

## Article

# Ecological Conditions of the Lower Dniester and Some Indicators for Assessment of the Hydropower Impact

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**Abstract:** The Dniester is one of the largest transboundary rivers of the Black Sea basin, and its lower reaches integrate the influence of climate change and hydropower plant (HPP) impact on the waterway. The decrease in precipitation and average annual air temperature increase and intensive hydroelectric construction have led to a decline in the total water content of the river, during the last 10 years, being below the long-term historical “norm”. The shifts in the river flow result in multidirectional seasonal dynamics of nutrient concentrations. During the modern period, a stabilization of nutrient concentrations takes place, being lower than at the peak of eutrophication in the 1970s–1980s, but higher than in the natural flow period. The construction of reservoirs leads to a long-term decline in silica concentrations, continuing in the modern period. The concentration of heavy metals and metalloids in water and bottom sediments of the river generally corresponds to the ecological status of “Moderate”. Biological communities show a high  $\beta$ -diversity of microalgae, but low diversity of plankton and benthic invertebrates. Biological communities respond to the impact of HPP in both the short- and long-term. Hydroelectric dams change the bioavailability of nutrients downstream which, in the long-term, causes shifts in phytoplankton composition, especially the reduction of Bacillariophyta due to the lack of silicates that are deposited in reservoirs. However, in the short-term, after the discharge from the HPP dam, the concentration of silicates and the proportion of diatoms increase. Long-term changes also include a decline in the proportion of Rotifera and an increase in Copepoda in the total abundance of zooplankton and the unification of the benthic community with an increase in the biomass of gastropods in the area, which can be considered as indicators of the impact of hydroelectric power plants. The saprobity index, calculated both for zooplankton and macrozoobenthos, characterised the water as moderately polluted; benthic biotic indexes (Biological monitoring working party (BMWP), Belgian Biotic Index (BBI), Danish Stream Fauna Index (DSFI)) calculated on macrozoobenthos described the condition as “low” quality.

**Keywords:** hydropower impact; dam; big river; river runoff; nutrients; metal pollution; long-term dynamics; phytoplankton; zooplankton; macrozoobenthos; patch dynamics; potamal; ponto-caspian region; Ukraine; Moldova

## 1. Introduction

The Dniester is the largest river in Western Ukraine and the Republic of Moldova. The total length of the Dniester is 1362 km. Ukraine owns the upper reaches of the Dniester and its estuarine part with a total length of 705 km, a section of the river 220-km long, is

adjacent to Ukraine and Moldova, and a part of the river, running for 437 km, is located in the territory of Moldova. The area of its basin is 72,100 km<sup>2</sup>, 26.4% of which is located in the territory of the Republic of Moldova, 0.6% in Poland, and 73% in Ukraine [1,2]. According to the sources of water supply, water regime, and physical and geographical features, the Dniester River basin is divided into three parts:

- Upper-Carpathian (from the source to the Nizhnee village, the mouth of the river Tlumach, length 296 km).
- Middle-Mohyliv-Podilskyi (from the Nizhnee village to Dubossary, length 715 km).
- Lower (from the dam of Dubossary Hydro Power Plant (HPP) to the mouth, length 351 km) [2].

The environmental state of rivers is primarily determined by their hydrological regime. At the same time, the Dniester ecosystem has suffered from eutrophication processes as a result of the so-called global “green revolution” because of the use of nitrogen and phosphorus fertilizers.

In the hydrological state of the Dniester River, the following periods may be distinguished:

- prior to 1954, the natural period without flow regulation and without significant eutrophication, when the hydrological and hydrochemical regimes were formed only under the influence of natural factors. During this period, significant fluctuations in water flow were associated with snow melting and frequent storm floods in the catchment area. Also, there was a time when significant anthropogenic eutrophication was absent.
- 1954–1987, the period of partial flow regulation. This period began while the Dubossary reservoir and the Dubossary hydropower plant (HPP) were put into operation, which led to a decrease in the flow rate and water turbidity. In the 1960s, the process of anthropogenic eutrophication began, and the 1970s were the time of the strong eutrophication impact.
- 1987–2009, when the Dniester reservoir and the Dniester hydroelectric (Dniester HES-1) power station were put into operation. During this period, the hydrological regime of the Dniester middle part was considered fully regulated. As well, the 1980s were a period of extremely high eutrophication levels. The collapse of the Soviet Union in 1991 triggered an economic downturn, followed by a decline in anthropogenic eutrophication.
- Since 2009, when the first hydroelectric unit of the pumped-storage power plant (PSPP) was put into operation, the reservoir is used as the lower reservoir of the PSPP. The morphometric characteristics of the buffer reservoir and the flow regime underwent some changes. Thus, the time since 2009 can be considered as a sub-period of the third (fully regulated) period.

The aim of our study was to evaluate the current ecological state of the Lower Dniester and to identify the indicators of the hydropower plants’ (HPPs) construction impact. For the complex assessment of the current environmental state, we used the data on river hydrology, standard hydrochemistry and pollution of water and bottom sediments, phytoplankton, zooplankton, and macrozoobenthos. The study was carried out under the project with code BSB165 HydroEcoNex.

## 2. Materials and Methods

### 2.1. Study Area and Sampling Sites

During the research period from 2018 to 2020, water and bottom sediment and biological samples were taken in the Lower Dniester at two stations: near Palanca village (51 km highway or 27 km of the Dniester from the confluence of the Dniester estuary; 46.419 N 30.17389 E), at a distance of 324 km from the Dubossary hydropower plant and near the Maiaky village (46.4128 N 30.2627 E) at a distance 15 km from the Dniester estuary (Figure 1).



**Figure 1.** Map of the investigated area of the Lower Dniester (HPP = hydropower plants; HGS = hydrological gauging stations).

The main difference between the selected stations is that Palanca is the furthest upstream point on the border of Ukraine with Moldova, and the Maiaky station is located below the confluence of the Turunchuk and Dniester rivers. The width of the river in the Palanca site is up to 80 m, and the average depth is 3.2 m. In 2018–2020, the average annual runoff volume reached about  $3.32 \text{ km}^3$ , the average annual discharge was  $105 \text{ m}^3 \text{ s}^{-1}$ , and the average flow velocity was  $0.32 \text{ m s}^{-1}$ , varying from  $1.1\text{--}1.2 \text{ m s}^{-1}$  during floods down to  $0.15\text{--}0.25 \text{ m s}^{-1}$  during the autumn–summer low-water period. The river width at the Maiaky site reaches up to 180 m, the average depth is 3.4 m, the average annual runoff volume is  $7.71 \text{ km}^3$ , and the average annual discharge is  $245 \text{ m}^3 \text{ s}^{-1}$ . Within the study period, the average flow velocity was  $0.35 \text{ m s}^{-1}$ , varying from  $1.25\text{--}1.35 \text{ m s}^{-1}$  during floods down to  $0.15\text{--}0.25 \text{ m s}^{-1}$  during the autumn–summer low-water. As mentioned, the Palanca site is the furthest upstream point on the border between Moldova and Ukraine (reference point of observation on the Dniester by the Institute of Zoology of Moldova), the Maiaky site is a hydrological, hydrochemical, and hydrobiological long-term research point, located in the Ukraine territory. The choice of these stations made it possible to make a comparison of the obtained data with published historical data [2–16]. The right bank of the Dniester, where samples were taken, is raised above the water level, to 10 m in the Palanca area and up to 20 m in the Maiaky area, with trees and shrubs on the bank and grassy-moss soil cover. Downstream of the Maiaky station, there are flooded areas and the shore is lowered. The bottom substrates of the river are represented by pelal (black and grey silts and sandy silts), particulate organic matter, psamal and akal mixture substrates (sands with granite gravel), and rare woody detritus increases in the section of the river in the Maiaky area. The high water plants are represented by a coastal strip of *Phragmites Adans.*, *Myriophyllum spicatum* L., etc. [11].

Sampling for plankton and hydrochemical data was carried out in flowing sections; samples were taken from the central part of the river by boat, and in the absence of a boat, they were taken by entering the river and using a throw-in container, at a distance of at least 4 m from the shoreline. Water column samples for biological (phyto- and zooplankton) and hydrochemical analyses were taken monthly. Bottom sediments for zoobenthos and pollution were sampled in the coastal part at depths of no more than

0.8–1.5 m. Zoobenthos samples and samples of water and bottom sediments for metal concentration were taken seasonally.

## 2.2. Hydrological Analysis

The most representative and comprehensive long-term hydrological data that could be used for reliable evaluation of the annual Dniester flow was collected at Bender hydrological gauging station.

The hydrological gauging station (HGS) near the city of Bender produces long-term data showing Dniester runoff from a catchment area of 66,100 km<sup>2</sup> (91.7% of the entire Dniester catchment area). The hydrological observations have been conducted here since 1881 [17].

For a comparative analysis of the total runoff of the Dniester River, starting from 1946, data on the measured level and discharge of water were used for:

- Zalishchyky HGS, catchment area 24,600 km<sup>2</sup>, the upper part of the Dniester basin.
- Mohyliv-Podilskyi HGS, catchment area 43,000 km<sup>2</sup>, middle part of the basin.
- Bender HGS, catchment area 66,100 km<sup>2</sup>, the lower part of the basin.

In addition, data from the Maiaky HGS cover a catchment area of 72,000 km<sup>2</sup>, located at the furthest downstream point, where daily monitoring measures only water level.

The data relating to water level and discharge daily observations, plus air temperature and precipitation, were taken from the archive of the Hydrometeorological Centre for the Black and Azov Seas, Odesa, Ukraine. The values of water discharge and runoff volume at the Maiaky HGS were obtained using calculated analytical formulas [17].

## 2.3. Chemical Methods

The concentrations of dissolved oxygen, total suspended solids, and nutrients were measured using standard methods [18,19]. The total number of samples was 58 for each parameter. The following parameters have been analysed: Temperature, pH, Dissolved Oxygen (DO), Total Organic Carbon (TOC), Biological Oxygen Demand (BOD<sub>5</sub>), Total Suspended Solids (TSS), dissolved inorganic nitrogen species (NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>), Total Dissolved Nitrogen (TDN), Total Organic Nitrogen (TON) as a difference between TDN and DIN, Dissolved Inorganic Phosphorus (DIP), Total Dissolved Phosphorus (TDP), Dissolved Organic Phosphorus as a difference between DIP and TDP, and silicates (Si).

In waters and bottom sediments in the Lower Dniester, the concentration of 10 heavy metals and metalloids was determined: highly hazardous As, Pb, Cd, Hg, Zn, Cr, moderately hazardous Cu, Ni, Co, and low hazardous Fe.

Surface water samples collected for metals analysis were filtered through a membrane with pore size of 0.45 µm. Dissolved metals were determined in seawater samples, acidified up to pH = 2 with Ultrapure HNO<sub>3</sub>.

Sediment samples were treated with a mixture of ultrapure acids HNO<sub>3</sub>, HCl, after which HF was added.

For instrumental analysis and quantification of metals, electrothermal furnace atomic absorption spectrometry (AAS-ET Analytik Jena AG ZEENIT 650P) was employed. Calibration for concentration of metals was undertaken with working standards for each element, starting from stock solutions of 1000 µg L<sup>-1</sup> (Sigma-Aldrich). At least three instrumental readings have been undertaken for each sample, with an average value reported. The work domains were as follows: water Cd 0–1 µg L<sup>-1</sup>; other metals 0–40 µg L<sup>-1</sup>; sediment Cd 0–2 µg L<sup>-1</sup>; other metals 0–80 µg L<sup>-1</sup>. Quality Control of the analysis results was carried out by control analysis of reference materials [20–27].

## 2.4. Biological Methods

Samples of phytoplankton were processed according to standard methods [19,28,29]. The total number of phytoplankton samples was 58 during 2018–2020. In 2020, phytoplankton samples were taken from the centre of the flowing reaches of Dniester from the

surface/subsurface and bottom layers of water using a Niskin's bathometer. The sample, with a volume of around 2 L, was decanted twice up to an approximated volume of 20 millilitres, from which several subsamples of 0.05 mL were examined. Species identification was carried out with the help of a light microscope LOMO MIKMED 5 ( $\times 600$ ) and appropriate keys [30–32].

