in Sections I and II was at the level: Chl-a - 25.2–34.8 μg/dm^3; PO_4^{3-} - 0.10–0.12 mgP/dm^3 (0.50–0.60 MPC); Turb - 3.3–14.1 NTU (0.94–4.04 MPC); TSS - 11.3–48.3 mg/dm^3 (0.45–1.93 MPC). In the water of the river delta (Section III) there was a reduction in the concentration of pollutants by 2.2–2.4 times. A similar seasonal decrease in the level of pollutants was in the Dnipro-Buh estuary, in particular, in the Eastern area (Section IV) – by 2.0–2.7 times, in the Central area (Section V) – by 1.9–3.0 times, in the Western area (Section VI) – by 2.2–3.8 times.

DISCUSSION

The Russian armed aggression, hostilities and destruction of the Kakhovka Reservoir have disrupted hydrological, biological and physical-chemical processes in the Dnipro-Buh estuary system. A decrease in the flow velocity, a fall in the water level by 16.4%, deterioration of water balance, stagnation and an increase in the water temperature, high accumulation pollutants, a significant increase in the levels of their maximum permissible concentrations in the surface waters according to fisheries, drinking, household and recreational norms were observed. In particular, in hot seasons there was an increase in the use of water resources, diffuse pollution, surface runoff and sewage, an acceleration in biological-chemical processes in the water areas. Therefore, the period of July–September is the most indicative period for establishing the spatio-temporal patterns of a change in the properties and environmental characteristics of surface water quality.

The war impact resulted in the annual deterioration of the hydrological regime and gradual saturation of the surface waters with biogenic elements by 1.4 → 2.1 times (Figure 14a) in the Lower Dnipro (Sections I and II). In 2022–2023, it caused an increase in the density of algal distribution and chlorophyll concentration by 1.5 → 2.9 times (Figure 14b), leading to deterioration of productivity and substantial hydro-biological pollution of the river and a change in the trophic status from "Mesotrophic" to "Polytrophic", a change in the water class from "Clean" to "Dirty". The river water turbidity (Figure 14c) and the content of Total Suspended Solids (Figure 14d) increased by 4.0 times.

There was a rise in the concentration of Chl-a by 1.3 times in the floodplain lakes of the river (Section III) as of 2022, in comparison with 2021. The floodplain lakes create a single water system in the Dnipro delta. Their trophic status mainly depends on a hydrological connection with the main river course which forms hydro-chemical

