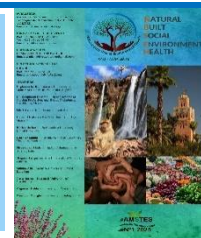




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Consequences of Sabotage of the Kakhovka Dam on the Waters of the Dnipro-Buh Estuary and the Black Sea

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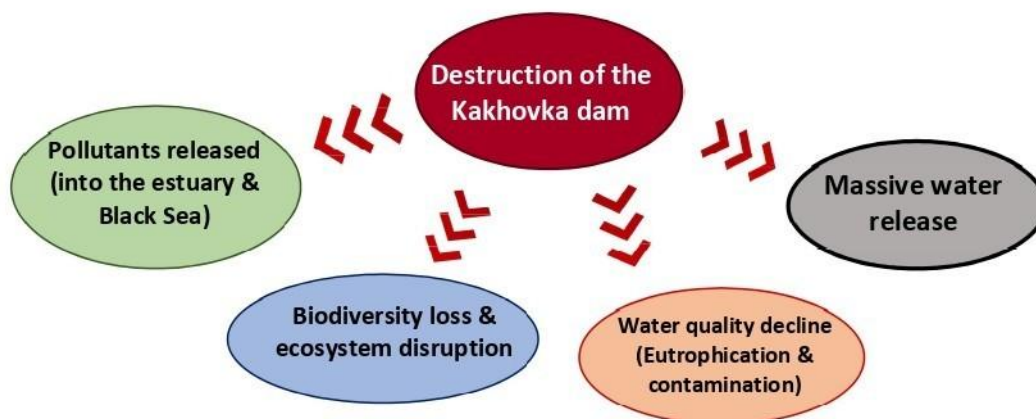
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Graphical Abstract

The destruction of the Kakhovka dam released pollutants up to 50 times above permissible levels across 6,800 km², severely impacting the Dniro-Buh estuary and the Black Sea. This disaster caused a deterioration in water quality, leading to eutrophication and excessive algal growth. The aquatic ecosystem is now disrupted, threatening biodiversity and hindering natural water regeneration.



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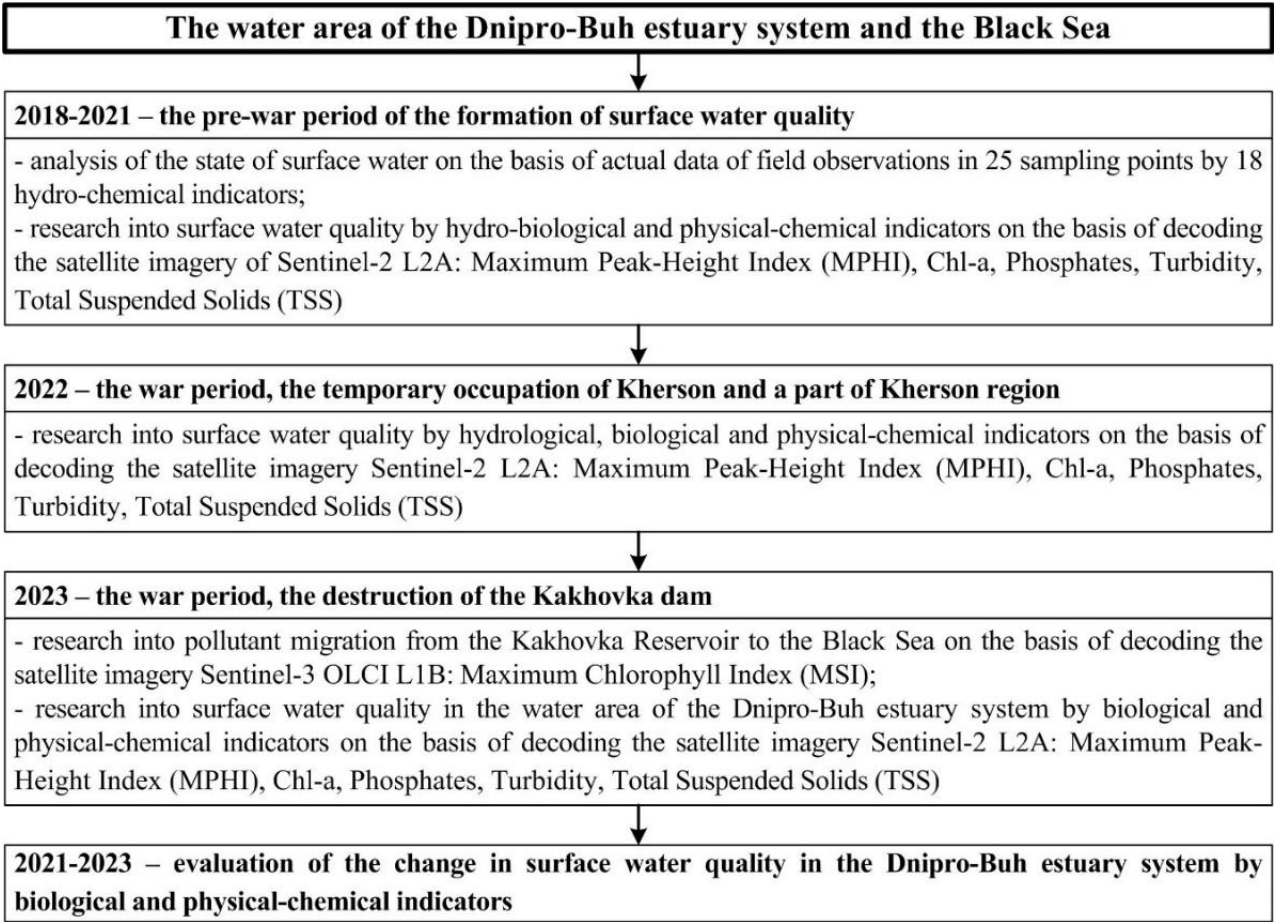
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Abstract: Sabotage of the Kakhovka dam released pollutants with concentrations up to 50 times their maximum permissible concentrations into 6,800 km² of the Dniro-Buh estuary and the Black Sea. The accumulation of biogenic elements doubled; there was a four-fold deterioration of physical and chemical properties, a three-fold increase in phytoplankton, and worsening of water quality to polytrophic status. The amplitude of freshwater flows to the estuary is now weakened and there is no effective mechanism to restore its status.

Keywords: *Armed aggression, Estuarine pollution, Spot samples, Remote sensing.*

Introduction

Russia’s threat is existential: Political, Economic, Cultural, Ecological. At a stroke, destruction of the Kakhovka Dam on 6th June 2023 damaged one third of Ukraine’s freshwater reserves and released the accumulated pollutants into the Dnipro-Buh estuary and the Black Sea [1-3]. However unsatisfactory its water quality, the Kakhovka reservoir supplied municipal and industrial needs, Europe’s biggest irrigation scheme [4, 5], and maintained the ecological flow of the lower Dnipro River and its estuary. In turn, the estuary is an important aquatic habitat [6,7]. When considering the necessity and feasibility of recreating the Kakhovka Reservoir, we should take account of changes in the hydrology and water quality of the Dnipro-Buh estuary which are the object of our research (Fig.1).



Materials and Methods

Table 1 lists our field observations and data of the State Environmental Inspectorate of the Southern Region (SEISR) of Ukraine that were used to trace surface water quality in 2018-23. Locations are plotted in Figure 2. Satellite imagery from the Sentinel 2 L2A and Sentinel-3 OLCI L1B, supplied by Copernicus Browser, was decoded to provide a dynamic spatial general view.

Table 1. Surface water samples from the Dnipro-Buh estuary.

№	Source of information	River	Name
Water samples 2018-21			
Dnipro river			
1	Authors	River bed	Ivanivka village shoreline
2	Authors	River bed	Ivanivka village 1, shallows
3	Authors	River bed	Ivanivka village 2, shallows
4	Authors	River bed	Ivanivka village, ship canal
5	Authors	River bed	ship canal
6	Authors	River bed	Kherson city 1, shallows
7	Authors	River bed	Kherson city 2, shallows
8	Authors	River bed	Rvach river 1, shallows
9	Authors	River delta	Rvach river 2, shallows
10	Authors	River delta	Rvach river, ship canal
11	Authors	River delta	Rvach river 3
Dnipro-Buh estuary			
12	Authors	Eastern	Shyroka Balka village
13	Authors	Eastern	Stanislav village, shallows
14	Authors	Eastern	Stanislav village, waterway
15	Authors	Eastern	Stanislav village, ship canal
16	Authors	Central	Oleksandrivka village
17	Authors	Central	Entrance to the Buh estuary 1
18	Authors	Central	entrance to the Buh estuary, 2
19	Authors	Central	entrance to the Buh estuary, ship canal
20	Authors	Central	Heroiske village, shallows
21	Authors	Western	Adzhyiol village, shallows
22	Authors	Western	Adzhyiol village, waterway
23	Authors	Western	Kutsurub village, shallows
24	Authors	Western	Pokrovski Khutory village, shallows
25	Authors	Western	Ochakiv city – exit from the estuary

Water samples 2023			
26	SEISR of Ukraine	Ingulets River bed	Darivka village, shoreline
27	SEISR of Ukraine	Dnieper River bed	Antonivka railway bridge
28	SEISR of Ukraine	Dnieper River bed	Kherson city, Mykola Sadovskyi Street
29	SEISR of Ukraine	Dnieper River delta	Koshova river, Kherson city, Prychalna street
30	Authors	Dnieper River delta	Pohorile lake
31	Authors	Dnieper River delta	Koshova River
32	Authors	Dnieper River delta	Chichkovate Lake
33	Authors	Dnieper River delta	Bezmen Lake
34	Authors	Dnieper River delta	Bile lake