Samples of zooplankton were processed according to standard methods [19,33]. The total number of zooplankton samples was 58 during 2018–2020. Samples were taken by a small Apstein-net, with mesh size of 100  $\mu\text{m}$ . The total volume of filtered water was 100–200 L per sample. The samples were concentrated to a volume of 20–100 mL, depending on visual analysis of suspended particles concentration in the water. Taxonomic analysis was carried out using a stereoscopic microscope Rubin MBS-10 ( $\times 28$ –98), light microscope LOMO MIKMED 5 ( $\times 300$ –600) and appropriate keys [34–36]. In order to analyse the community structure and the share of higher taxa, Shannon's index was used. The environmental status of zooplankton was evaluated according to Pantle–Bukh recommendations based on project and own published data [4,5,37].

Samples of zoobenthos were collected according to standard methods with an Ekman bottom grab (sampling area 0.025  $\text{m}^2$ ) or D-net (sampling area 0.025  $\text{m}^2$ ), and a rectangular dredge with a sampling track of 8 m. This was washed through a sieve (mesh 0.5  $\text{mm}^2$ ). For qualitative samples, a pond net, with manual collection from various substrates, was used [19]. The total number of samples was 24 (Maiaky-12, Palanca-12). Invertebrates were preserved in 4% formaldehyde, then analysed using a stereoscopic microscope Rubin MBS-10 ( $\times 28$ –98) and light microscope LOMO MIKMED 5 ( $\times 300$ –600) (UkrSCES), with Axio Imager A.2 microscope (Zeiss) ( $\times 600$ ) and a SteREO Discovery.V8 binocular microscope (Zeiss) ( $\times 16$ –120) (Institute of Zoology). The specimens were identified with appropriate keys [35,38–41]. To assess the structure of communities, we used indicators and indices recommended by European and American scientists for assessing the impact of hydraulic structures on aquatic ecosystems: abundance, biomass, ratio of taxonomic groups, Shannon's index, proportion of functional feeding groups (FFG), Zelinka–Marvan saprobity index and saprobity index in modification for Romanian waters, UK Biological Monitoring Working Party (BMWP), Belgian Biotic Index (BBI), Danish Stream Fauna Index (DSFI), Lotic-invertebrate Index for Flow Evaluation (LIFE), and Potamon Type Index (PTI) [37,42–49].

The historical data on the Lower Dniester, covering all the periods indicated above, were taken from literature, in order to analyse the long-term dynamics of the ecosystem components [2–16].

### 2.5. Data Analysis

The calculations were carried out using MS Excel 2019. Correlation analysis for phytoplankton and zooplankton organisms and measured hydrological or chemical parameters was undertaken with Primer 7 and Statistica 10. The structure and functional composition of macrozoobenthos and its environmental state were estimated with the free software Asterics 4.0.4 [50].

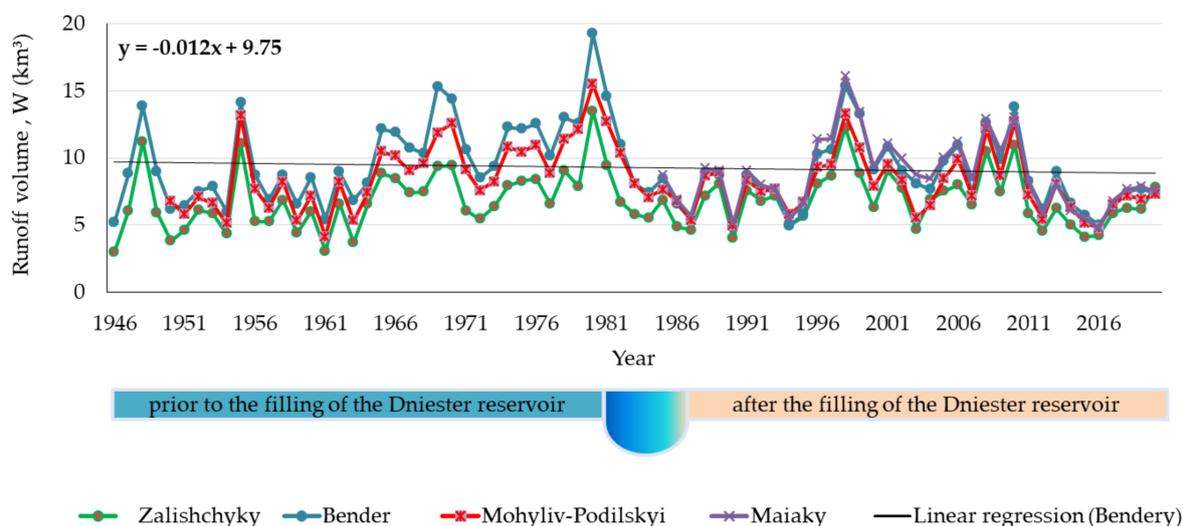
Taxon names are given according to WORMS ([www.marinespecies.org](http://www.marinespecies.org), accessed on 18 October 2021), Algae Base ([www.algaebase.org](http://www.algaebase.org), accessed on 18 October 2021) and Fauna Europea (<https://fauna-eu.org>, accessed on 18 October 2021).

## 3. Results

### 3.1. Runoff State of the Lower Dniester

The current environmental and anthropogenic conditions have led to a decrease in the total volume of the Dniester River, which for almost 10 years has not been able to reach the value of the statistical "norm", estimated as a long-term average of 9.2–10.2  $\text{km}^3$ . The phase of low volume, which began in 2011 (Figure 2), reached a minimum value in 2016, with annual runoff volume of 4.74  $\text{km}^3$  at the outlet section at the Maiaky HGS (catchment area 72.000  $\text{km}^2$ ). In 2018, 2019, and 2020 the annual runoff at the Maiaky HGS

was 7.67, 7.89, and 7.57 km<sup>3</sup>, respectively. Low flow-rates in the same years, due to releases from the Dniester reservoir, were kept at a level of 145–155 m<sup>3</sup> s<sup>-1</sup> at the Maiaky HGS. At the same time on the Dniester River, in the Chobruch-Olonesti section, the estimated discharge reached 65 m<sup>3</sup> s<sup>-1</sup>, and on the Turunchuk River, on the Chobruch-Belyayivka section-85 m<sup>3</sup> s<sup>-1</sup>. The maximum average daily discharge during the floods of 2018, 2019, and 2020 at the Maiaky HGS reached values of 850, 1100, and 1300 m<sup>3</sup> s<sup>-1</sup>.



**Figure 2.** Combined hydrograph of annual runoff volumes for the 1946–2020 period within selected hydrological gauging stations.

### 3.2. Hydrochemistry of the Lower Dniester

In the modern period, three key factors have affected the nutrient regime of the Lower Dniester:

- (1) Stabilization of nutrient runoff by reducing the use of fertilizers in the catchment area.
- (2) Smoothing flow variability, as a result of the system of reservoirs.
- (3) Transformation of river runoff because of climate change, as well as massive deforestation in the upper catchment, where the bulk of the runoff originates.

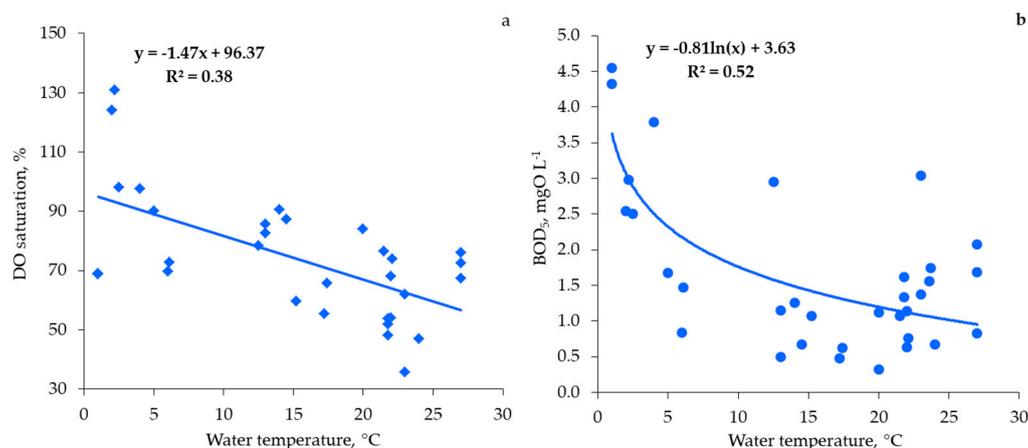
The temperature conditions are characterised by significant annual variation (from 1° to 27 °C) since seasonal air temperature variations in temperate latitudes are high. During the period of study, we observed winter water temperatures in the range of 1.0–4.0 °C with an average value of 2.4 °C. The average value in spring was of 12.5 °C and varied in the range 5.0–17.3 °C. In the summer, the highest values of water temperature occur (mean 23.4 °C, minimum 22.0 °C, maximum 27.0 °C). Cooling of air in autumn leads to decrease in water temperature down to an average value of 15.5 °C with cooling of water from 23.7 °C in September to 6.1 °C in November.

In the annual dynamics of dissolved oxygen, a winter peak and a summer minimum are normal. Moreover, only winter concentrations are close to saturation level. The average value of oxygen saturation in the winter is 98% with fluctuations from 69% to 127% (Table 1), equivalent to 9.8 to 12.3 mg L<sup>-1</sup>. In the spring, the average saturation is 81% (8.5 mg L<sup>-1</sup>), and in the summer 63.5% (5.5 mg L<sup>-1</sup>). In the autumn, there is a slight increase in concentration. The decline in DO level relates to consumption for the oxidation of organic matter. Since respiration depends on the water temperature, the decrease in the DO concentration seems to be as expected (Figure 3). It is most likely that the low oxidation rate of organic matter at low temperatures in situ is responsible for high BOD<sub>5</sub> values in the cold period, as can be seen from Figure 3b. The TOC values are also maximum in winter, which is consistent with a high BOD<sub>5</sub>.

**Table 1.** Seasonal variations of nutrients of the Lower Dniester in 2018–2020 (above the line, average values and standard error; below the line, range of variation).