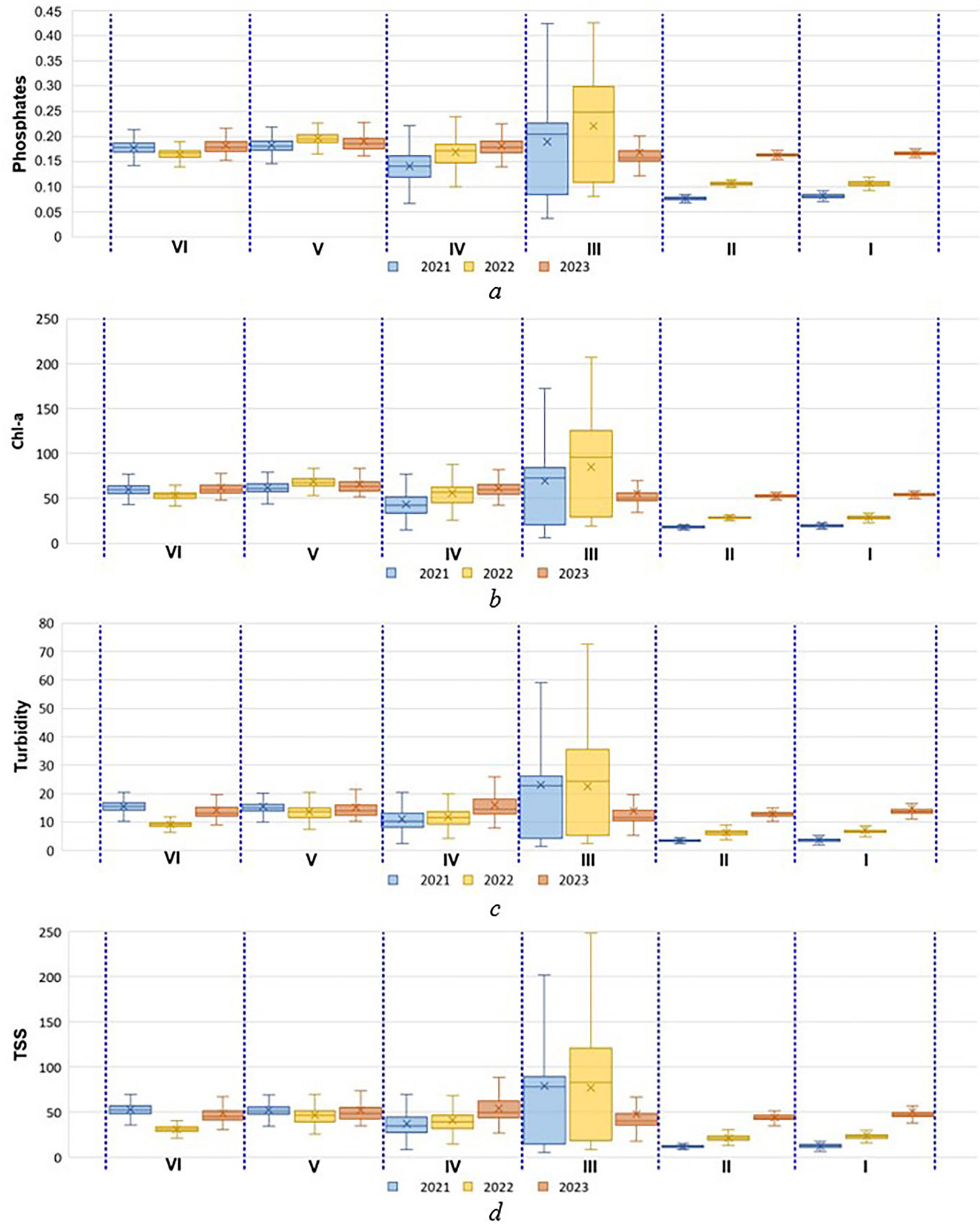

Figure 14. Spatio-temporal patterns of water quality formation in the Dnipro-Buh estuary system, July–September, 2021–2023: a – concentration of phosphates, mgP/dm^3); b – concentration of Chl-a, μg/dm^3; c – water turbidity, NTU; d – total content of suspended solids, mg/dm^3

and hydro-biological regimes throughout the year. Primary and secondary production contributes to intensive growth of bottom sediments and accelerated eutrophication. In this regard, the volumes of water runoffs affect the balance of nutrients in the lakes, accelerating or restraining the level of sedimentation. The volumes of runoffs and floods contribute to evacuation of bottom sediments having a positive environmental effect of water purification. This temporary effect was observed in 2023, at the time of the destruction of the Kakhovka hydroelectric power station dam, the water masses caused the flushing of floodplain lakes, the transport of pollutants and algal biomass by the flow to the Dnipro-Buh estuary and the Black Sea. The concentration of biological and physical-chemical substances in the floodplain lakes dropped by 34.6–55.6%.

The Dnipro waters account for 93.5% of causal relationships of hydrological, biological and physical-chemical processes in the Dnipro-Buh estuary system. Therefore, the Russian armed aggression resulted in degradation of the estuary water resources. In particular, in the Eastern area of the estuary (Section IV) there was an increase in the average seasonal concentration of Chl-a by 42.0%, PO_4^{3-} - by 21.4%, Turb - by 97.8%, TSS - by 78.7%; in the Central area (Section V) there was a rise in the content of Chl-a - by 6.5%, PO_4^{3-} - by 5.6%, Turb - by 6.7%, TSS - by 6.7%; additional accumulation of pollutants was insignificant, varied between 0.5 and 1.2% in the Western area (Section VI). A decrease in the intensity of pollutant concentration from the Eastern to the Western areas was determined by gradual solution of substances in the estuary water.