The Dnipro-Buh estuary stretches from the former Kakhovka dam and the estuary of the Southern Buh River to the Kinburn spit, where it joins the Black Sea. The hyper-ecosystem encompasses 810 km² with a total length of 150.8 km (Fig. 1). The near-estuary between the Kakhovka dam and the city of Kherson and the delta includes numerous channels and floodplain lakes with a length of 94.4 km and an area of 492 km². Until 6/6/2023, its hydrology and ecology

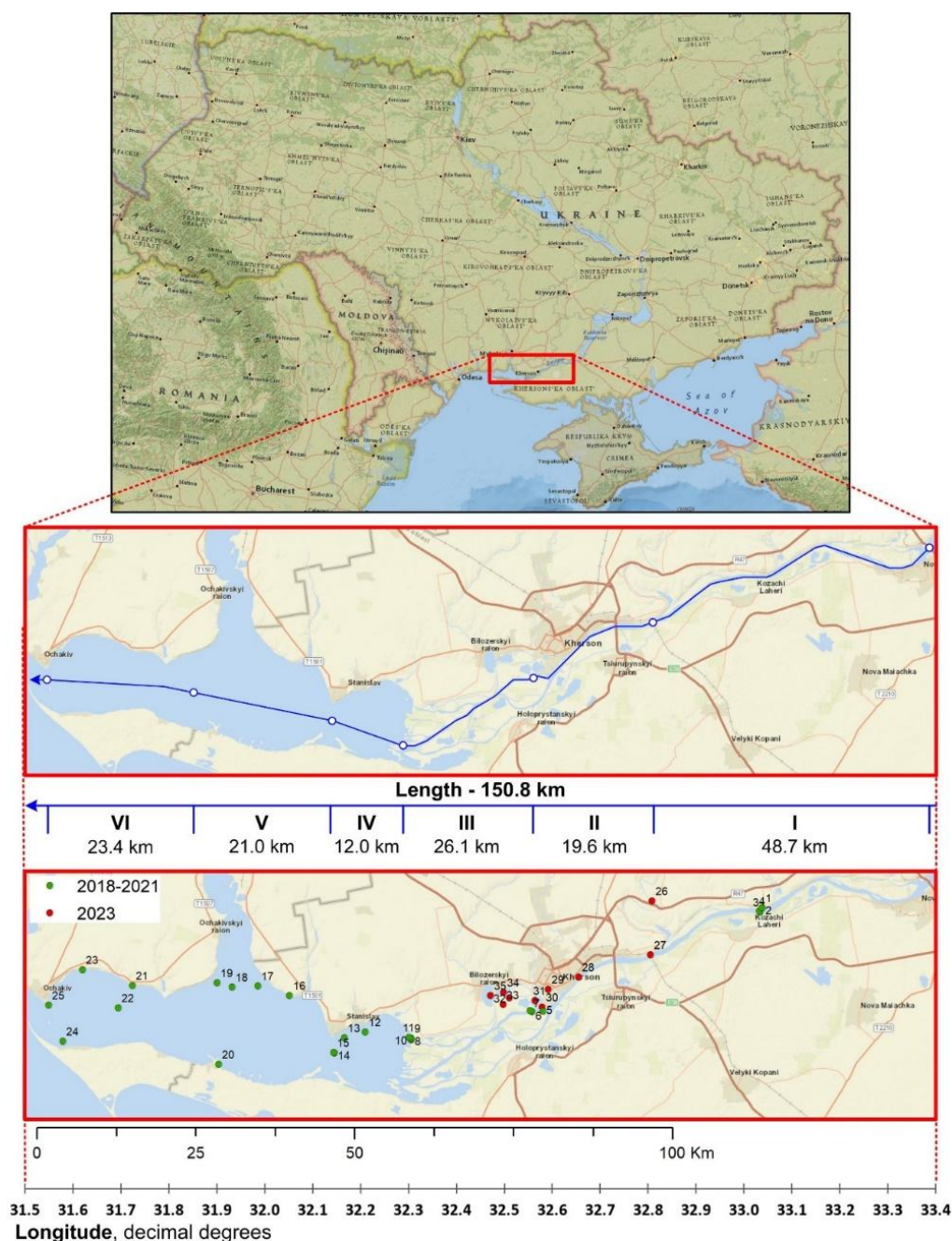


Figure 1. The water area of the Dnipro-Buh estuary system.

Lower Dnipro: length of the river course 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 bridge to the beginning of the Dnipro delta within the city of Kherson; III, from the beginning of the delta to the Dnipro mouth. **Dnipro-Buh estuary:** length 56.4 km: IV, Eastern section; V, Central section; VI, Western section depended on the water flow through the Kakhovka hydroelectric plant and its dam. Now it is governed by the operation of the Dnipro hydroelectric plant, 230km upstream.

The 48.7 km reach from the Kakhovka dam to the Antonivka railway bridge receives surface waters similar to those of the Lower Dnipro but the 19.6 km reach from the Antonivka bridge to the beginning of the Dnipro delta receives the brackish Inhulets River and surface runoff from Kherson. Pollution of the Inhulets River stems from mine waters and wastewater from Kryvyi Rih and the Inhulets mine-processing plants that add dry residues of 2,150-3,900 mg/dm³, including chloride (425-1,365 mg/dm³) and sulphate (670-842 mg/dm³) [8]. Surface runoff from Kherson adds oil products entering the suburban river area with untreated municipal wastewater, so this section of the Dnipro River is classed as *dirty – very dirty* by the norms of water suitability for fisheries.

The third section of 26.1 km from the beginning of the delta to the Dnipro mouth is characterized by inflow of sewage from Kherson and stagnant lake waters with a low or medium flow capacity. The city's treatment plants, built in 1975, have a capacity of 45-50 thousand m³ of wastewater per day: filtration and primary settling tanks retain heavy pollution and effect 35-40% treatment; subsequent digestion by aerobic microorganisms achieves up to 90% treatment [9]. But, over the period 2016-21, sewage discharge into the Dnipro exceeded the *maximum permissible concentrations* (MPC) of suspended solids by 4.2 times, phosphate by 3.6 times, dry residue by 1.3 times, sulphate by 1.7 times, chloride by 1.2 times, sodium+potassium, by 2.6 times, ammonium nitrogen by 3.8 times, and oil products by 2.0 times. Moreover, releases of untreated sewage add 400 tonnes of surface-active agents, nitrogen oxides, sulphur, phosphorous and oil products [9].

After the Danube delta, the Dnipro delta is the second largest in Ukraine extending over about 350 km², including channels, floodplain lakes, backwaters, tributaries, and several small islands. The Dnipro-Buh estuary is an open, oligohaline water body with an average depth of 3.5-4 m and greatest depth 12 m. It connects with the Black Sea by a 3.6 km-wide strait between the Ochakiv Cape and the Kinburn Spit. The southern shore is low and sandy; the northern shore mostly high (up to 20-35 m) with steep, sandy clay banks and some sand and shell spits. The estuary proper comprises the Eastern section (IV) fed by the Dnipro which contributes 94 per cent of the outflow; the Central section (V) under the influence of river and sea waters that are vertically stratified, which brakes the mixing process and leads to anaerobic zones in hot weather; and the Western section (VI), also under the influence of river and sea waters. The average salinity is 3.6‰ but 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 and Techniques

We calculated the intensity of saturation of floating blue-green algae (cyanobacteria) with the Chl-a pigment ($\mu\text{g}/\text{dm}^3$) using the Maximum Peak-Height Index (MPHI) [10]:

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

where B4, B5, and B8 are the reflectance and $\lambda B4 = 665\text{nm}$, $\lambda B5 = 705\text{nm}$, and $\lambda B8 = 842\text{nm}$ are the central wavelengths of the corresponding bands of Sentinel-2 L2A. MPHI ranges from -1.0 to 1.0; a value higher than 0.004 indicates presence of Chl-a in the blue-green algae of the surface water.

The content of phosphate (mgP/dm^3) was calculated on the basis of the established dependence (authors' research):

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

The turbidity of the surface water (Turb, NTU) was determined by this formula [11]:

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

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

Total Suspended Solids (mg/dm^3) was calculated on the basis of the established dependence [12]:

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

Table 2 presents the ecological classification of surface water quality [13].

Table 2. Classes and categories of surface water quality.

Water Quality Classes	I	II		III		IV	V
Water Quality Categories	1	2	3	4	5	6	7
Chl-a, $\mu\text{g}/\text{dm}^3$	<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

Class I waters are the least polluted with hydro-chemical and hydro-biological indicators close to natural values. Class II waters are changed in comparison with natural values but these changes do not disrupt the ecological balance. Class III waters significantly polluted, close to the limit of ecosystem sustainability. Classes IV-V waters are severely impaired [14]. Maximum permissible concentrations (MPCs) of substances in the waters of the river and estuary were determined by the most stringent standards of surface water quality and water bodies for potable, household, recreational and fishing purposes in Ukraine and the EU (Tab.3) [15].

Table 3. Surface water quality standards.

Indicator		Standards of water quality		
		for fishing	for drinking	for household and recreational purposes
Total Suspended Solids, mg/dm ³	TSS	≤25	≤25	≤30
Turbidity, NTU	Turb	≤3.5	≤3.5	≤5
Reaction	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
Chloride, mg/dm ³	Cl ⁻	≤300	≤200	≤200
Sulphate, 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
Phosphate, mg/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 pollutants to the Black Sea after the destruction of the Kakhovka dam was calculated using the Maximum Chlorophyll Index (MCI) [16]:

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

where B10, B11 and B12 are the reflectance and $\lambda_{B10} = 681$ nm, $\lambda_{B11} = 709$ nm, and $\lambda_{B12} = 754$ nm are the central wavelengths of the corresponding bands of Sentinel-3 OLCI L1B.