Season	DO	TOC	BOD <sub>5</sub>	TSS	Nitrogen Species						Phosphorus Species			Silicate
					NH <sub>4</sub> <sup>+</sup>	NO <sub>2</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	DIN	DON	TDN	DIP	DOP	TDP	
					mgN L <sup>-1</sup>						mgP L <sup>-1</sup>			
Winter	98.0 ± 12.0	7.3 ± 2.0	3.37 ± 0.45	8.2 ± 5.6	0.093 ± 0.020	0.021 ± 0.010	1.76 ± 0.42	1.87 ± 0.42	1.09 ± 0.18	2.95 ± 0.48	0.084 ± 0.004	0.024 ± 0.004	0.107 ± 0.007	2.87 ± 0.23
	68.9–127	4.2–11.8	2.50–4.44	1.9–25.1	0.050–0.144	0.010–0.050	0.99–2.74	1.08–2.88	0.59–1.36	1.88–3.89	0.075–0.091	0.013–0.032	0.088–0.121	2.39–3.29
					0.064 ± 0.030	0.032 ± 0.010	1.66 ± 0.24	1.88 ± 0.28	0.78 ± 0.19	2.66 ± 0.47	0.065 ± 0.006	0.018 ± 0.001	0.083 ± 0.005	2.28 ± 0.30
Spring	81.1 ± 6.9	5.0 ± 1.5	0.97 ± 0.25	30.6 ± 7.2	0.030 ± 0.014	0.010 ± 0.016	1.66 ± 0.24	1.88 ± 0.28	0.78 ± 0.19	2.66 ± 0.47	0.065 ± 0.006	0.018 ± 0.001	0.083 ± 0.005	2.28 ± 0.30
	60.6–90.2	3.4–9.6	0.55–1.67	13.3–45.1	0.131–0.085	0.060–0.038	1.27–2.37	1.50–2.52	0.51–1.23	2.10–3.75	0.055–0.077	0.016–0.020	0.075–0.093	1.71–3.13
					0.085 ± 0.039	0.038 ± 0.004	1.17 ± 0.14	1.30 ± 0.14	1.10 ± 0.24	2.50 ± 0.11	0.061 ± 0.014	0.036 ± 0.015	0.097 ± 0.009	3.44 ± 0.34
Summer	63.5 ± 5.5	6.4 ± 1.5	1.23 ± 0.23	24.1 ± 4.3	0.039 ± 0.016	0.004 ± 0.031	1.17 ± 0.14	1.30 ± 0.14	1.10 ± 0.24	2.50 ± 0.11	0.061 ± 0.014	0.036 ± 0.015	0.097 ± 0.009	3.44 ± 0.34
	47.3–71.9	4.3–10.7	0.63–1.67	17.4–36.6	0.170–0.025	0.047–0.034	0.94–1.58	1.08–1.62	0.55–1.44	2.17–2.84	0.023–0.087	0.008–0.063	0.082–0.123	2.89–4.41
					0.025 ± 0.004	0.034 ± 0.004	0.55 ± 0.24	0.58 ± 0.27	1.55 ± 0.47	1.68 ± 0.38	0.091 ± 0.019	0.050 ± 0.015	0.141 ± 0.015	4.23 ± 0.27
Autumn	67.4 ± 4.3	5.4 ± 1.1	1.51 ± 0.39	19.5 ± 5.2	0.004 ± 0.016	0.004 ± 0.018	0.55 ± 0.24	0.58 ± 0.27	1.55 ± 0.47	1.68 ± 0.38	0.091 ± 0.019	0.050 ± 0.015	0.141 ± 0.015	4.23 ± 0.27
	55.3–78.4	2.4–8.5	0.72–2.95	7.6–39.0	0.035	0.040	0.09–1.43	0.15–1.48	0.62–2.69	0.89–2.84	0.022–0.137	0.018–0.102	0.103–0.184	3.44–4.83

Abbreviations: DO-Dissolved Oxygen, TOC-Total Organic Carbon, BOD<sub>5</sub>-Biological Oxygen Demand, TSS-Total Suspended Solids, TDN-Total Dissolved Nitrogen, TON-Total Organic Nitrogen as a difference between TDN and DIN, DIP-Dissolved Inorganic Phosphorus, TDP-Total Dissolved Phosphorus, DOP-Dissolved Organic Phosphorus.



**Figure 3.** Saturation of dissolved oxygen (a) and biochemical oxygen demand (b) vs. water temperature.

Winter is the period for maximum concentrations of nitrogen species (ammonium, nitrates, total nitrogen). Due to the decomposition of plankton and detritus, an increase in the concentration of dissolved nutrients in winter is a common occurrence, when the content of suspended matter is released into a dissolved form. The concentrations of ammonium, nitrates, and total nitrogen decrease until autumn, and in the winter, a rapid rise in their concentrations is again observed. Conversely, the minimum concentrations of organic nitrogen were observed in spring, and then increased until autumn and fell back in winter. During the season of maximum plant growth, there is an accumulation of organic nitrogen and an accompanying decrease in inorganic nitrogen (Table 1) as a result of the transformation of ammonium and nitrates into an organic form as a result of primary production processes.

The phosphorus level shows a statistically significant increase in its organic form (DOP) from spring to autumn. The amount of dissolved inorganic phosphorus (DIP) decreased in the summer, probably because of consumption by phytoplankton.

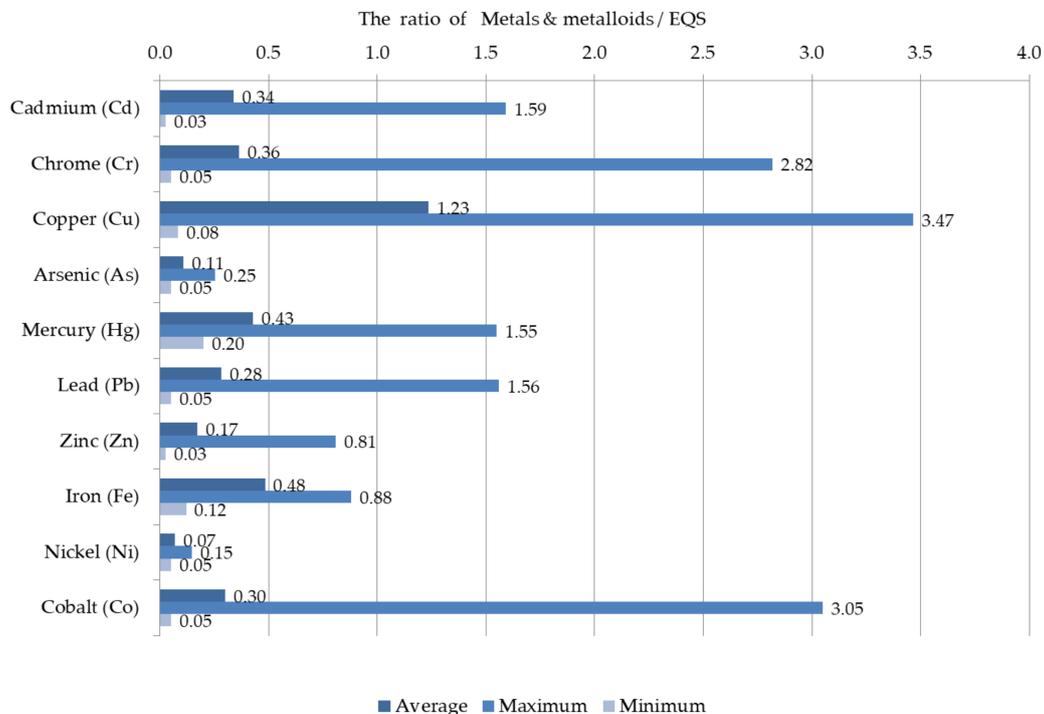
Silicate concentrations were at their minimum in the spring and increased towards the autumn. This is most likely to be caused by peculiarities in the distribution of inflowing water during the observation period. A decrease in the concentration of silica with an increase in inflow is associated with dilution. Total suspended matter (TSS) directly depends on the runoff value; an example is shown by the data from 2019 (Supplementary Materials Figure S1).

The total suspended matter reached maximum values in the spring (average  $31 \text{ mg L}^{-1}$ ) and then decreased until winter ( $8 \text{ mg L}^{-1}$ ).

During 2018–2020, the concentration of heavy metals in water varied from analytical zero to  $44.0 \text{ } \mu\text{g L}^{-1}$ . This maximum value ( $44.0 \text{ } \mu\text{g L}^{-1}$ ) was observed for iron, for which the environmental quality standard (EQS) is  $50.0 \text{ } \mu\text{g L}^{-1}$ . Cobalt was not found in the area of Maiaky and only once was noted at the station at 51 km in the Dniester River. According to the highest value of the average concentrations, the elements are arranged in the following sequence:  $\text{Fe} > \text{Cu} > \text{Zn} > \text{Pb} > \text{Cr} > \text{Co} > \text{As} > \text{Ni} > \text{Cd} > \text{Hg}$ , and according to the ratio of the average concentration to the ecological quality standard (EQS), in the sequence:  $\text{Cu} > \text{Fe} > \text{Hg} > \text{Cr} > \text{Cd} > \text{Co} > \text{Pb} > \text{Zn} > \text{As} > \text{Ni}$ .

In all water samples in 2018 and 2019, copper concentration exceeded the environmental quality standard (EQS =  $3.0 \text{ } \mu\text{g L}^{-1}$ ) by 1.1–3.5 times. In 2020, no excess of copper EQS was observed in water samples. In terms of average concentrations of the studied elements in water, only copper concentration exceeded the EQS [27]. The maximum concentrations of a number of heavy metals in some cases also exceeded their environmental quality standard (Figure 4):

- in winter, chromium in 2.8 times (EQS = 5.0  $\mu\text{g L}^{-1}$ ), cadmium in 1.6 times (EQS = 1.0  $\mu\text{g L}^{-1}$ ), mercury in 1.6 times (EQS = 0.1  $\mu\text{g L}^{-1}$ ).
- in spring, lead in 1.6 times (EQS = 10.0  $\mu\text{g L}^{-1}$ ).
- in summer, cobalt in 3.0 times (EQS = 5.0  $\mu\text{g L}^{-1}$ ).

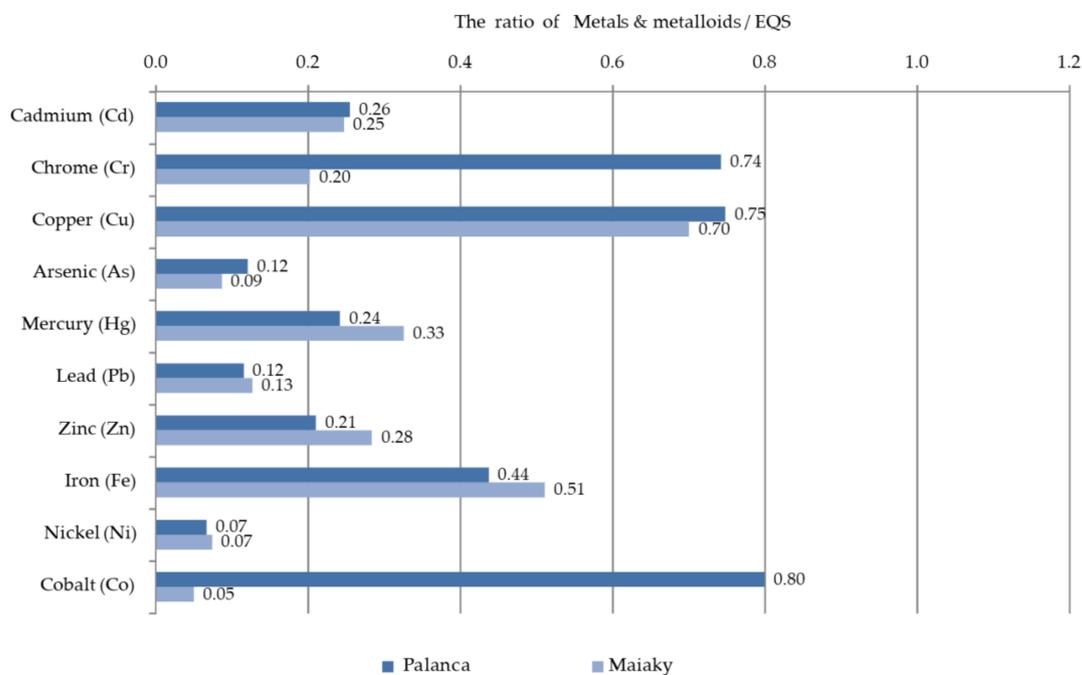


**Figure 4.** The ratio of average and extreme concentrations of heavy metals and metalloids to their environmental quality standards (EQS) in the waters of the Lower Dniester.

It should be noted that heavy metals such as mercury, lead and cadmium, for which an excess of threshold limit concentrations was observed, belong to the most toxic elements of the I hazard class. Copper belongs to the II class (moderately hazardous pollutants) [51]. At the station at Maiaky, the average concentration of copper in winter and spring exceeded the environmental quality standards by 1.8 times and 2.5 times, respectively; also in winter, the concentration of mercury was 1.5 times higher than the EQS (Supplementary Materials Figure S2).