According to the hydro-biological characteristic of the Chl-a content, about 15.7% of the Dnipro-Buh estuary system lost their seasonal background values. This caused the progression of eutrophication processes in 94.8% of the estuary system area and deterioration of water quality to the polytrophic state. According to the level of biogenic pollution by PO_4^{3-}, the water area lost patches with Clean Enough water, whereas the patches with moderately polluted and dirty water expanded by 15.3% (77.2 → 92.5%). An increase in the concentration of non-organic and organic suspended solids (TSS), active development of plankton organisms affected organoleptic properties of water and caused a reduction in the transparency of the water layer by 28.0% in the water area (42.2 → 70.2 %) and deterioration of the water quality to the level – moderately polluted and dirty.

Water quality is a crucial aspect in ensuring safety and sustainability of water resources, involving the indicators which determine the health of water ecosystems (Kutishchev et al., 2022). Evaluation of water quality involves examination of hydro-biological, physical-chemical and biological indicators, each of them giving a unique vision of the water area state (Kutishchev et al, 2021). Hydro-biological indicators are often represented by the density and activeness of phytoplankton development, which allow establishing the environmental balance of productivity and the level of eutrophication of water systems. Temperature, transparency or turbidity and electrical conductivity are important physical indicators of water quality (Seifi et al., 2020). Presence and concentration of chemical substances are crucial markers for evaluating water quality. Health of water flora and fauna is a reflection of the overall well-being of a water body. Monitoring of these indicators contributes to understanding a potential impact of different stressors on water flora and fauna (Gaikwad et al., 2020).

Eutrophication is a systematic reaction of a freshwater ecosystem to the intensity of the impact of anthropogenic factors characterized by the volumes of erosive nutrient inputs, the frequency of uncontrolled surface runoffs, discharges of conditionally treated wastewater and sewage, the level of regulation of natural sources. The main indicators of eutrophication intensity are the concentration of Chl-a and nutrients (nitrogen and phosphates), transparency or turbidity, and water temperature (Katkaew and Chamchoi, 2024). Chlorophyll is widely used for representing plankton biomass in water bodies, the development of which depends on the level of phosphorous enrichment in water and sediments. In particular, the conducted research established strong ($r \geq 0.7$) and medium ($0.5 \leq r \leq 0.7$) correlations between productivity and the intensity of oxygen consumption by anaerobic bacteria as a result of oxidation of organic matter, dry residue, presence of chlorides and sulfates in freshwater sources which affects the quality of habitats for aquatic organisms and water supply. A higher level of eutrophy causes the denitrification activity of denitrifying bacteria. A high concentration of Chl-a in phytoplankton contributes to a reduction of dissolved oxygen at night. To maintain the bio-integrity of different types of water bodies, the maximum amount of oxygen should not exceed 4.15–4.19 mg/dm^3, phosphates - 28.25–29,42 mgP/dm^3 (Katkaew and Chamchoi, 2024), Chl-a - 30 µg/dm^3 (Wei et al, 2022). The background concentration of Chl-a in the Dnipro waters in the period of high temperatures in 2021 was 18.0–19.8 µg/dm^3, which corresponded to the initial eutrophic state and slightly polluted state of water. The background concentration of Chl- in the water of the Dnipro-Buh estuary amounted to 33.7–64.1 µg/dm^3, varying between the euplytrophic and polytrophic states. Hostilities in the territory of Ukraine caused considerable deterioration of the water to Polytrophic conditions of the formation of surface waters throughout the Dnipro-Buh estuary system in 2022–2023. This led to disruption of the bio-integrity of the water bodies, additional accumulation of nutrients and an increase in the background concentration of Chl-a in the Dnipro river to the level of 52.6–54.5 µg/dm^3 and in the Dnipro-Buh estuary to 59.7–82.1 µg/dm^3.