Correlation and regression were used to find relationships between concentrations of substances in the water. MS Excel 2016 was used to create graphs and perform cross-sectional analysis. Image processing, mapping and spatio-temporal analysis employed ArcGis 10.6.

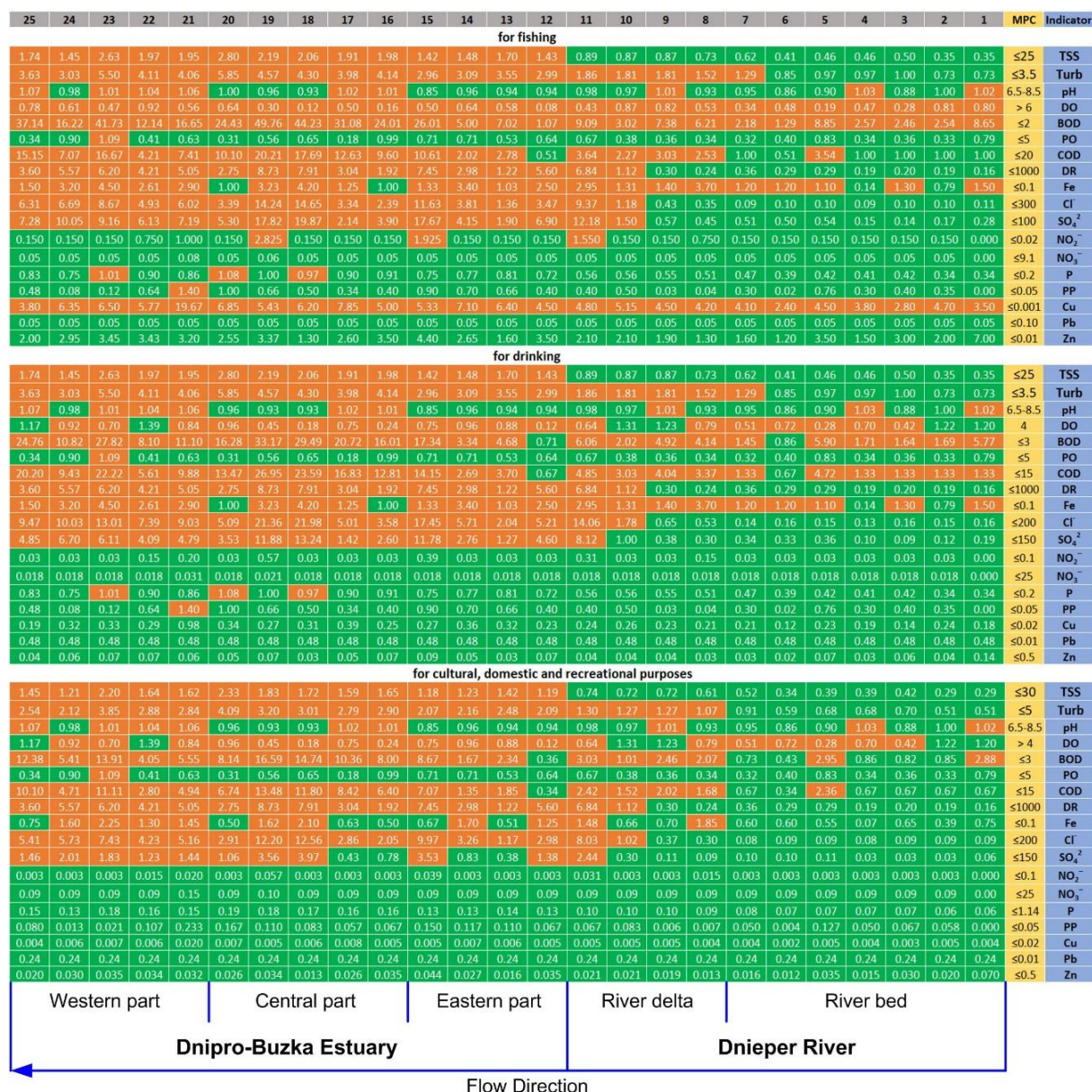
Results

Water quality in 2018-2021

In the pre-war period, surface water quality in the Dnipro-Buh estuary was driven by climate and human activities. Pollutants go with the flow, accumulating in excess of MPCs in the lower reaches of the river and the estuary, leading to eutrophication. In the spring floods, the Dnipro carries organic compounds, manganese, turbidity, chemical and biological oxygen demand from the upper reaches that drain upland peat bogs; but discharges from city sewage treatment plants have increased tenfold in the last decade and illegal construction in the water protection zone has caused bank abrasion. Above all, the cascade of huge reservoirs does not allow the river to function naturally. Increased anthropogenic load led to imbalance and a loss of self-regulation, self-purification and self-regeneration. Warm weather brought algal blooms, deoxygenation and mass fish deaths and microbiological and viral pollution of surface water required the closure of beaches.

During July-October 2018-21, MPCs of various contaminants were exceeded according to distance downstream from the Kakhovka Reservoir (Fig. 2). In particular, in the riverbed waters (samples 1-7), there was a deficiency in dissolved oxygen from 20 to 80% of the norm, and excess biological oxygen demand by 1.3-8.9 times from the multiplication of aerobic bacteria, causing fish kills. There was also an excess of chemical oxygen demand by 1.3-4.7 times, indicating input of untreated wastewater with organic and mineral substances, including humic substances, sulphides and iron. The concentration of iron exceeded the MPC for fisheries by 1.1-1.5 times. The excess of copper was 2.4-4.7 times MPC; enough to disrupt homeostasis and cause pathological changes of fish liver and other organs; human consumption of such fish is dangerous.

The waters of the delta (samples 8-11) were characterized by medium and low retention time but stagnation in floodplain lakes considerably worsened water quality. The turbidity of the surface waters was 1.3-1.9MPC, indicating the presence of fine impurities and plankton. Sentinel 2 L2A imagery (Fig. 3) also indicates algal blooms, turbidity and accumulation of suspended solids in the floodplain lakes. In July-October 2021, the average turbidity in the lakes varied from 13.5-26.9NTU (*i.e.* 3.8-7.4MPC), the maximum value being 52.5-74.1NTU (15-21MPC).



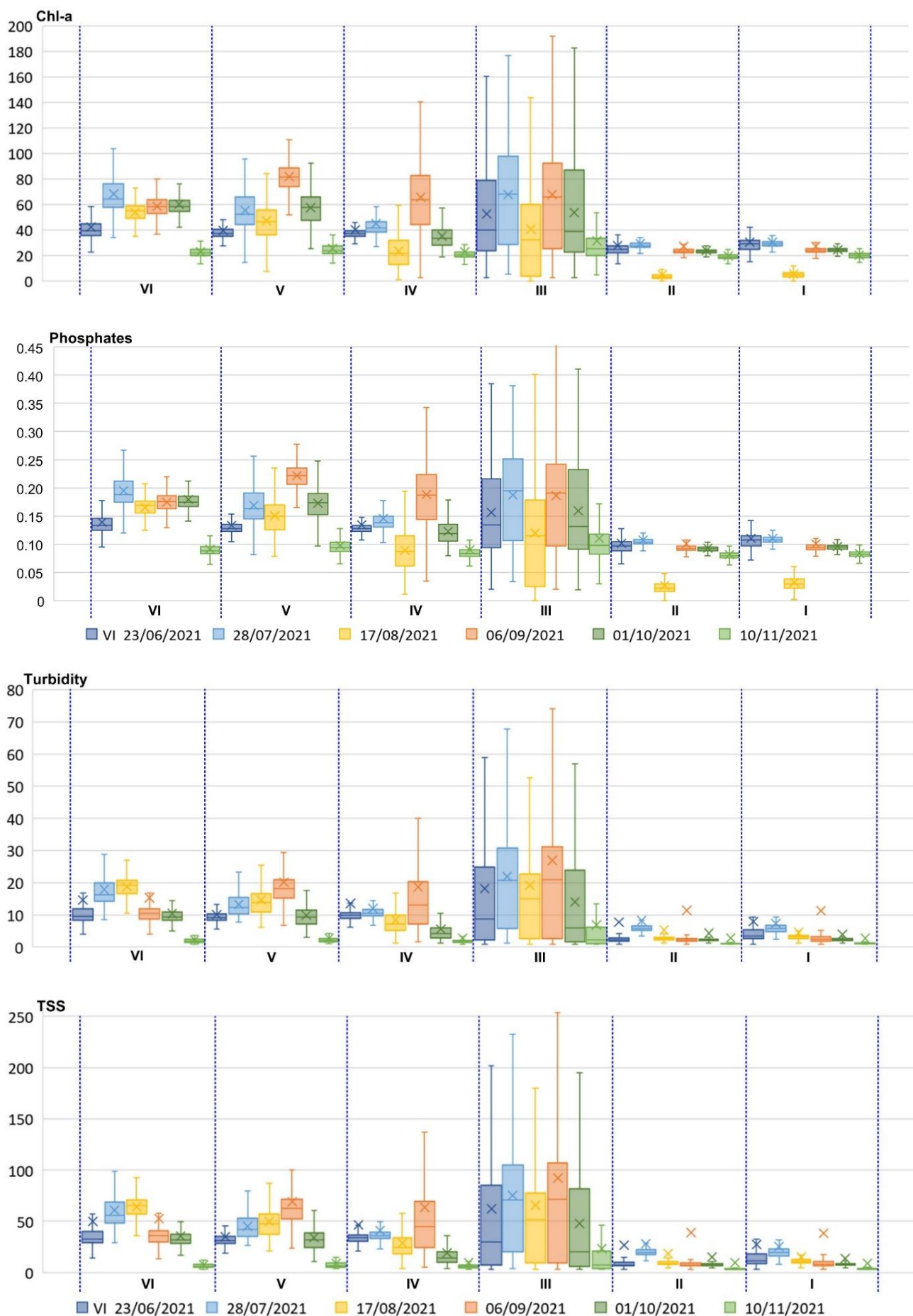


Figure 3. Surface water quality in the Dnipro-Buh estuary, 2021.