In bottom sediments, the concentration of heavy metals varied within the range of 0.17–83.7  $\text{mg kg}^{-1}$  of dry weight [52]. According to the highest average concentrations in bottom sediments, heavy metals were ordered in the following sequence: Zn > Cr > Ni > Cu > Fe > Pb > Co > As > Cd > Hg, and according to the ratio of the average concentration to the ecological quality standard (EQS) [53,54], in the sequence: Ni > Cu > Cr > Co > Zn > Cd > Hg > As > Pb > Fe (Supplementary Materials Figure S3). For iron concentration in bottom sediments, no environmental standard has been established; therefore, for Fe, the concentration of 200  $\text{mg kg}^{-1}$  was conventionally taken as the standard. In the bottom sediments, the concentration of heavy metals did not exceed their environmental quality standard (EQS). The maximum concentrations of all elements except copper also corresponded to a good ecological state and did not exceed their respective EQS values (Supplementary Materials Figure S3). Exceeding the ecological quality standard by 1.2 times (EQS = 35.0  $\text{mg kg}^{-1}$ ) for the copper concentration in the bottom sediments was noted in only one sample at the Palanca station in September 2020. Quasi-synchronous observations carried out at two stations: Palanca station and at Maiaky station (5 km downstream in the area of confluence of the Turunchuk arm with the main channel of the river Dniester), showed that the concentration of Cd, Cr, Cu, As, and Co decreased by 40%

on average, and the concentration of Hg, Pb, Zn, Fe, and Ni, on average, increased by 22%. The concentrations of mercury and zinc in this part of the river increased on average by 35%, and of iron by 17% (Figure 5).



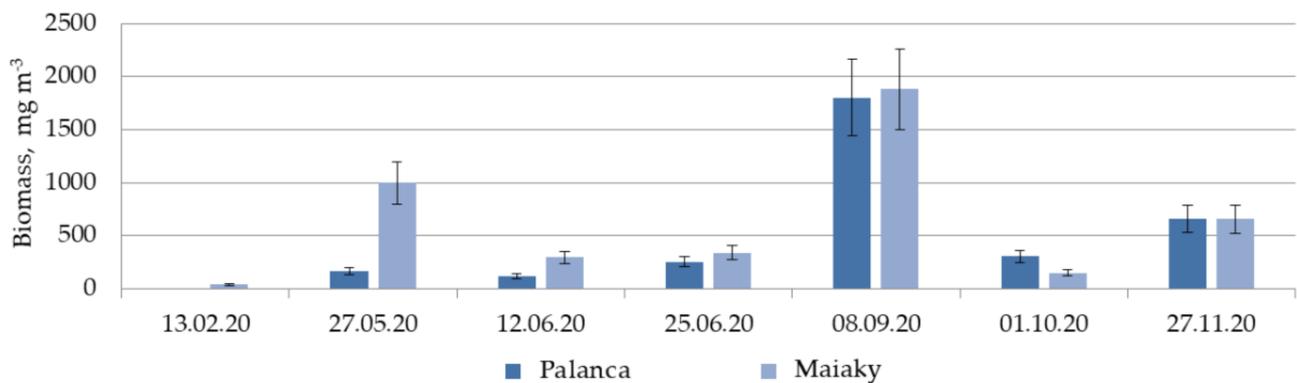
**Figure 5.** The ratio of the average concentrations of heavy metals and metalloids to their environmental quality standards (EQS) in bottom sediments in the lower reaches of Palanca and Maiaky of the Dniester River.

### 3.3. Phytoplankton

The peculiarities of phytoplankton in 2018 and 2019 are described in our previous papers [16,55], and here is the integrated picture for all the periods of our study (2018–2020). During the period of study, we found 264 taxa of microalgae, belonging to 11 classes: Bacillariophyceae (111), Chlorophyceae (58), Trebouxiophyceae (21), Ulvophyceae (1), Conjugatophyceae (1), Euglenoidea (20), Chrysophyceae (4), Cyanophyceae (34), Dinophyceae (12), and Imbricatea (1), and an uncertain taxon of flagellate (1). The contribution of different classes in the total phytoplankton diversity is shown in (Supplementary Materials Figure S4). The basis of taxonomic diversity was formed by diatoms, green algae, and cyanobacteria, which is usual for freshwater phytoplankton. The basis of phytoplankton biomass during the study period belongs to Bacillariophyta. There was no significant correlation between phytoplankton biomass and any of the measured hydrophysical or hydrochemical parameters (Supplementary Materials Figure S5). The regression analysis for the pairs of the key factors of phytoplankton development and biomass of microalgae also gives low values of correlation. Multiple regression coefficients are 0.367 for temperature and pH, 0.377 for temperature and DIP, 0.320 for temperature and DIN, 0.435 for temperature and silicates, 0.441 for pH and DIP, 0.356 for pH and DIN, 0.468 for pH and silicates, 0.326 for DIP and DIN, 0.368 for DIP and silicates, and 0.230 for DIN and silicates. For multiple factors of temperature, pH, DIP, DIN, and silicates, multiple regression coefficients figured as 0.406. The highest multiple regression coefficient of 0.494 is observed for a combination of three factors: DIP, silicates, and pH. The addition of temperature to these three factors did not change the value of multiple regression coefficients within three significant digits and replacing any of these factors with temperature makes the value of multiple regression coefficients lower.

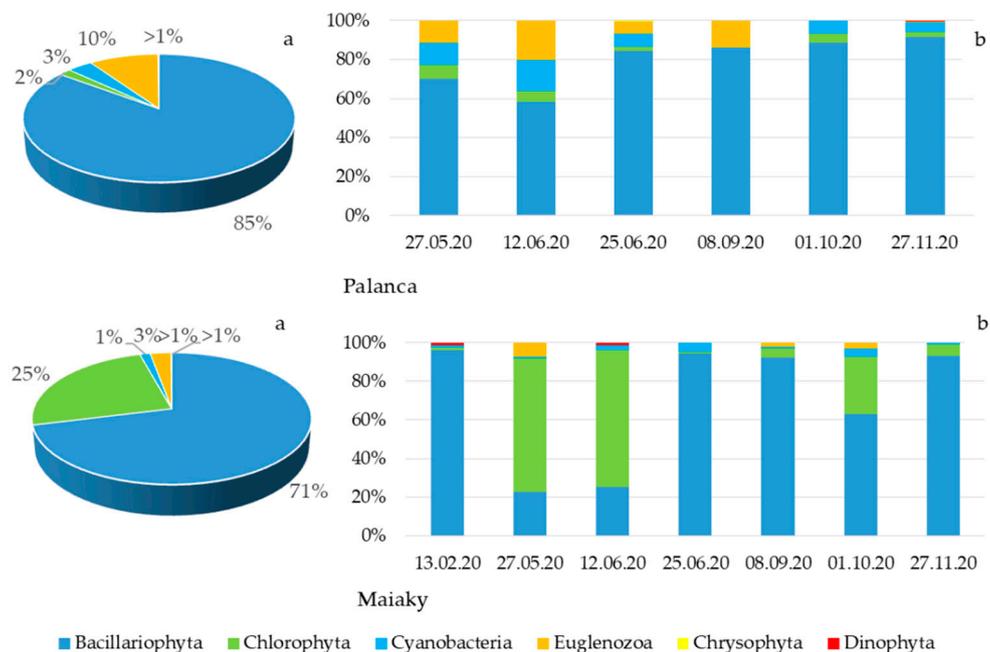
In 2020, we have also compared the parameters of the phytoplankton community in two sites of the Lower Dniester—Palanca and Maiaky (after the confluence of the Dniester

with its arm Turunchuk). At Palanca, the average biomass was lower than at Maiaky ( $550 \pm 262$  and  $621 \pm 243 \text{ mg m}^{-3}$ , respectively). For almost all the samples, the biomass in Maiaky was higher than in Palanca (Figure 6), but this difference did not exceed the standard deviation.



**Figure 6.** Seasonal changes of phytoplankton biomass (average  $\pm$  SE) in two sites of the Lower Dniester (2020).

The comparison of the taxonomic structure of the phytoplankton community at these two sites (Figure 7) shows the higher contribution of green algae to the total biomass at Maiaky station, especially in the spring and early summer period. The analysis of vertical distribution of phytoplankton shows no consistent difference in quantitative characteristics between surface and bottom layers (Supplementary Materials Figure S6), but in the summer period, the share of diatoms in the bottom layer was higher. Nevertheless, the data were not sufficient for detailed analysis.



**Figure 7.** The contribution of different classes in phytoplankton biomass of the Lower Dniester in 2020. (a) Total biomass per year; (b) seasonal changes of biomass.

### 3.4. Zooplankton

During the period of study (2016–2020), 47 taxa of planktonic invertebrates were identified. The most diverse were Rotifera (25 taxa), 8 taxa belonged to Cladocera, 4 taxa to Copepoda, and 10 taxa were assigned to the group Varia (other organisms) (Supplementary

Materials Figure S7). Over the studied period, the most common taxa ranged by their frequency were *Brachionus calyciflorus* Pallas, 1776, *Acanthocyclops vernalis* (Fischer, 1853), *Chydorus sphaericus* (O. F. Müller, 1776), *Aplanchna priodonta* Gosse, 1850, *Brachionus plicatilis* Müller, 1786, *Brachionus diversicornis* (Daday, 1883), *Brachionus quadridentatus* Hermann, 1783, and *Lecane lunaris* (Ehrenberg, 1832). Species number per sample varied from 5 to 19 and had an average at  $13 \pm 2$ . The abundance and biomass of planktonic invertebrates varied significantly with the average over the studied period of  $10449 \pm 3923$  ind.  $m^{-3}$  (min–max range: 133–64683 ind.  $m^{-3}$ ) and  $205 \pm 89$  mg  $m^{-3}$  (min–max range: 0.84–1605 mg  $m^{-3}$ ). A statistically valid difference was shown both for seasonal (Table 2) and inter annual (Supplementary Materials Table S1) variation in abundance and in biomass. Shannon's index ranged from 0.86 to 3.26 (median = 2.71); it was the highest in spring and the lowest in late summer. Nearly all the taxa were common for a  $\beta$ -mesosaprobic zone. Saprobity index by zooplankton indicators [37] varied from 1.25 in winter 2018 to 3.02 in autumn; on average, it was 1.83, which corresponds to moderately polluted waters (Supplementary Materials Figure S8). No valid statistical variation, in species composition allowing generalized characteristics of the zooplankton for the Lower Dniester to be assessed, was found within the studied sites during 2018–2020.

**Table 2.** Seasonal variation of zooplankton abundance and biomass (Average  $\pm$  SE) in the Lower Dniester in 2016–2020.

Season	Characteristic	Rotifera	Copepoda	Cladocera	Varia	Total *
Spring	Abundance, ind. $m^{-3}$	5575 $\pm$ 3660	17,689 $\pm$ 16,033	1490 $\pm$ 941	312 $\pm$ 103	25,067 $\pm$ 17,668
	Biomass, mg $m^{-3}$	12.3 $\pm$ 7	412.7 $\pm$ 396.3	84.4 $\pm$ 45	5.7 $\pm$ 3.6	515.1 $\pm$ 436.6
Summer	Abundance, ind. $m^{-3}$	3594 $\pm$ 963	5310 $\pm$ 1789	2463 $\pm$ 1046	1758 $\pm$ 425	13,125 $\pm$ 2497
	Biomass, mg $m^{-3}$	10.5 $\pm$ 4.6	68.1 $\pm$ 22.7	207.6 $\pm$ 99.4	7 $\pm$ 1.4	293.2 $\pm$ 113.6
Autumn	Abundance, ind. $m^{-3}$	394 $\pm$ 235	265 $\pm$ 107	155 $\pm$ 131	53 $\pm$ 29	867 $\pm$ 439
	Biomass, mg $m^{-3}$	2.2 $\pm$ 1.1	2.3 $\pm$ 0.9	4.7 $\pm$ 3.7	0.2 $\pm$ 0.1	9.3 $\pm$ 5.2
Winter	Abundance, ind. $m^{-3}$	128 $\pm$ 33	70 $\pm$ 10	55 $\pm$ 45	25 $\pm$ 5	278 $\pm$ 93
	Biomass, mg $m^{-3}$	0.1 $\pm$ 0.1	0.3 $\pm$ 0.1	1 $\pm$ 0.3	0.2 $\pm$ 0.2	1.7 $\pm$ 0.5

\* Total Abundance KW-H (3;54) = 18.9549;  $p = 0.0003$ ; Total biomass KW-H (4;54) = 14.4447;  $p = 0.0024$ .