According to the data of the Sentinel 2 L2A satellite images, as on the end of March 2024, in the water area of the Dnipro-Buh estuary system, an abnormally high concentration of phytoplankton (Figure 15a), suspended substances, organics and zooplankton (Figure 15b) was recorded, which is an atypical phenomenon for this period of the year. In the hydrobiological samples of surface waters, a large mass of dead suspended and organic substances was recorded. A high density of plant residues and the protozoa is observed in suspended and organic matter. At the end of the growing season, plant residues form a strengthening siderative surface on the drained territory of the Kakhovka Reservoir, but they are washed away by spring floods and enter the surface waters of the Dnipro-Buh estuary. In particular, the increase in dead residues and protozoa is caused by their washing by floodwaters from the bottom cells of the active silt of the drained reservoir. A large number of protozoa was recorded, primarily *Oxytricha fallax*, *Vorticella microstoma*, *Uronema nigricans*, *Pseudoglaucoma muscorum*, which are common for the polysaprobic zone (polluted water) with a weak stream and significant zones of stagnation of water masses.

The increase in the concentration of phytoplankton in the Dnipro-Buh estuary system is caused by the movement of microscopic diatoms *Melosira varians* (filamentous) through the water masses of the destroyed Kakhovka Reservoir. This led to the transfer of colonial diatom

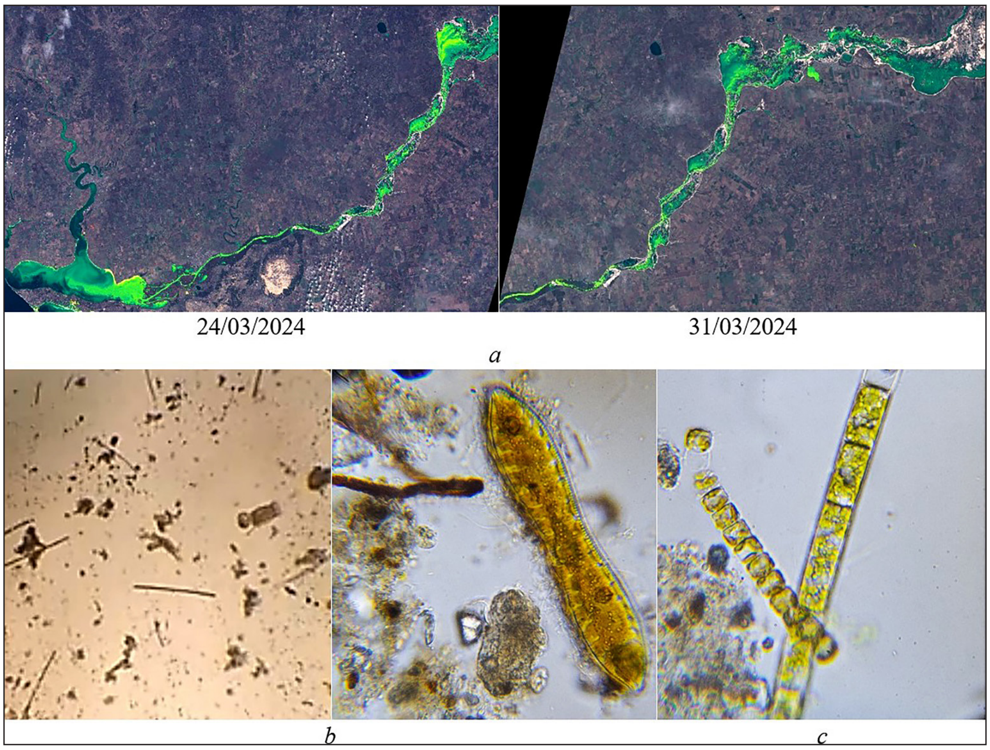

Figure 15. Distribution and development activity of the colonial diatom *Melosira varians* in the water area of the Dnipro-Buh estuary system: a – data from Sentinel 2 L2A satellite images; b – surface water quality under a microscope (suspended substances, organic matter, zooplankton); c – diatom algae *Melosira varians*