The dry residue (DR) measures the total amount of mineral salts and organic matter dissolved in water. In the period 2018-2021, DR was 1.1-6.8 MPC and, at the river mouth (samples 10 and 11), the content of chloride exceeded the MPC for drinking water by 1.8-9.4 times, the content of sulphate by 1.5-12.2 times. As well as tasting salty, salinity disrupts water-salt metabolism, suppresses gastric secretions, impedes food digestion and complicates hypertension; it also corrodes metal pipes and equipment used for transporting and storing water, and an increase in the sulphate content against the backdrop of the deficiency in dissolved oxygen, releases hydrogen sulphide. Sample 11 also exhibited excess nitrite, by 1.6 MPC, and a 4.2-5.2 MPC excess of copper.

In short, the surface waters of the Dnipro-Buh estuary in July-October were eutrophic or polytrophic. Throughout the estuary, there were mosaic processes of accumulation of pollutants and an increase in their quantity in the direction of water movement – from the western to the eastern section of the estuary and entry to the Black Sea shallows. The greatest pollution and a substantial phytoplankton biomass were observed at the beginning of September 2021 (satellite image dated 06/09/2021) when the concentration of Chl-a in the western section of the estuary ranged between 2.5 and 140 $\mu\text{g}/\text{dm}^3$ with a mean of 66 $\mu\text{g}/\text{dm}^3$; in the central section of the estuary, Chl-a ranged from 52-111 $\mu\text{g}/\text{dm}^3$ with a mean of 82 $\mu\text{g}/\text{dm}^3$; and in the eastern section ranged from 37-80 $\mu\text{g}/\text{dm}^3$ with a mean of 59 $\mu\text{g}/\text{dm}^3$. The minimum value of Chl-a was registered at the beginning of November when falling temperatures curtailed plankton growth; as of 10/11/2021, Chl-a ranged from 12.8 to 36.4 $\mu\text{g}/\text{dm}^3$.

Phytoplankton depend on the availability of phosphate. Their values change synchronously so that, on 06/09/2021, the mean phosphate concentration was 0.18mgP/dm³ (0.9 MPC) in the eastern section of the estuary, ranging from 0.03-0.35 mgP/dm³ (0.15-1.75MPC); in the central section the mean was 0.22 mgP/dm³ (1.1 MAC), ranging between 0.16-0.28 mgP/dm³ (0.8-1.4 MPC); and in the western section 0.17 mgP/dm³ (0.9MPC), in the range of 0.14-0.22 mgP/dm³ to 0.70-1.1 mgP/dm³. On 10/11/2021, the concentration of phosphate in the estuary water varied between 0.09 and 0.15 mgP/dm³ (0.5-0.8 MPC). In the same vein, turbidity and a high concentration of suspended solids (TSS) were observed in July-September 2021 when turbidity varied between 1.2 and 40.0NTU (0.3-11.4 MPC) and TSS varied between 4.1 and 136.9 mg/dm³ (0.2-5.5 MPC).

In summary, the July-October period throughout 2018-21 saw MPCs exceeded by most indicators *in all sections of the estuary*; in particular dissolved oxygen (0.08-0.8 MPC), biological oxygen demand (1.1-49.8 MPC), chemical oxygen demand (2.0-20.2 MPC), dry residue (1.2-8.7 MPC), iron (1.0-4.2 MPC), chloride (1.4-14.7 MPC), sulphate (1.9-19.9 MPC) and, sporadically, nitrite (1.6-2.8 MPC).

Water Quality in 2022

The Russian invasion of February 24, 2022, brought occupation of the Kherson region, seizure of water infrastructure, and transfer of enormous volumes of water from the Kakhovka reservoir to the occupied territories. According to the State Environmental Inspectorate of Ukraine, theft from the Kakhovka and the North Crimean main canals reached 50 m³/s; losses \$US 860,000 per day. Further water discharges to the Lower Dniro created significant fluctuations of the water level in the Kakhovka Reservoir (Fig. 4).

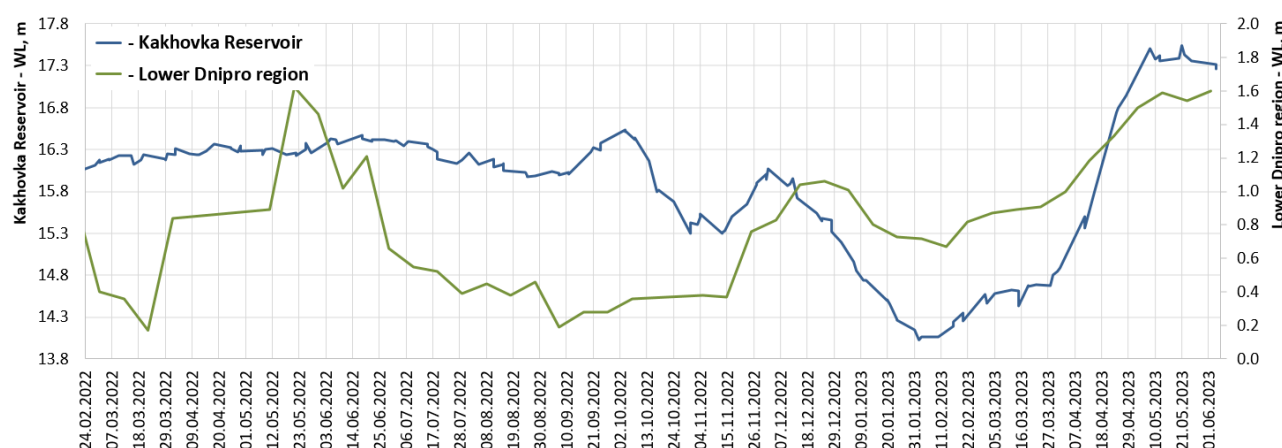


Figure 4. Dynamics of the water level in the Lower Dniro from the Russian invasion on 24.02.2022 to the destruction of the Kakhovka dam on 06.06.2023.

From the onset of hostilities until the liberation of Kherson (11/10/2022), unauthorised water discharges from the Kakhovka Reservoir produced pulses of flushing of the Lower Dniro and the estuary (Fig. 5). The water level in the Lower Dniro reached 1.46-1.62 m compared to the normative level of 0.57 m which reduced the background concentrations of pollutants in the river and the estuary: in particular, phosphate to (0.10±0.01 mgP/dm³), Chl-a (27.0±5.0 µg/dm³), turbidity (11.0±9.5 TU), and total suspended solids (37.5±32.6 mg/dm³).

From July to the second decade of September 2022 water levels in the reservoir and the Lower Dniro were lowered by diversion of water to the left bank of Kherson region and Crimea. Lesser river flow and stagnation of surface waters greatly increased the concentration of pollutants in the estuary in this warm season: there was a high concentration of phosphate in the river delta (0.18-0.22 mgP/dm³) and a record increase in the floodplain lakes (up to 0.44-0.45 mg/dm³ or 2.2-2.3MPC). The mean phosphate accumulation in different sections of the estuary ranged from 0.16-0.25 mgP/dm³ with spots of maximum concentration from 0.33-0.37 mgP/dm³ (1.7-1.9 MPC).