In terms of the annual course of zooplankton development, early spring was characterised by low abundance and species diversity. Only rotifers, mainly of the genera *Brachionus* Pallas, 1766 and *Asplanchna* Gosse, 1850, were relatively numerous in the samples. Although in some years other genera dominated, for example, in the winter of 2019–2020, rotifers of the genus *Notholca* Gosse, 1886 prevailed. There was also a representative of Cladocera *Chydorus sphaericus* (O.F. Müller, 1776), rotifers of the genera *Brachionus*, *Asplanchna*, *Filinia* Bory de St. Vincent, 1824 as well as copepod nauplii. Only in early spring, tardigrades (presumably of the genus *Hypsibius* Ehrenberg, 1848) were occasionally present in plankton samples, probably migrating into the water column from the bottom. As the temperature rose, an increase in diversity and abundance of plankton organisms was observed, with the appearance of the Copepoda genera *Acanthocyclops* Kiefer, 1927, *Eucyclops* Claus, 1893, and *Eudiaptomus* Kiefer, 1932 and different Rotifera. Later, in summer, the abundance and diversity of Cladocera increased (KW-H (3; 54) = 8.8684;  $p = 0.0311$ ). In August, the quantitative indicators of zooplankton began to decline. In September, in some years, there was an insignificant maximum in the zooplankton development, caused by rotifers and copepods; nevertheless, the average abundance and biomass in autumn were significantly less than those in spring and summer (KW-H (3;54) = 16.2681;  $p = 0.0010$ ) (Table 2). After that, in October–November, the quantitative indicators of zooplankton decreased still further, reaching the winter level by November–December.

A negative correlation between the total abundance and runoff volume was already noted [56]. However, during the succeeding studies, a clear correlation between these indicators was not found [57]. There were also no statistically valid correlations between the indicators of zooplankton and phytoplankton biomass (Supplementary Materials Figure S9), as well as any measured hydrophysical and hydrochemical parameters, except

water temperature, for which the correlation with different zooplankton indicators ranged from 0.55 to 0.63. A weak negative correlation was observed with most chemical parameters such as salinity, pH, oxygen, phosphorus, and nitrogen.

### 3.5. Macrozoobenthos

In 2018–2020, the total taxa composition of the riverine macrozoobenthos of the Lower Dniester covering all two sites of investigation (Maiaky and Palanca) consisted of 108 species from 44 families. Species number varied from 1 to 18 per sampling area of 0.025 m<sup>2</sup> and up to 40 species in the drag-samplings (Table 3). The most diverse taxa were Diptera (23), Gastropoda (22), Oligochaeta (18), and Crustacea (11); species numbers in the other groups did not exceeded 5. The most frequent taxa were *Aulodrilus pluriset*a (Piguet, 1906), *Branchiura sowerbyi* Beddard, 1893, Corixidae Gen. sp., *Dreissena polymorpha* (Pallas, 1771), *Esperiana esperi* (Férussac, 1823), *Katamysis warchowskyi* Sars, 1877, *Limnodrilus* spp., *Limnomysis benedeni* Czerniavsky, 1882, *Lithoglyphus naticoides* (C. Pfeiffer, 1828), *Polypedilum (Uresipedilum) convictum* (Walker, 1856), *Psammoryctides barbatus* (Grube, 1861), *Tubifex tubifex* (Muller, 1774), *Viviparus ater* (De Cristofori and Jan, 1832), *Viviparus contectus* (Millet, 1813), and *Viviparus viviparus* (Linnaeus, 1758). Sensitive Ephemeroptera, Plecoptera, and Trichoptera (EPT) taxa were found accidentally in dredge samples within the Palanca sampling points: 3 October 2018 *Ecnomus tenellus* (Rambur, 1842) 28 October 2019, *Mystacides longicornis* (Linnaeus, 1758), Polycentropodidae, 22 October 2020-*Agraylea* sp. All of listed EPT species had low number (1–80 ind./sample) and did not influence the total abundance of the bottom community. *Branchiura sowerbyi*, an alien warm water species from Asia, was present in all biotopes such as silt, sand, and aquatic vegetation. Previously, it was known mainly from the Danube region and was rare in Dniester [58–61]. Other invasive species, known for the Dniester basin such as *Ferrissia californica* (Rowell, 1863), *Macrobrachium nipponense* (de Haan, 1849), *Physella acuta* (Draparnaud, 1805), *Dreissena rostriformis bugensis* Andrusov, 1897, *Potamopyrgus antipodarum* (J.E. Gray, 1853) were not a significant element of the fauna in terms of general abundance or biomass.

**Table 3.** Benthic community state of the Lower Dniester within natural flow [3,9] and modern periods, calculated using with Asterics 4.04.

Biotic Characteristics	1949–1951		2018–2020	
	Average ± SE	Range	Average ± SE	Range
Abundance, ind. m <sup>-2</sup>	3914 ± 828	1463–6432	14,528 ± 3552	107–58,764
Biomass, g m <sup>-2</sup>	29 ± 9	7.27–56	799 ± 230	0.76–3411
Number of Taxa	11 ± 3	3–21	8 ± 1	1–40
Shannon Index	0.81 ± 0.16	0.22–1.25	1.28 ± 0.08	0.1–1.85
Saprobic Index (Zelinka & Marvan)	2.14 ± 0.09	1.9–2.32	2.25 ± 0.06	1.94–3.27
Romania Saprobic Index	2.28 ± 0.11	1.98–2.5	2.2 ± 0.06	1.96–3.08
BMWP Score	19 ± 6	8–47	14 ± 1	1–32
BMWP N taxa	5 ± 1	2–10	4 ± 1	1–7
Average BMWP score per Taxon	4.1 ± 0.15	3.75–4.7	3.43 ± 0.18	1–4.57
DSFI Diversity Groups	—	0–1	—	0–3
DSFI	—	—	—	—
BBI	3.5 ± 0.24	3–4	3.9 ± 0.11	3–5
Potamon Type Index	3.45 ± 0.58	1.87–5	3.05 ± 0.19	1.67–5
Functional Feeding Groups				
% Grazers and scrapers	20.02 ± 11.03	0–68.18	11.53 ± 2.46	0–47.41
% Miners			1.29 ± 0.75	0–15.82
% Shredders			0.73 ± 0.36	0–7.71
% Gatherers/Collectors	34.91 ± 15.29	3.05–95.04	47.92 ± 6.9	0–92.4
% Active filter feeders	20.71 ± 12.2	0–77.88	7.29 ± 1.83	0–40
% Passive filter feeders	3.42 ± 3.39	0–20.36	1.03 ± 1.02	0–22.37

Table 3. Cont.

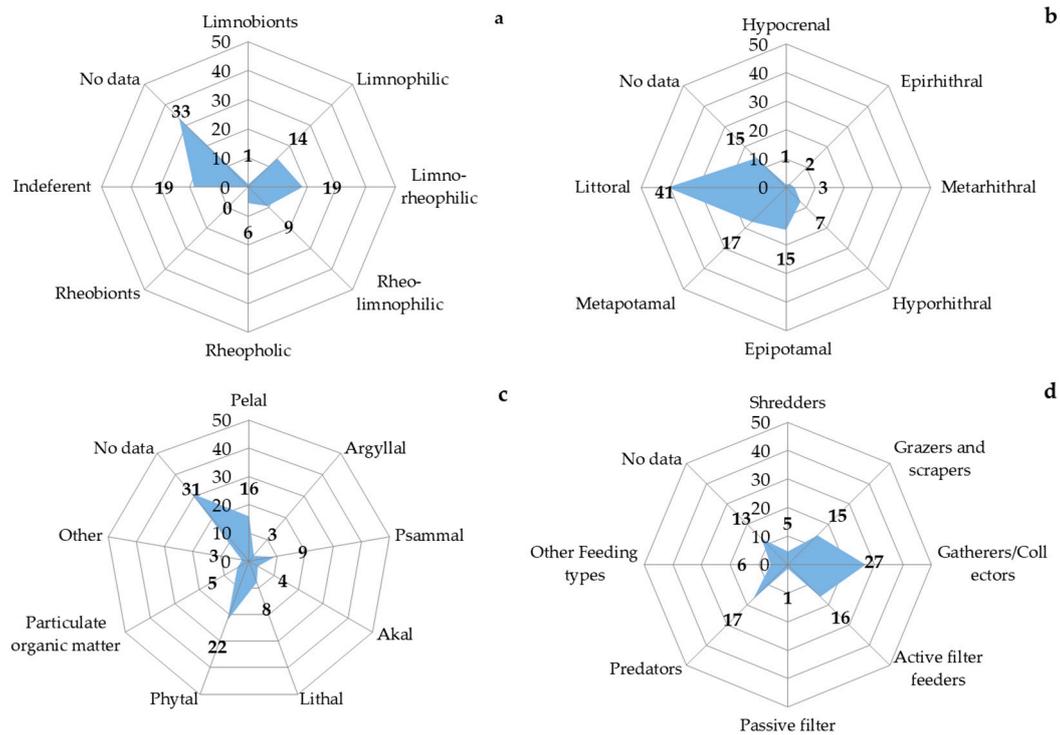
Biotic Characteristics	1949–1951		2018–2020	
	Average $\pm$ SE	Range	Average $\pm$ SE	Range
% Predators	0.64 $\pm$ 0.58	0–3.5	2.71 $\pm$ 1.26	0–20
% Parasites			0.74 $\pm$ 0.48	0–10.33
% Other Feeding types			0.19 $\pm$ 0.08	0–1.34
LIFE Index	6.83 $\pm$ 0.2	6–7.5	5.17 $\pm$ 0.25	3–7

Abbreviations: BMWP-Monitoring Working Party, BBI-Belgian Biotic Index, DSFI-Danish Stream Fauna Index, LIFE-Lotic-invertebrate Index for Flow Evaluation.

During all the years of investigation (2018–2020), *Viviparus* spp. (*V. ater*, *V. connectus*, and *V. viviparus*) have been the dominant taxa covering all the biotopes and their share of biomass varied from 50 up to 90% ( $600 \pm 205 \text{ g m}^{-2}$ ). Other gastropods such as *Lithoglyphus naticoides* and *Esperia esperi* comprised 30–40%, but their share in the abundance was rather low. On the other hand, Tubificidae worms together made about 55% of the total abundance ( $10,800 \pm 3050 \text{ ind. m}^{-2}$ ) without a significant share in biomass. *Polypedilum* spp. was common in both sites of investigation, but only in Palanca were significant values reached ( $4972 \pm 1670 \text{ ind. m}^{-2}$  and  $5.0 \pm 2.7 \text{ g m}^{-2}$ , with the maximum at  $14,080 \text{ ind. m}^{-2}$  and  $37 \text{ g m}^{-2}$ ). The composition of other subdominants with the joint share of about 10% of biomass was different depending on site and time. The abundance and biomass of community varied significantly with the average of  $14,500 \pm 3500 \text{ ind. m}^{-2}$  and  $0.8 \pm 0.2 \text{ kg m}^{-2}$  and with the highest figures of  $58,800 \text{ ind. m}^{-2}$  and  $3.4 \text{ kg m}^{-2}$  (Table 3).

Nearly 67% of taxa have full or partly autecological characteristics in the Asterics database. Among the species, littoral species dominated (about 40%), and close values indicated common taxa for the potamal (31%). Groups within current velocity had the next ranking species: limno-rheophilic (18.5%), indifferent to the current velocity species (18.5%), limnophilic (13.9%), and the share of other species did not exceed 10% (Figure 8). Rare occurrence of such sensitive taxa as Ephemeroptera, Plecoptera, and Trichoptera both in modern and historical data [9] did not allow to compute DSFI. In both periods, Gather/Collector was dominating both in taxa number (27%) and total abundance and biomass (up to 92%) in composition of FFG.

Based on taxa composition, the Potamon Type Index characterised the environmental state as “bad”. In 2018–2020, species indicating  $\beta$ -mesosaprobic (27 from 54 saprobity indicators) and  $\alpha$ -mesosaprobic (17 from 54) conditions were the most abundant in all the samples, resulting in saprobic index calculated both in classic Zelinka and Marvan and Romanian version which did not exceed 2.5, and characterised the status as moderate. According to the BMWP and BBI indices, the modern condition of the lower reaches on investigated two sampling points during 2018–2020 of the Dniester River can be described as “poor”. The LIFE index in this section of the river also had an average of values (5–7), which is typical of weakly flowing streams, and its changes both with correlation with annual runoff were not statistically significant.