Melosira varians by the river stream, which was accompanied by an increase in their share in the water area of the Dnipro-Buh estuary (Figure 15c) from 15.0 to 86.7%. These algae, having natural cryophilicity (cold tolerant), formed large volumes of biomass. It is worth emphasizing that a slight increase in water temperature up to 5 °C is a favorable condition for the intensive reproduction of *Melosira varians*, at a time when the vegetation period of other algae has not yet begun. As the water temperature rises, the number and biomass of diatoms sharply decrease, as the intensive development of lower and higher plants begins. Reverse processes of development of *Melosira varians* are observed in autumn, when the water temperature drops, when blue-green and green algae, which are the main ones during the summer period, begin to die. At this time, the concentration of biogenic elements increases against the background of a decrease in water temperature, which is a favorable condition for the active development of representatives of diatom algae.

The current state of the surface water quality in most part of the estuary system corresponds to the quality of Moderately Polluted and Dirty water. Significant deterioration of the ecological condition of the Dnipro-Buh estuary system necessitates continuous monitoring of the surface water quality, analysis of the living conditions of aquatic animals, search for solving the problem of quality water supply for residents of rural territories.

CONCLUSIONS

The full-scale Russian invasion has led to man-made disasters and destruction of natural ecosystems in the South of Ukraine causing deterioration in the functioning of the Dnipro-Buh estuary system and affecting the Black Sea. In 2022, the Lower Dnipro was actively used by the occupation forces for military logistics of the enemy, transportation of equipment and weapons. In particular, the aggressors' seizure of the hydraulic structures, unauthorized discharges from the Kakhovka Reservoir, illegal water withdrawal and transfer of large volumes of surface waters to the temporarily occupied left bank of Kherson and Zaporizhzhia regions and the Autonomous Republic of Crimea have disrupted the hydrological, biological and physical-chemical regimes of the estuary system. The situation became more complicated after the destruction of the Kakhovka hydroelectric power station dam on 06/06/2023, that was a large-scale man-made disaster causing negative environmental and socio-economic consequences. Large volumes of biological and physical-chemical substances were transferred to the Black Sea. According to some indicators, the excess of their concentration in the water masses amounted to 1.1–51.8 MPC, causing pollution of the Black Sea by freshwater flows to the Dnister mouth and lower. The area of water pollution reached about 6800 km^2, including about 40% of the sea area with a high level of pollutant concentration. Due to the dam destruction and the drainage of the Kakhovka Reservoir, the South of Ukraine has lost an important area of artificial freshwater accumulation with an area of 2155 km^2 and deterioration of seasonal characteristics of the hydrological regime of the Dnipro-Buh-estuary systems by 1.42–1.82 times. In turn, this has caused an increase in the saturation of the river water with biogenic elements by 2.1 times, led to a rise in the density of algal distribution and chlorophyll concentration by 2.9 times, resulted in the deterioration of transparency and an increase in the amount of total suspended solids by 4.0 times. Over the war period, the degraded area of the Dnipro-Buh estuary system has increased by 15.7–28.0%. In 2023, about 94.8% of the water area corresponded to the Polytrophic state according to its hydro-biological characteristics. According to physical-chemical characteristics of Turbidity and Total Suspended Solids, about 70.2% of the water areas was characterized by a significant level of disruption of the hydro-ecosystem sustainability and ecological regression. The obtained results are an important evidence of the consequences of the ecocide caused by the Russian armed aggressors against Ukraine. In particular, the research provides important information for developing the measures and implementing technologies for the post-war restoration of the ecological conditions of water bodies and providing their zonal bio-integrity and balance.

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