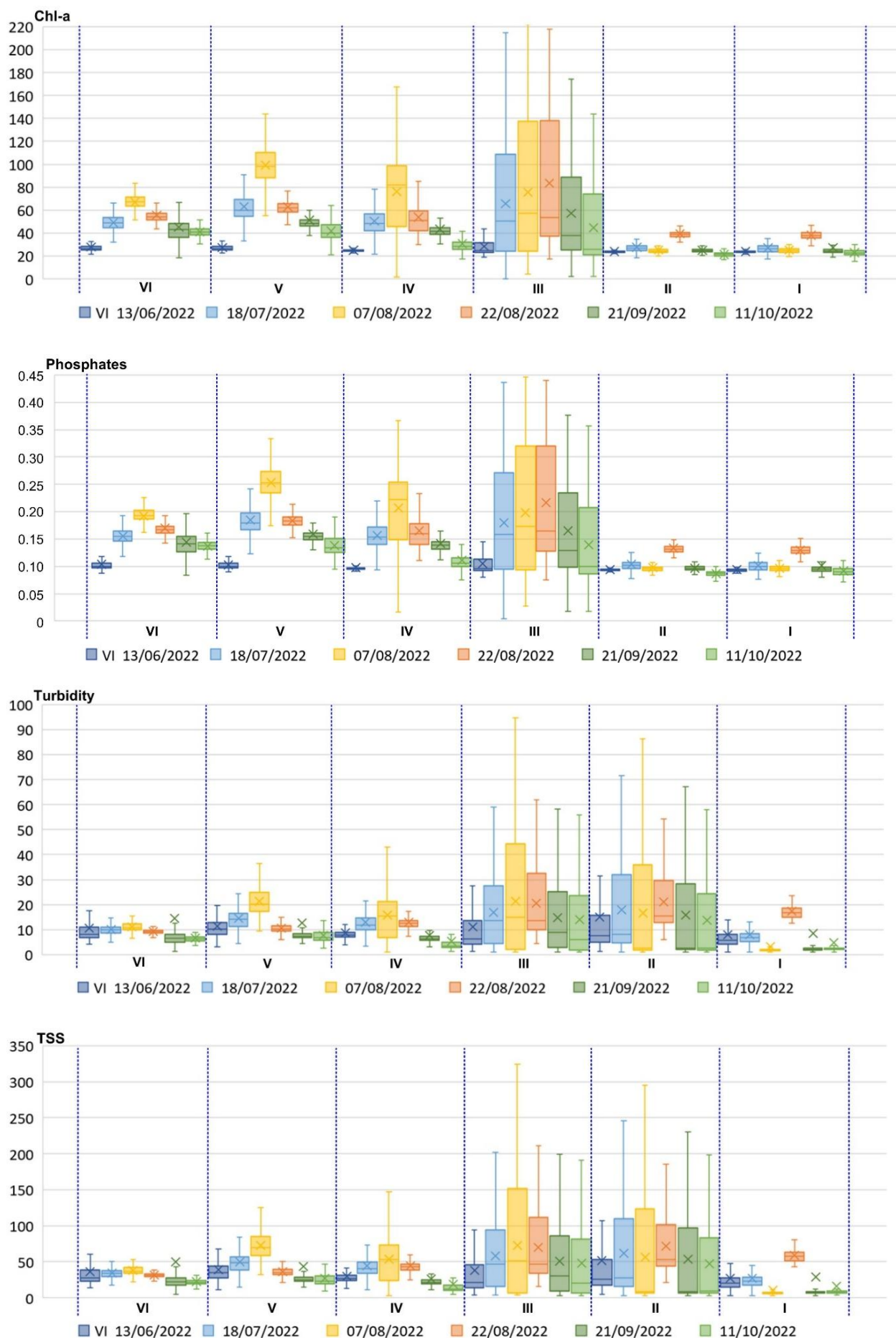


Figure 5. Surface water quality in the Dnipro-Buh estuary, 2022.

This accelerated the growth of algal blooms, shown by a rise in Chl-a content in the delta from 65.6 to 83.5 µg/dm³ with the spots of maximum concentration of 215-222 µg/dm³. The content of Chl-a in the estuary ranged from 49.1-99.2 µg/dm³ with a maximum of 144-168 µg/dm³. At the same time, occupying troops initiated shoreline destruction and diffuse pollution of the water sources in Section III of the Dnipro river area where turbidity varied between 4.3-24.7 MPC and TSS from 2.1-11.8 MPC.

During their retreat from the right bank to the left bank of the Dnipro from 04 to 30/10/2022, the occupying forces unloaded water to the main canals on the left bank and maintained spate flows in the lower reaches of the river; the reservoir level dropped sharply from 16.51 to 15.30 m, and the outflow was more than 2.6 BCM. After the Ukrainian army liberated the right bank of Kherson on 11.10.2022, Russian troops who remained in control of the dam kept the river in spate to prevent Ukrainian forces from crossing. A total outflow of 4.5 BCM brought a record decrease in the level of the reservoir from 16.07 to 14.03 m. The critical minimum water level was registered on 02/02/2023.

In the following period of winter water accumulation and spring floods, clearly with evil intent, Russian forces raised the water level in the reservoir to a record high of 17.5 m, 1.5 m above the norm, raising the water volume of the reservoir from 18.2 to 21.5 BCM. At 2.50 am on 06/06 2023, they detonated the dam.

Water Quality in 2023

At that time, the water level in the reservoir was 17.26 m. At 8:00 a.m on June 9 the water level in the reservoir had fallen to 11.74 m; at noon on June 11 the water level was 9.17 m; the losses being 17.5 BCM or 84 per cent of the storage. Some 600 km² of land along the Lower Dnipro was flooded, with a rise of water levels of 5.6-6.8 m in different places [1]. Hundreds of people drowned and innumerable plants and animals were destroyed along with the main water source for cities, towns and villages and 800 thousand ha of irrigated land; the emergency zone covered 180 settlements with over 900 thousand people. Washouts and bank abrasion created diffuse pollution of the Lower Dnipro and transport of pollutants to the Dnipro-Buh estuary and Black Sea. Sentinel satellite imagery from 08/06/2023 (Fig.6) shows concentrations of various pollutants in the Dnipro delta and estuary much in excess of their background values.

The maximum content of phosphate reached 0.21-0.23 mgP/dm³, exceeding its background value by 1.4-3.1 times, and Chl-a reached 77.5-86.9 µg/dm³, i.e. polytrophic levels. Turbidity was 33.9-50.7 NTU, exceeding the background level 3.5-8.7 times. Total suspended solids reached 116-173.5 mg/dm³ (4.6-6.9 MPC); chloride 3500-4200 mg/dm³ (17.5-21 MPC) sulphate 1,420-1,700 mg/dm³ (14-17 MPC);

and dry residue 8000-8700mg/dm³ (8.0-8.7 MPC). There was a sharp increase in biological oxygen demand to 90-103.5mgO₂/dm³ (45-52 MPC) and chemical oxygen demand to 370.0-425.6mgO₂/dm³ (18.5-21 MPC), and lack of oxygen caused mass fish kills.

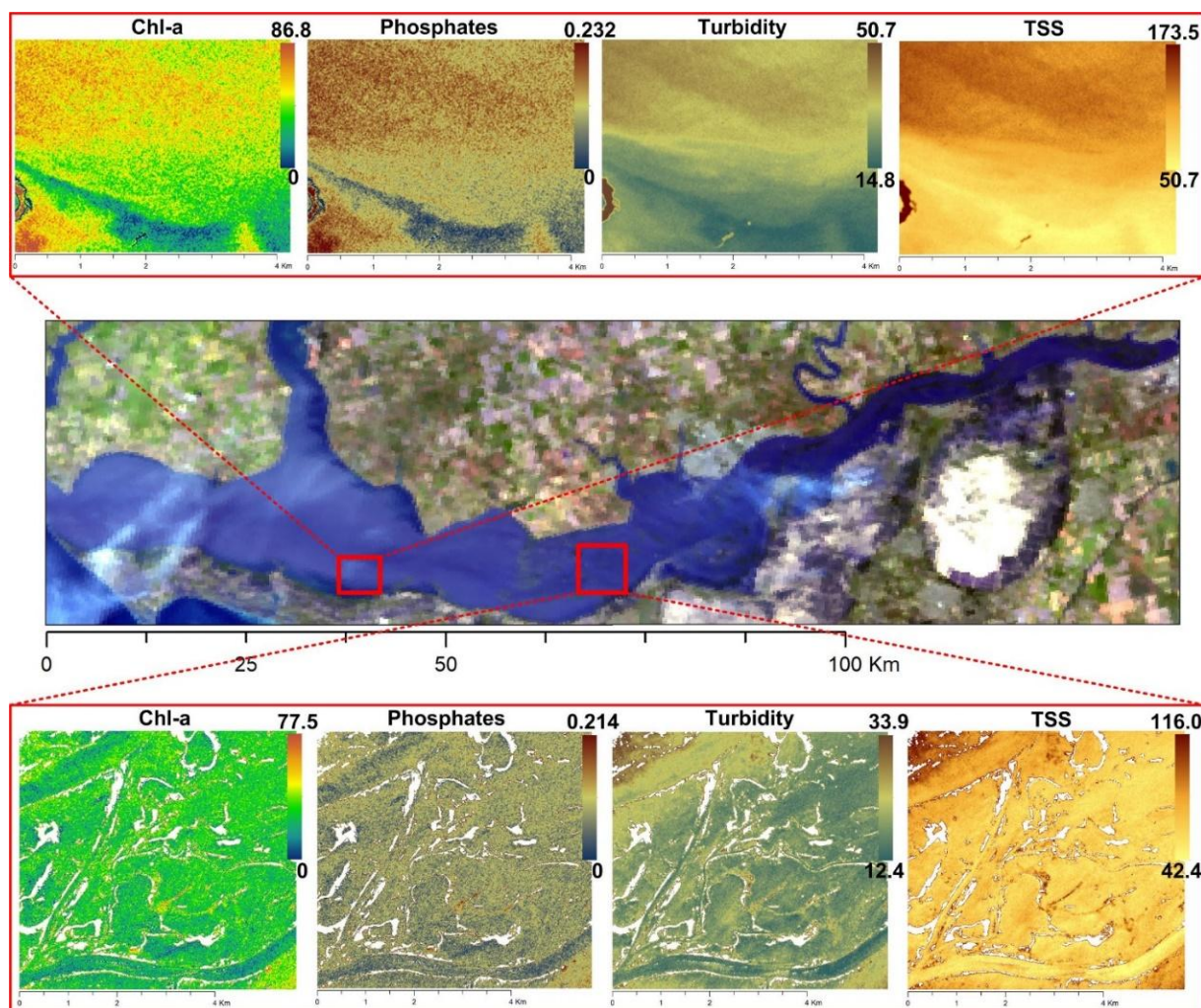


Figure 6. Transport of pollutants by surface flow in the Dniro-Buh estuary, as of 08/06/2023.

Calculation of Maximum Chlorophyll Index (MSI) according to the Sentinel-3 OLCI L1B imagery shows that polluted waters reached the Black Sea below the mouth of the Dniester River, the polluted area extending some 6800 km² by June 26, 2023 (Fig. 7).

At that time, in the coastal area of Odesa, the salinity of the sea decreased from 11.0 to 4.2g/dm³ and MPCs were exceeded for copper by 895 times, zinc 45 times, arsenic 3 times, and oil products by twice [1]. According to our calculations, the MCI in the Black Sea was 0.03, corresponding to a concentration of Chl-a of about 91.0 µg/dm³; phosphate 0.24 mgP/dm³ (1.2 MPC), turbidity 26.0NTU (7.4 MPC), total suspended solids 83.4 mg/dm³ (3.3 MPC), dry residue 9,220 mg/dm³ (9.2MPC), chloride 4260mg/dm³ (14.2MPC), sulphate 1,770 mg/dm³ (17.7 MPC), biological oxygen demand 110 mgO₂/dm³ (55.0MPC), chemical oxygen demand 451 mgO₂/dm³ (22.6 MPC). The MPC values were

calculated for fisheries; the maximum value of pollutant concentration was taken as 100%, and the sea areas with different levels of pollution were calculated on the basis of the ratio. The concentrations of pollutants were calculated in relation to the share of the total area of pollution in the Black Sea (6,800km²) where 29.3% of the water area was characterized by 0-10% of pollutant concentration, 31.8% of the water area accumulated 20-30% of pollutants, 22.9% of the water area had 30-40%; and 16.0% of the territory had >40%. One hundred and fifty dolphin deaths were officially recorded.