**Figure 8.** Autecological preference composition (%) of macrozoobenthos in the Lower Dniester in 2018–2020 calculated using total taxa list with Asterics 4.04. (a) Current preference, (b) zonation, (c) biotope, and (d) functional feeding group.

#### 4. Discussion

##### 4.1. Long-Term Dynamics of the Runoff

In official documents, as well as in various publications, it is usual to describe the annual runoff of the Dniester River at about 10.2 km<sup>3</sup> [17]. This value (as will be shown below) is based on its average value, usually obtained from the longest available series of representative observations. However, how true is it today? The data relating to long-term observations on water discharge at the hydrological stations Zalizhchyky, Mohyliv-Podilskyi, Maiaky (Ukraine), and Bender (Moldova) were used initially. The choice of these stations was dictated, on the one hand, by the need to correctly identify the impact of the functioning of the Dubossary hydroelectric complex and its reservoirs, as well as climate change on the river flow below the dam, and, on the other hand, by the accessibility of available information.

Long-term hydrological data on the Lower Dniester runoff should be distinguished into two main periods: 1946–1981 before the filling of the Dniester reservoir, and 1987–2020 when the Dniester reservoir and HES-1 were put into operation. The influence of Dubossary HPP, put into operation in 1955, was not taken into account, because of its low impact on the total discharge of the river. The main difference between these periods is that the first one is characterised by stable climate, and the other one is characterised by a global warming influence, starting in the middle of 1990s. The combined hydrograph of annual runoff volumes for the period from 1946 to 2020 for each of the four stations is shown in Supplementary Materials Figures S10 and S11. A trend line with a linear regression coefficient  $-0.012$  (Figure 2) shows a downward trend in the total discharge of the Dniester River at all the stations. We suggest that this trend is due to general climatic changes that began to manifest themselves in the mid-1980s.

The degree of the Dniester reservoir impact on the Lower Dniester total discharge, regarding the influence of climatic changes, can be calculated by the analysis of the statistical relationship between the runoff at the Bender HGS and Zalizhchyky HGS before and after the reservoir was filled.

The runoff data at the Bender HGS should be divided into two periods:

- (1) 1946–1981, the period prior to the filling of the Dniester reservoir (Supplementary Materials Figure S10). The linear regression equation is:

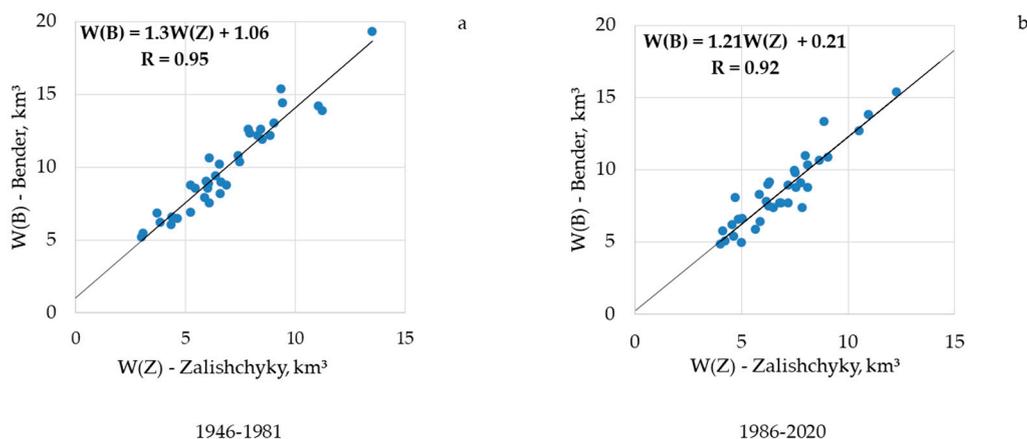
$$y = 0.19x - 6.82 \quad (1)$$

- (2) 1987–2020, the period after the filling of the Dniester reservoir (Supplementary Materials Figure S11). The linear regression equation is:

$$y = -0.017x + 8.89 \quad (2)$$

The series of runoff data from 1946 to 1981 (the year when the Dniester reservoir began to fill) may be considered homogeneous, since the main influence on the discharge was exerted by natural factors. The 1986–2020 data series is also homogeneous because of the emergence of a significant factor influencing the Lower Dniester flow. This factor is the reservoir, capable of holding up to 1/3 of the total annual river flow. At first time interval, the trend line has a positive regression coefficient of 0.19 and shows that the water content acquired a local growth trend (1). For the second period, a trend line with a negative regression coefficient of  $-0.017$  shows a decrease in the annual runoff (2).

Dependence of the Dniester annual river flow volume at Bender HGS on the flow volume at Zalishchyky HGS, for the periods 1946–1981 and 1986–2020, is shown in the Figure 9.



**Figure 9.** The annual runoff volume  $W(B)$  at Bender and  $W(Z)$ -Zalishchyky HGS statistical dependence for the period of (a) 1946–1981 and (b) 1986–2020.

The regression line on each of the graphs demonstrates a close linear relationship between the volumes of annual runoff in Bender HGS and Zalishchyky HGS. The correlation coefficient between the runoff in Bender and Zalishchyky is  $R = 0.95$  (for the observation period 1946–1981) and  $R = 0.92$  (for the observation period 1986–2020). These correlation coefficient values suggest a very high statistical dependence of the annual runoff in Bender with the corresponding runoff in Zalishchyky.

The linear regression equations for these periods are the following:

$$W(B) = 1.30W(Z) + 1.06 \quad (3)$$

$$W(B) = 1.21W(Z) + 0.21 \quad (4)$$

The analysis of linear regression Equations (3) and (4) shows that the multiplier of the variable in the first regression equation is 1.3. This value allows us to conclude that in the period of high-precipitation years (1946–1981), the annual runoff in the catchment area

from the Zalizhchyky HGS to Bender HGS due to lateral inflow increased, on average, by 1.3 times.

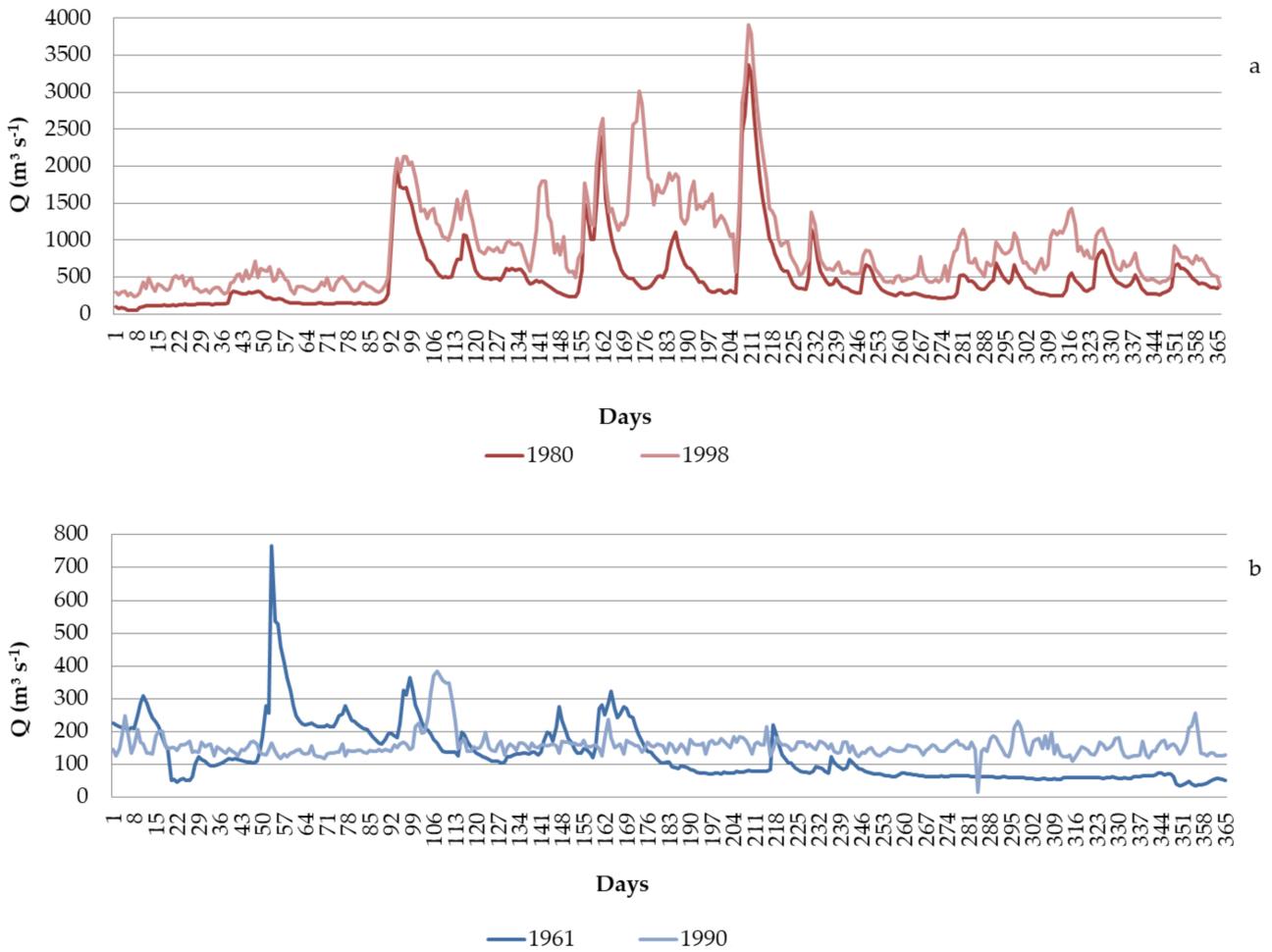
After the onset of a prolonged phase of lowering water volume and filling the reservoir, the same river flow increment coefficient (the coefficient of linear regression in the second equation) had decreased to 1.2, i.e., by 8.3% from 1986 to the present. This difference between the coefficients contains, in an implicit form, irrecoverable losses from the reservoir by evaporation and infiltration into the groundwater horizons that do not have a recharge into the river channel, as well as irreversible losses for water management needs.

The value of the constant in these linear regression equations is also significantly different, which can be interpreted as the runoff increase in the Zalizhchyky–Bender section because of groundwater supply. If the volume of the annual runoff in Zalizhchyky is theoretically equal to zero, in 1946–1981, the runoff in Bender could reach a value up to 1 km<sup>3</sup>. In the period with a steady downward trend in water availability (1986–2020), groundwater reserves and possible insignificant surface runoff from the catchment area between Zalizhchyky and Bender may provide only a runoff of 0.21 km<sup>3</sup>, if there is no discharge through the Dniester HPP dam.