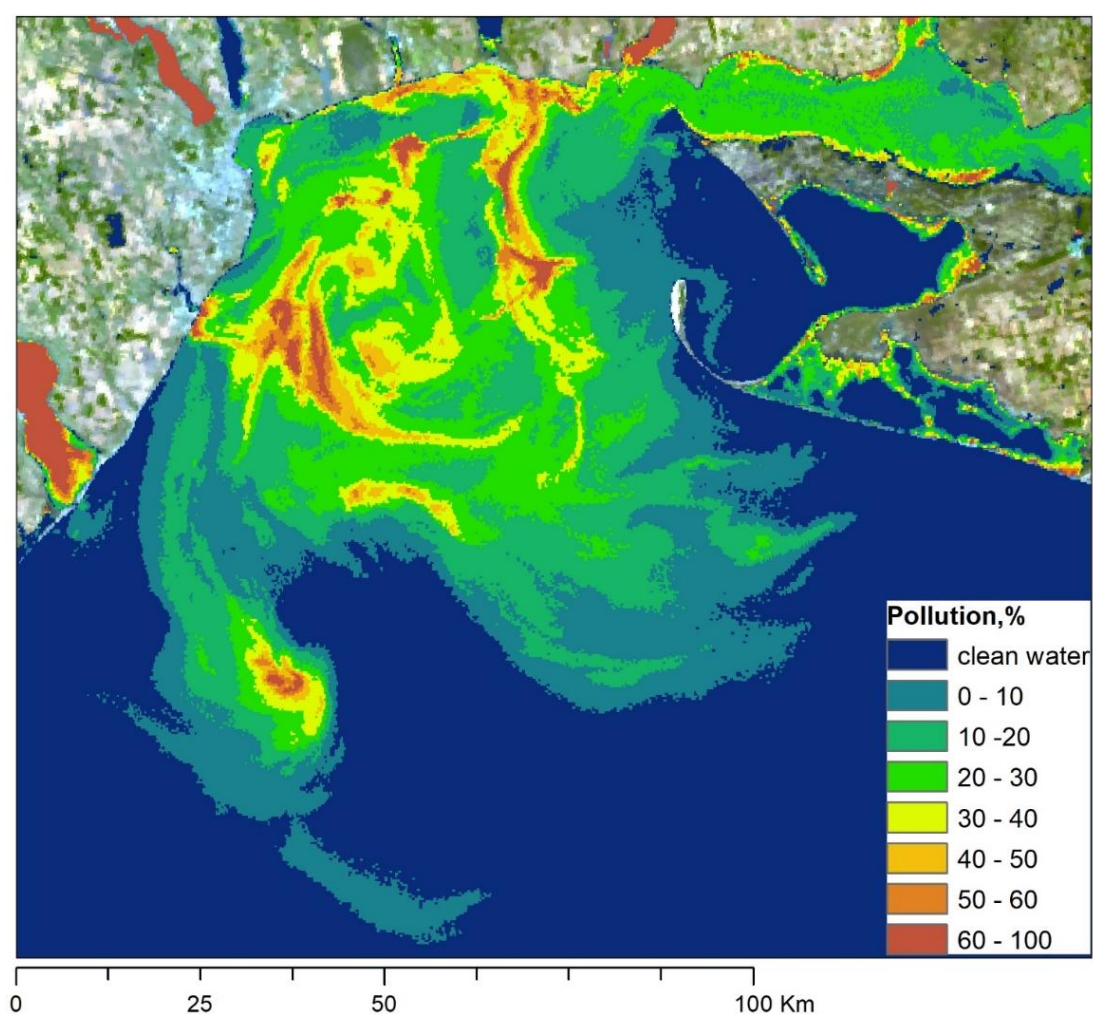


Figure 7. Spread of polluted waters in the Black Sea, 10-26/06/2023.

Destruction of the Kakhovka dam drained the reservoir that had extended over 2155 km², adding 230 km to the length of the Dnipro river bed that now has to be flushed by discharges from the smaller Dnipro reservoir upstream. Compared to the situation in 2018-21, the maximum seasonal fluctuations of the water level in the Lower Dnipro have decreased by 1.4-1.8 times, resulting in stagnant zones

in the Dnipro-Buh estuary and a sharp deterioration of water quality. Data of the State Environmental Inspectorate of the Southern Region of Ukraine were used to identify regularities of a change in dissolved oxygen (DO , mgO_2/dm^3).

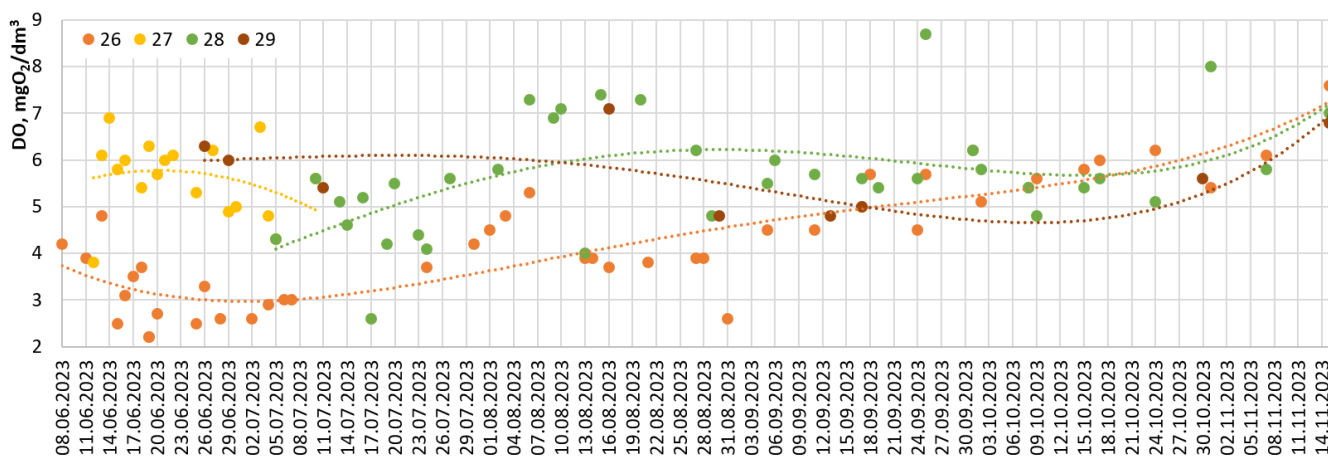


Figure 8. Dissolved oxygen in the waters of the Lower Dnipro and Inhulets River.

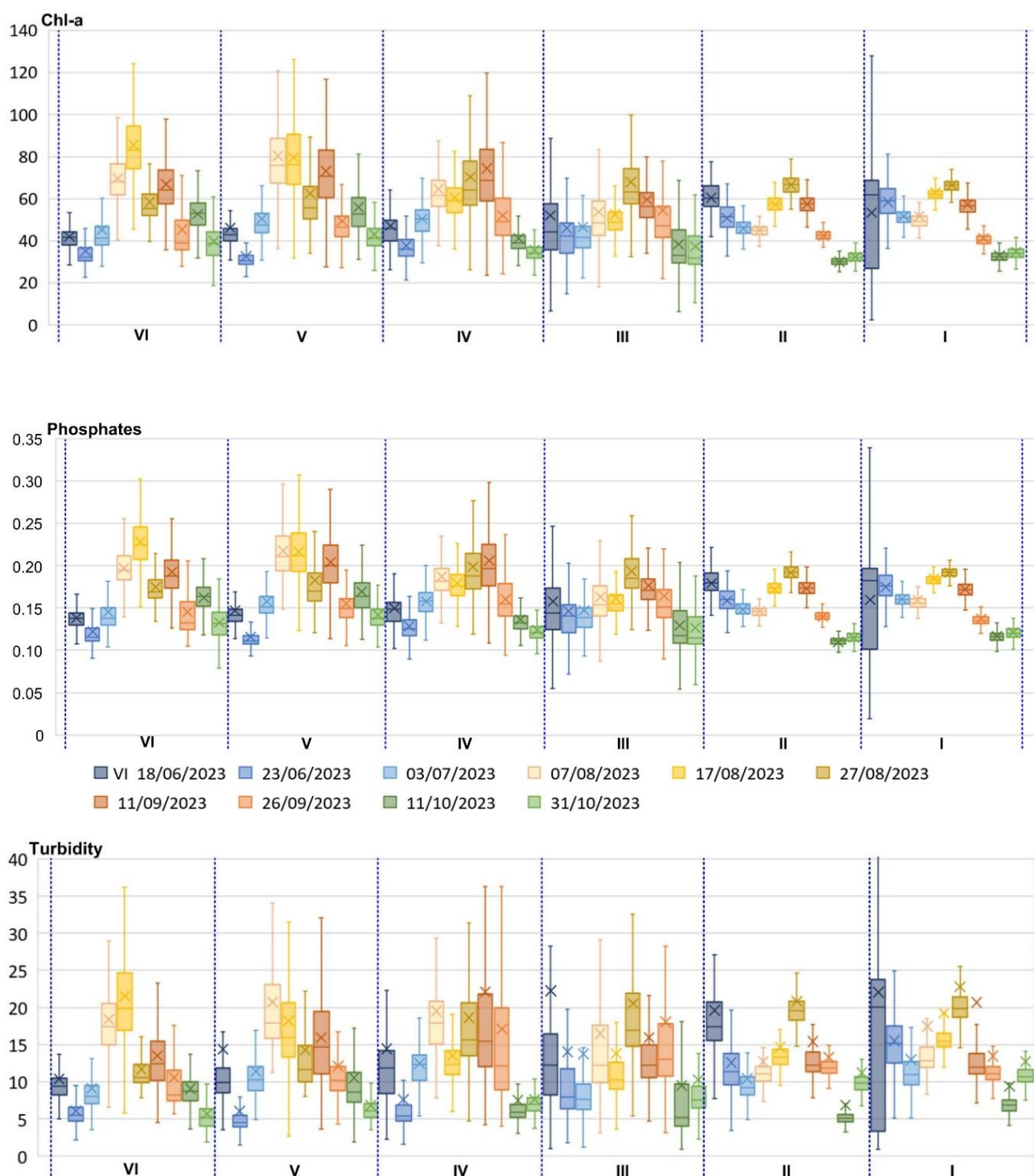
The deluge of polluted water sharply decreased dissolved oxygen in the period 08-15/06; DO reached a critical $4.8 \rightarrow 2.5 \text{ mgO}_2/\text{dm}^3$ ($0.80 \rightarrow 0.42 \text{ MPC}$) in the Inhulets River (sample 26) and in the Lower Dnipro near the Antonivka railway bridge (sample 27), DO fell from 6.9 to $5.8 \text{ mgO}_2/\text{dm}^3$ ($1.15 \rightarrow 0.97 \text{ MPC}$). In the period 15-25/06 when the water gradually receded, DO in the Inhulets River varied between 3.7 and $2.2 \text{ mgO}_2/\text{dm}^3$ ($0.62 \rightarrow 0.37 \text{ MPC}$); in the Dnipro River from 6.3 to $5.3 \text{ mgO}_2/\text{dm}^3$ ($1.05 \rightarrow 0.88 \text{ MPC}$).

As of June 18, 2023, there was a record high level of pollutants in the Lower Dnipro (Fig. 10).

In Sections I - III from the dam to the river mouth, Chl-a varied from $53.3\text{--}128.0 \text{ }\mu\text{g}/\text{dm}^3$ to $42.0\text{--}77.60 \text{ }\mu\text{g}/\text{dm}^3$; phosphate from $0.20\text{--}0.34 \text{ mgP}/\text{dm}^3$ ($1.0\text{--}1.7 \text{ MPC}$) to $0.1\text{--}0.25 \text{ mgP}/\text{dm}^3$ ($0.8\text{--}1.3 \text{ MPC}$); turbidity from $22.1\text{--}54.0 \text{ NTU}$ ($6.3\text{--}15.4 \text{ MPC}$) to $16.5\text{--}28.3 \text{ NTU}$ ($4.7\text{--}8.1 \text{ MPC}$); and total suspended solids from $76\text{--}185 \text{ mg}/\text{dm}^3$ ($3.0\text{--}7.4 \text{ MPC}$) to $57\text{--}97 \text{ mg}/\text{dm}^3$ ($2.3\text{--}3.9 \text{ MPC}$). From the end of June to the beginning of July 2023, pollutant concentrations in some riverbed areas were reduced as much as 3-fold by flushing into the estuary.

After the flood receded and until the beginning of August 2023, there was low but gradually increasing concentration of dissolved oxygen from 2.5 to $5.3 \text{ mgO}_2/\text{dm}^3$ ($0.42 \rightarrow 0.88 \text{ MPC}$) in the Inhulets River; from 4.3 to 5.8 ($0.72 \rightarrow 0.97 \text{ MPC}$) in the Dnipro River in Kherson (sample 28); and from 5.3 to 6.0 ($0.9 \rightarrow 1.0 \text{ MPC}$) within the river delta (sample 29). Chl-a varied between 46.6 and

67.2 $\mu\text{g}/\text{dm}^3$; phosphate 0.15-0.19 mgP/dm^3 (0.8-1.0 MPC); turbidity 10.5-17.3 NTU (3.0-4.9 MPC); and total suspended solids 35.9-59.2 mg/dm^3 (1.4-2.4 MPC). Low values of pollutants were observed in the estuary in relation to the background values of 2021, in particular: Chl-a, 27.8-69.8 $\mu\text{g}/\text{dm}^3$; phosphate 0.10-0.20 mgP/dm^3 (0.5-1.0 MPC); turbidity 3.5-18.6 NTU (1.0-5.3 MPC); and TSS 12.0-63.6 mg/dm^3 (0.5-2.5 MPC).



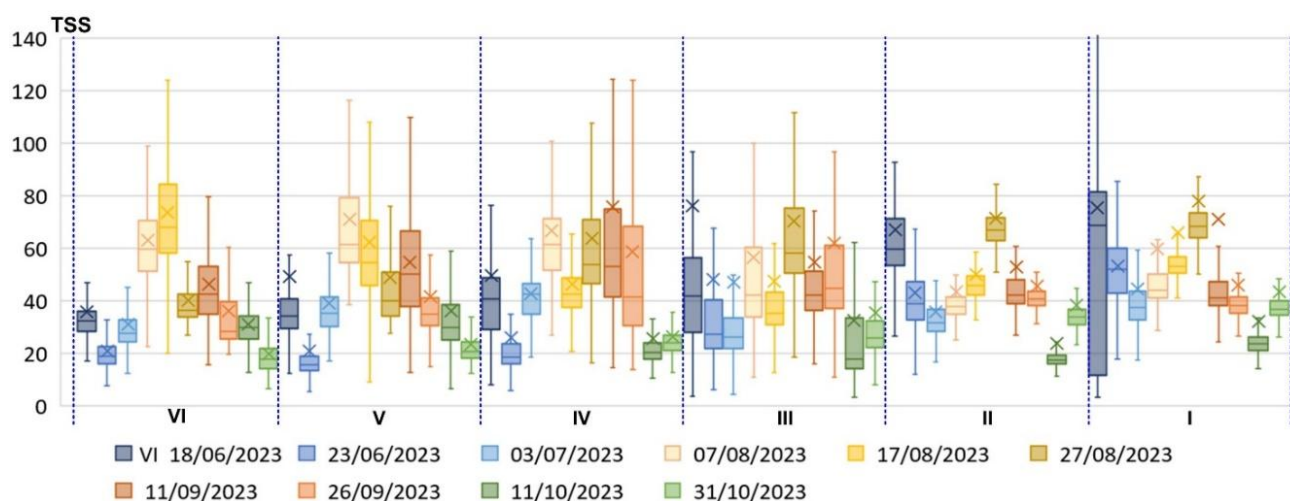


Figure 10. Water quality in the Dnipro-Buh estuary, 2023.

The seasonal maximum concentration of dissolved oxygen in samples 28 and 29 was registered at $6.9 \rightarrow 7.3 \text{ mgO}_2/\text{dm}^3$ (1.25 $\rightarrow$ 1.22 MPC) in the period of August 05-25 thanks to rainfall and slight flushing of the Lower Dnipro. But in the lower reach of the Inhulets riverbed there was a reversal, DO $5.3 \rightarrow 3.73 \text{ mgO}_2/\text{dm}^3$ (0.9 $\rightarrow$ 0.6 MPC) caused by accumulation of organic matter and an algal bloom. In this same period, there were concentrations of pollutants at the level of 1.1-5.5 MPC in the surface waters of the Dnipro riverbed and delta and they accumulated in the estuary at the level of 1.9-9.7 MPC.

Hot weather, systematic accumulation of pollutants and algal blooms caused eutrophication in the lower part of the river until the third decade of September: deficiency of dissolved oxygen (1.0 $\rightarrow$ 0.8 MPC) was observed in 80% of water samples and, in Dnipro riverbed Sections I and II, a polytrophic state prevailed with Chl-a, $54.9\text{-}78.7 \text{ }\mu\text{g}/\text{dm}^3$, phosphate $0.17\text{-}0.22 \text{ mgP}/\text{dm}^3$ (0.9 -1.1 MPC), turbidity 14.6-25.5 NTU (4.2-7.3 MPC), and TSS $50.0\text{-}87.3 \text{ mg}/\text{dm}^3$ (2.0-3.5MPC). The maximum content of pollutants in the waters of the estuary in the direction east $\rightarrow$ central $\rightarrow$ west varied at the level $4.3\text{-}9.0 \rightarrow 3.0\text{-}6.4 \rightarrow 2.2\text{-}4.6$ MPC.

As of September 25, dissolved oxygen peaked at $8.7 \text{ mgO}_2/\text{dm}^3$ (1.5MPC) thanks to water discharges from the Dnipro reservoir and flushing of the Lower Dnipro riverbed. In this period, pollutant concentration in the Dnipro riverbed was reduced by 40-47 %. The satellite image of September 26 shows a substantial release of pollutants in the Eastern estuary at the level of 5.0-10.4 MPC.

The seasonal decrease in surface and water temperatures from early October led to an increase in the concentration of dissolved oxygen in all the water samples by early November: $6.8 \rightarrow 7.6 \text{ mgO}_2/\text{dm}^3$ (1.1 $\rightarrow$ 1.3MPC). From 11-31 October 2023, the concentration of pollutants in the Lower Dnipro

decreased: in Sections I and II, Chl-a 25.2-34.8 $\mu\text{g}/\text{dm}^3$; phosphate, 0.10-0.12 mgP/dm^3 (0.5-0.6 MPC); turbidity, 3.3-14.1 NTU (0.9-4.0 MPC); TSS, 11.3-48.3 mg/dm^3 (0.5-1.9 MPC). In the delta (Section III), pollutant concentrations fell by 2.2-2.4 times, and in the estuary by 2.0-2.7 times in the eastern section (IV), by 1.9-3 times in the Central area (V), and by 2.2-3.8 times in the western area (VI).