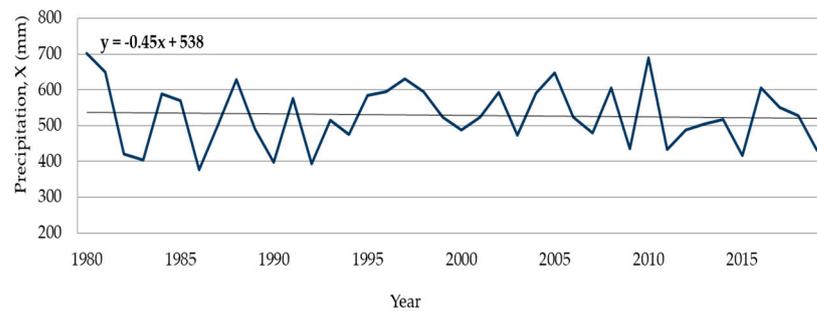
The impact of the Dniester HPP and the reservoir is clearly visible on the shape of the hydrograph of average daily discharges in the Mohyliv-Podilskyi HGS. Comparison of the hydrographs “before and after” demonstrates a significant difference in the daily fluctuations in water level and discharge. Before the appearance of the HPP dam, the diurnal variation of the river levels had a smooth appearance both in the low-water period and during floods. After the HPP commissioning, the course of the levels and, accordingly, the hydrograph of water discharges took the form of a sinusoid with a high frequency of daily fluctuations (Figure 10). A decrease in the maximum flow rates during floods, due to the transforming and smoothing effect of the Dniester and the Dubossary reservoirs, leads to a significant deterioration in the “washing” of the riverbed and cleansing from silt deposits, especially in the lower river. This negative phenomenon is especially manifested in years of medium and low water levels. The positive effect of the influence of the Dniester reservoir is illustrated (Figure 10), where the hydrographs for years with a minimum annual runoff of about 4 km<sup>3</sup> are shown. In 1961, when the Dniester runoff depended only on climatic factors, the water discharge in Mohyliv-Podilskyi decreased to 50 cubic meters per second during low-water periods. In 1990, as in other dry years (in particular in 1987, 1994, 1995, 2015, 2016), the availability of water reserves in the reservoir made it possible, through regular releases, to ensure the minimum water discharge within 120–150 cubic meters per second, practically throughout the entire low-water period. This operating mode of the Dniester reservoir improved the filling of the Lower Dniester channel with the water necessary for its ecosystem.

It should be emphasized that the problem of a decrease (lack or deficit) of runoff in the Middle and Lower Dniester, which manifested itself after the construction of the Dniester reservoir, is largely because of a significant decrease in inflow from the Dniester tributaries flowing into the main river below the Mohyliv-Podilskyi HGS. The long-term tendency towards a decrease of precipitation on the territory of the Middle and Lower Dniester (Figure 11), a stable tendency towards an increase in the average annual air temperature (Figure 12), largely determines the conditions for the runoff formation on the catchments of these rivers.

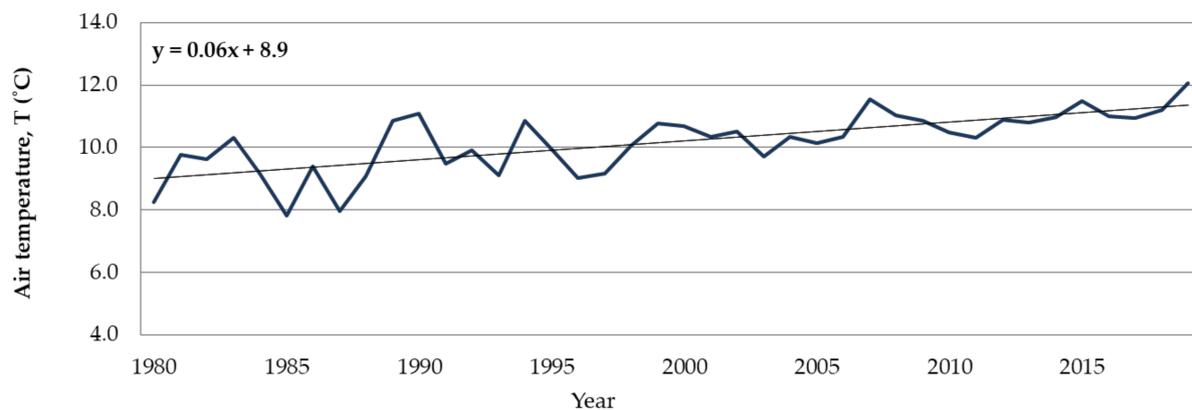
The conditions have already led to the decrease in the total water volume of the Dniester River, which, for almost 10 years, has not been able to reach the value of the statistical “norm”. To date, the norm or long-term average value of the total annual runoff of the Dniester, with different assessment methods, is taken to be from 9.2 to 10.2 km<sup>3</sup> [17,62].



**Figure 10.** The annual hydrographs of water discharges at Mohyliv-Podilskyi HGS. (a) “Before and after” years with the maximum annual runoff (1980 and 1998) and (b) “before and after” years with the minimum annual runoff (1961 and 1990).



**Figure 11.** The sum of annual precipitation, averaged over the Middle and Lower Dniester basin in the 1980–2020 years.



**Figure 12.** Average annual air temperature in the catchment area of the Middle and Lower Dniester, T (°C).

#### 4.2. Chemical Conditions

Dams break down the river continuum, interrupting the organic matter and heavy metal transport in a lotic system and affect the chemical and biological characteristics of the river ecosystem [63–66]. The Dniester, with its high anthropogenic impact caused by HPP constructions, agriculture, and further influence by climate change, shows shifts in its water quality over the last 70 years.

In 2018–2020, the concentrations of ammonia and nitrite were very similar to 2003–2004. These values are 7–8 times lower than in 1985–1988. We also observed a tendency for all types of phosphorus to decrease by 1.5 times from the 1980s to the present. Concentrations of total dissolved nitrogen (TDN) in all periods (except the 1950s) remained at the same level (Supplementary Materials Table S2).

Analysing the historical data on the Lower Dniester, nitrates and dissolved inorganic nitrogen (DIN) were the lowest in the 1950s. Unfortunately, during the 1950s, no studies of organic forms of nutrients in the water of the Dniester River were carried out, as specified by [13,67,68]. Studies carried out in 1977–1978 showed that, in comparison with 1952–1954, the concentration of nitrites and nitrates in the water of the Dniester River increased 2.5 times. The concentration of dissolved inorganic phosphorus (DIP) also doubled [13,67,68]. Between 1985 and 1988, the concentration of ammonia tripled over that of the 1950s (Supplementary Materials Table S2). Nitrite has increased 5.5 times since the 1950s, and 2.5 times since the 1970s. We found no pattern in nitrate and dissolved organic nitrogen concentrations from the 1970s to the present. Perhaps this is due to the variability of river runoff, which strongly affects the concentration level and the degree of transformation of nutrients [69,70]. Nitrates and phosphates were at the same level in the 1970s and 1980s and dissolved organic phosphorus (DOP) increased by 1.5 times. It is safe to say that the 1970s–1980s were a time of intense eutrophication of the Dniester River [13,67,68]. In 1987, the commissioning of the Dniester reservoir and hydroelectric power station smoothed out the annual fluctuations in the Dniester River flow. In the 1990s, during a period of industrial and agricultural decline in the region under consideration, simultaneously with a decrease in the Dniester runoff, there was a tendency towards a decrease in the concentration of nutrients and an increase in the concentration of dissolved organic matter coming from the estuary to the coastal zone [68–71].

Silicates require special consideration since their concentrations do not depend on eutrophication. Today, a consistent halving of silicate concentration compared to the 1950s is observed. This is due to the sedimentation of Si with a sink out of diatom phytoplankton in Dniester's reservoirs. In reservoirs, the sedimentation of suspended matter occurs as a result of the slowdown of the river flow in lentic systems. This process leads to an increasing of water transparency. This is advantageous to the phytoplankton, leading to growth and an increase in biomass. The dominant group of phytoplankton of Dniester's reservoirs is diatoms, which take up Si to build frustules. The trend of long-term depletion in dissolved

silicates is illustrated below (Figure 13). As we can see, the concentrations of silicates in the Lower Dniester have a long-term tendency to decrease, and their concentration is inversely related to the runoff value. A decrease in the concentration of Si with an increase in runoff is clearly associated with dilution.

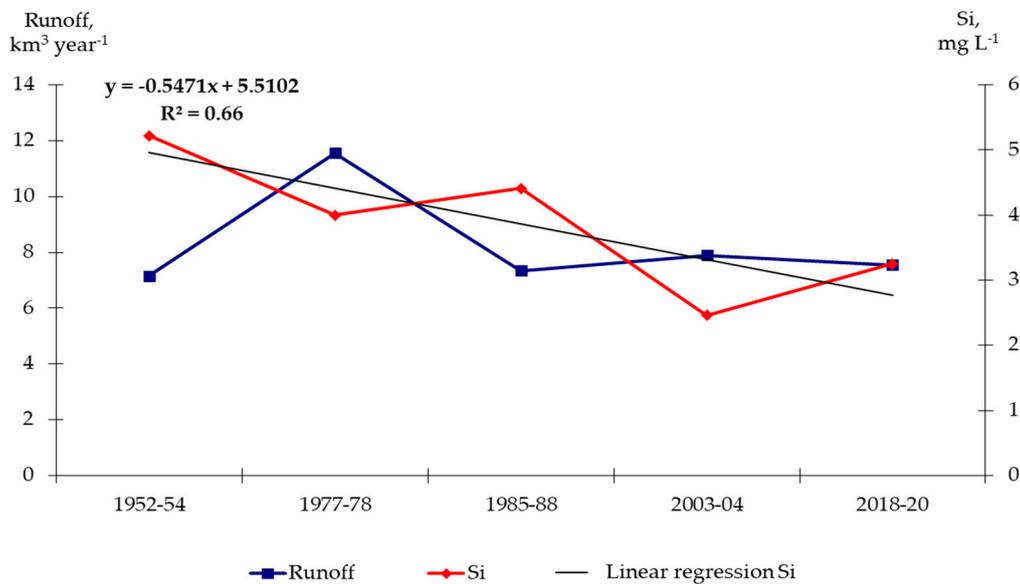


Figure 13. Long-term trend in silicates’ concentration and its relationship with runoff value [13,67,68].

Long-term decrease in silicates on the one hand and the process of eutrophication of the river, on the other hand, lead to a change in the ratio of nutrients in the ecosystem. Figure 14 shows the atomic ratios of inorganic nitrogen and phosphorus to silica. As illustrated, the increase in the proportion of phosphorus and nitrogen during the period of hard eutrophication persists to this day. Based on the results obtained, we can state the stabilization of this biogeochemical ratio in the last 40 years.

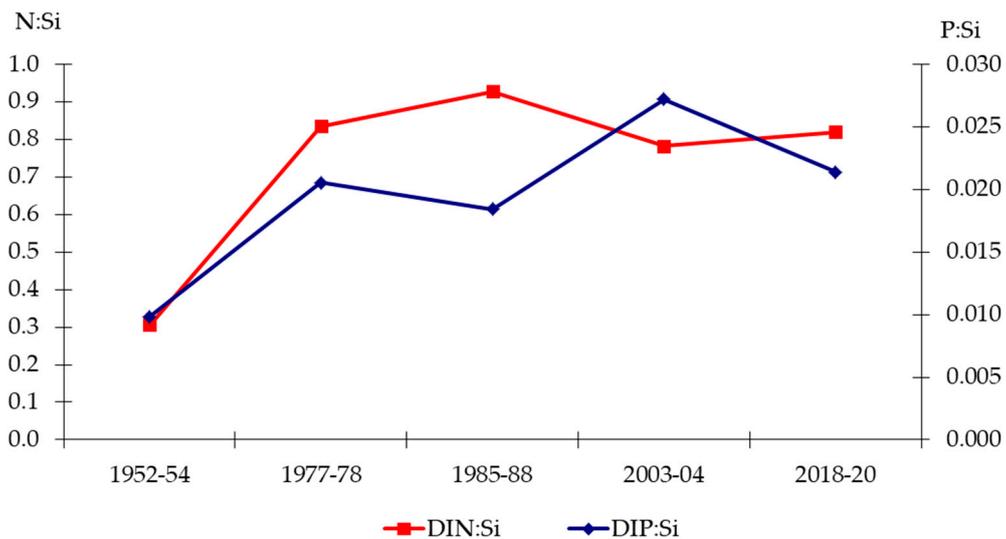


Figure 14. Long-term changes in an atomic ratio of inorganic nitrogen and phosphorus to silicate [13,67,68].

Uncontrolled input of heavy metal and metalloids from numerous sources, such as industrial, mining, municipal sewage, and agriculture, have contributed to the increased pollution in rivers and lakes all over the world [72]. These elements are generally accumulated in the sediments, which become a source of water pollution [73]. In the biological,

ecological and biochemical researches, most often Cr, Co, Ni, Cu, Zn, Mo, Cd, Hg, Pb, less often Ti, V, Mn, Fe, Sr, As, and some other elements are studied [74]. A priority group of toxicants have been identified among heavy metals (cadmium, copper, arsenic, nickel, mercury, lead, zinc, and chromium) as the most hazardous to human health. According to our data, an active re-mobilization process of heavy metals and metalloids take place in the Lower Dniester, while their concentrations in the water often exceed the EQS there, whereas the ones in bottom sediments are usually lower than the EQS. This process could be related to the increasing average annual temperature under climate change and the decline in the general discharge of the river.