Discussion

The wartime disruption of hydrology and biophysical processes in the Dnipro-Buh estuary can hardly be exaggerated: lesser flow velocity, lower water levels, worse water balance, stagnation and an increase in the water temperature and accumulation pollutants beyond maximum permissible concentrations – particularly in July-September with increased demands on water resources, diffuse pollution, surface runoff and sewage, and acceleration of biochemical processes.

The Lower Dnipro has been transformed from mesotrophic to polytrophic, water class from *clean* to *dirty*, saturation of surface waters with biogenic elements has increased twofold (Fig. 11a). In 2022-3, compared to 2021, algal chlorophyll density increased by 1.5→2.9 times (Fig. 11b) and turbidity (Fig. 12a) and total suspended solids (Fig. 12b) increased 4-fold.

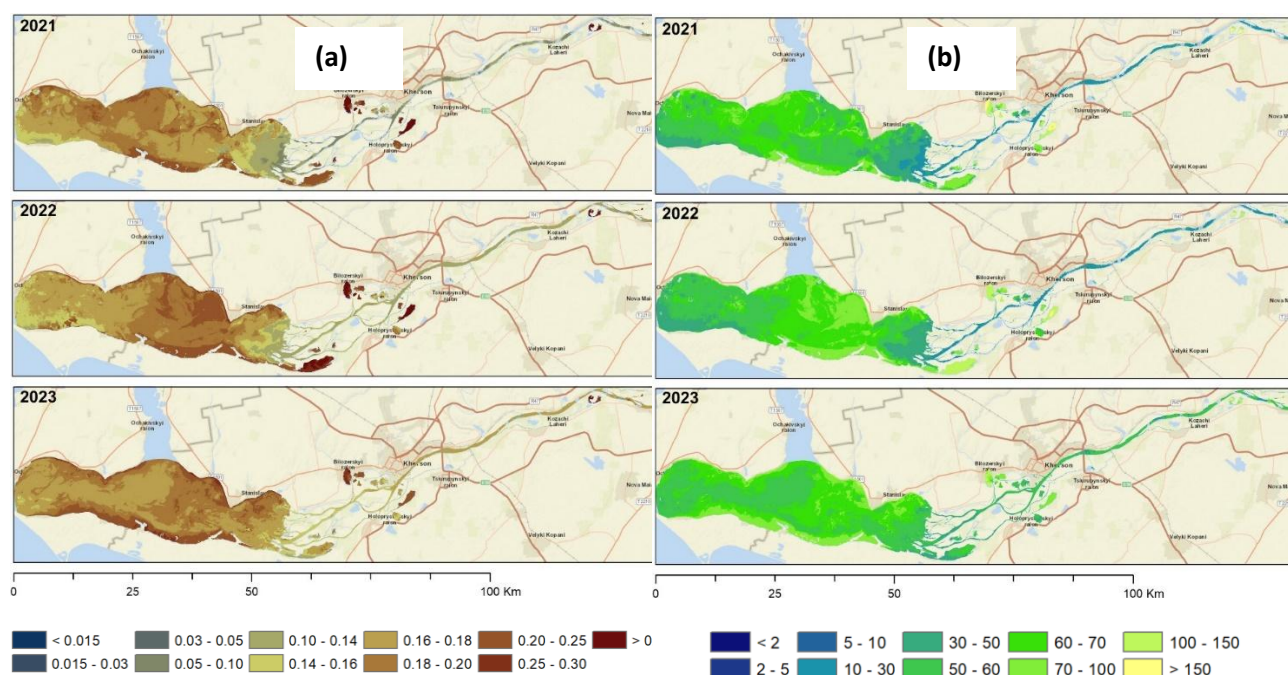


Figure 11. Concentration of phosphate (a, mgP/dm^3) and Chl-a (b, $\mu\text{g}/\text{dm}^3$) in the Dnipro-Buh estuary, July-September, 2021/23.

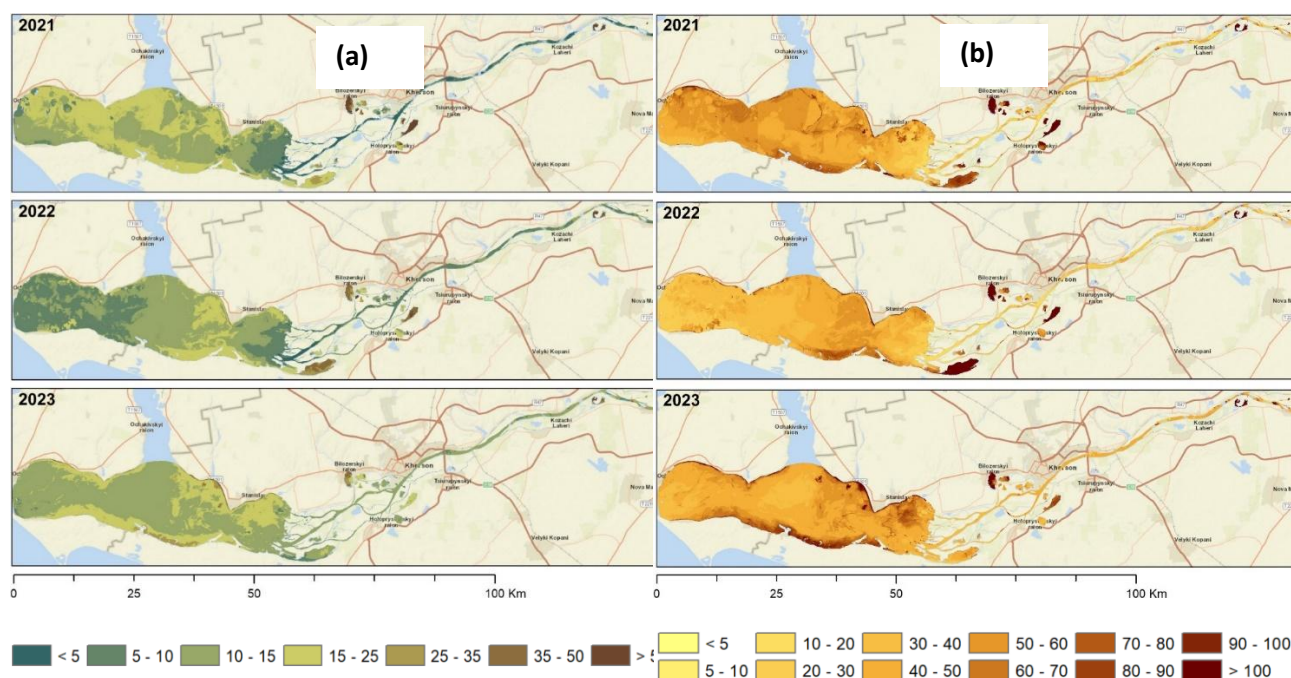


Figure 12. Water turbidity (a, NTU) and total content of suspended solids (b, mg/dm³) in the Dniro-Buh estuary, July-September, 2021/3.

In the floodplain lakes of the delta (Section III), Chl-a increased by 1.3 times in 2022 compared to 2021. Their trophic status depends on a hydrological connection with the main river channel. Primary and secondary production contributes to intensive growth of bottom sediments; eutrophication and the volumes of runoff affect the balance of nutrients in the lakes - accelerating or restraining sedimentation. Floods flush out the bottom sediments, as we saw at the time of the destruction of the Kakhovka dam when the concentration of biological and physical-chemical substances in the floodplain lakes dropped by 35-55%.

Since the waters of the Dniro River account for well over 90 per cent of the activity of the Dniro-Buh estuary, the overwhelming effect of the destruction of the Kakhovka dam has been degradation. In the Eastern area of the estuary (Section IV) there was an increase in the average seasonal concentration of Chl-a by 42%, phosphate by 21%, turbidity by 98 %, TSS by 79%; in the Central area (Section V) there was a rise in the content of Chl-a 6.5%, phosphate by 6 %, turbidity and TSS by 7%; although additional accumulation of pollutants was insignificant in the Western area (Section VI). The estuary as a whole has become polytrophic. According to the level of biogenic pollution by phosphate, the water area lost patches with *Clean Enough* water, whereas the patches with *Moderately Polluted* and *Dirty* water expanded from 77.2→92.5% and this has slighted the integrity of the ecosystem.

Conclusions

- The pre-war management of aquatic ecosystems might be described as negligent but the Russian assault has brought catastrophic destruction of both water infrastructure and the natural ecosystems in the South of Ukraine, in particular the Dnipro-Buh estuary.
- Sabotage of the Kakhovka dam on 06/06/2023, released more than 20BCM of stored water carrying a mass of pollutants down the Lower Dnipro to the Dnipro-Buh estuary and the Black Sea. The excess concentration of pollutants amounted to 1.1-51.8 MPC, extending over about 6800km².
- As well as the loss of one third of the country's engineered fresh water reserves, the destruction of the Kakhovka dam and reservoir eliminated the main mechanism for flushing the lower Dnieper and its estuary.
- In turn, this has more than doubled the saturation of the river water with biogenic elements; increased growth of algal blooms threefold; and brought a 4-fold deterioration of transparency and total suspended solids. Compared to the pre-war period, the degraded area of the Dnipro-Buh estuary has increased by 15-28 %. In 2023, 95% of the water area was polytrophic; and more than 70% of the water areas have experienced disruption of hydro-ecosystem sustainability and ecological regression.

Acknowledgments

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Geolocation

Polygon coordinates: 30.380493,45.859787; 30.405213,46.734336; 32.609619,46.706099; 33.299011,46.826471; 33.381409,46.71363; 32.274536,46.415353; 32.26355,45.848311; 30.380493,45.859787

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