During observations in the area of the Maiaky village, the average heavy metal concentration in Dniester bottom sediments was established during the high water period (water level at the Maiaky post of >120 cm) and dry period (water level of <100 cm) [52]. It is noted that during the dry season, the concentration of most studied heavy metals (Cd, Cr, Cu, As, Pb, Zn, Fe, Ni) on average, increases by 29%. The maximum increase in concentration was noted for the following elements: Ni by 76%, Cu by 46%, Cr by 37%, Cd by 35%, and Fe by 15%. This fact can be explained by an increase in metabolic processes at the bottom sediment–water interface during the flood period. The concentration of mercury and cobalt decreased during the flood runoff by 32% and 11%, respectively.

The analysis of the average concentration of toxic metals in bottom sediments in the area of 51 km and the Maiaky village showed that their concentrations did not differ significantly, and the average values of all the elements did not exceed their environmental quality standard (EQS). In this area, there was a clear decrease in their concentrations in bottom sediments along the course of the river.

In general, by the concentration of toxic heavy metals and metalloids in water and bottom sediments, the lower reaches of the river Dniester can be assessed as of moderate ecological state. For the most toxic heavy metals, mercury, lead and cadmium, exceeding the EQS was noted only in single cases. The average concentration exceeded EQS only for copper, which belongs to the II hazard class.

#### 4.3. Biological Conditions

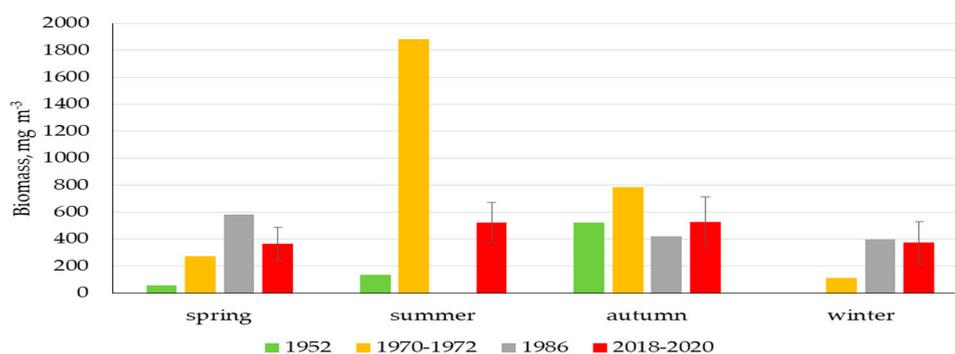
Plankton communities are sensitive to environmental changes in rivers, streams, and lakes. The construction of the HPP can affect plankton due to changes in sediment charge, flows, temperature, water quality, food availability, and other physicochemical parameters of the water. Affected organisms are mainly phytoplankton, zooplankton, planktonic microorganisms, and ichthyoplankton [75–77]. Dam building usually leads to an increase in the abundance and biomass of phytoplankton communities in reservoir areas, as well as significant changes in reproduction patterns, composition, and abundance of many algal groups, especially diatoms [63,75–77]. Zooplankton react to damming in an exponential reduction of cladocerans and a decreased number of rotifers in the lower reaches with distance from the main dams and copepod abundance increasing as in lentic water bodies [66,75–77].

During 2018–2020, a high species diversity of microalgae was observed. The basis of taxonomic diversity was formed by diatoms, green algae, and cyanobacteria, which is usual for freshwater phytoplankton, including rivers under HPP impact [75,78,79]

Comparing with studies of 1970–1972 [15] that were also carried out in the area of Maiaky village, evident changes in the structure of the phytoplankton community can be seen (Supplementary Materials Figure S12). It is known that due to the precipitation of silicates in hydropower reservoirs, diatoms lack dissolved silicates, and the dominant phytoplankton functional group shifted from diatoms (Bacillariophyta) to green algae (Chlorophyta) along the flow direction below the dam [55,80]. In the spring period in 2018–2020 the same diatom–green complex of species as in 1970–1972 was observed, but with a higher component of diatoms and lower component of green algae. This increase may be evidence of adaptation of the phytoplankton community and a partial return to the pre-regulated state comparing with the first decades after hydropower construction.

In the summer period, the situation has worsened, with the proportion of Bacillariophyta decreased, and a development of cyanobacteria and dinoflagellate blooms. This situation is common for waters affected by upstream dams [55,75,80,81]. In the autumn period, it is similar to the period of 1970–1972, with an increased component of Chlorophyta and a small decrease of Cyanobacteria. Changes in the contribution of different microalgae in total biomass for the winter period were greater. In 1972, Chlorophyta predominated, and the part of Cyanobacteria was quite high. In 2018–2020, the main contribution belonged to Bacillariophyta, the contribution of Cyanobacteria was less than 1%. A decrease in the proportion of cyanobacteria may indicate a decrease in water trophicity in these periods. However, it is necessary to note that these differences may be caused by hydrological peculiarities of certain years, because from year to year, the ratio of the phyla varied significantly.

Compared to the previous studies of the regulated period (1970–1972 and 1986) (Figure 15), we noticed a decrease of phytoplankton biomass. However, for most of the year, phytoplankton biomass was higher than in the pre-regulated period. In the autumn period during 2018–2020, the average biomass became even lower than in the pre-regulated period. This may be the result of decreasing phosphorus concentration to pre-eutrophication values. Only in winter, the average biomass was higher than in 1972, but lower than in 1986 (Supplementary Materials Figure S12). Active development of microalgae in winter may be due to higher winter temperatures and the absence of stable ice cover, as the result of global climatic changes [65,75,79].



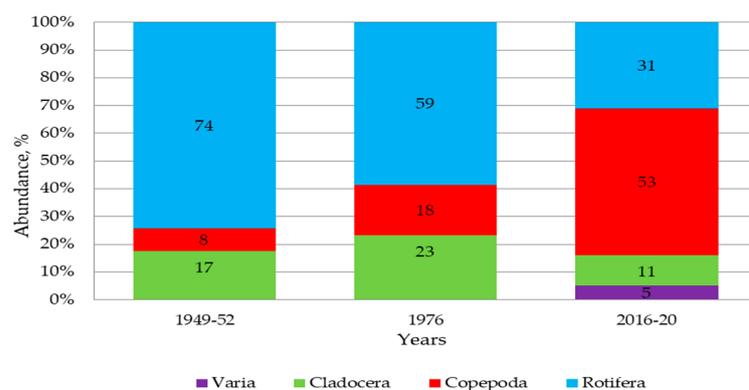
**Figure 15.** Long-term changes in the average  $\pm$  SE biomass of phytoplankton (1952 and 1970–1972 according to [15], 1986 according to [8], 2018–2020 project data).

A similar situation is known from other big rivers impacted by dams [70,72,77]. Thus, we need to keep in mind that the 1970s and 1980s were also periods of eutrophication, and it is difficult to separate the consequences of de-eutrophication and the long-term consequences of hydropower construction work [8,15,45,72,78].

No significant correlation between phytoplankton biomass and any of the measured hydrophysical or hydrochemical parameters was found for the Lower Dniester, while many authors have shown that Cyanobacteria in the sediment and water column in particular are significantly influenced by temperature, total carbon, maximum flow velocity, and DIN, and the eukaryotic phytoplankton are influenced by total phosphorous, temperature, total carbon, maximum flow velocity, and total nitrogen [78,82] (Supplementary Materials Figure S5). The regression analysis for the pairs of the key factors of phytoplankton development and biomass of microalgae also gives rather low values of correlation. The highest multiple regression coefficient of 0.494 is observed for a combination of three factors: DIP, silicates and pH. Thus, at the present time, it is impossible to identify the main factor determining the development of phytoplankton. For the prediction of microalgae development, it is necessary to carry out a comprehensive assessment of the combined action of hydrological and hydrochemical factors. The analysis of phytoplankton vertical distribution shows no consistent difference in quantitative characteristics between surface and bottom layers, but in the summer period, the component of diatoms in the bottom layer was higher.

Species diversity of zooplankton in Lower Dniester could be described as relatively low (only 47), when the other long-term studies on low-land rivers show up 115–150 in both compared periods 1960s and 2000s [83]. However, the figures obtained in our study were comparable with historical data [7,12]. The values of Shannon index of 2.7 are typical of slow-flowing rivers and reservoirs [63].

After the start of the Dubossary HPP exploitation, the component of Rotifera in the total abundance in the zooplankton community declined two times down to 31% during the modern period, but their share in species diversity is still relatively high (25 species). On the other hand, the role of copepods, representing only by 4 species, increased 6.6 times up to 53% of total abundance [16,56,57,84]. In 2016–2020, Copepoda predominated among plankton invertebrates during all seasons, which is common for natural and artificial lentic water bodies (Figure 16).



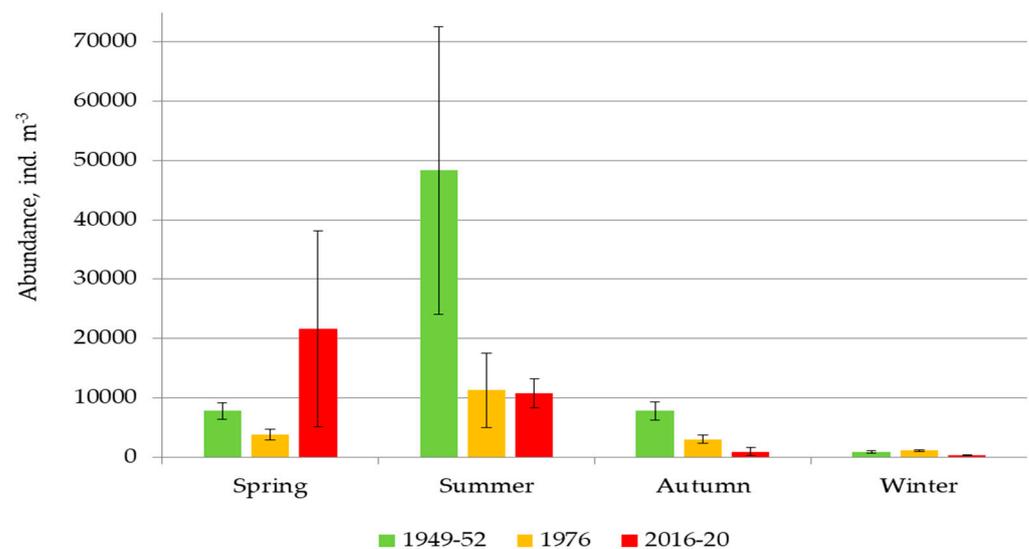
**Figure 16.** Long-term changes in zooplankton community structure in the Lower Dniester (1949–1952 according to [7], 1976 according to [12], 2016–2020 according to [4,5] and project data).

Earlier, Naberezhny A.I. [12,16,57] mentioned the change in the ratio of rotifers during the years with the high discharge of the Dniester, but during our recent studies, we have not received clear confirmation of this fact [12,16,57]. These shifts in the community composition may be related with an increase in average seasonal temperatures, and may also be caused by changes in seasonal water fluctuations in the Dniester Delta [2,11].

In comparison with the period of eutrophication (1970s), we noticed an increase in the average seasonal and average annual abundance of zooplankton. However, in comparison with the pre-eutrophication period, the biomass remained low (Figure 17).

According to historical data in the Lower Dniester, both in the 1950s and in the 1970s, the maximum abundance of zooplankton was observed in summer and the minimum in winter [9,11,12]. Spring and autumn were comparable by abundance [9,11,12]. Today, the maximum of average seasonal abundance has shifted from summer to spring, and the average autumn biomass has decreased. Perhaps this is related with a warmer spring, which quickly warms up the river to summer temperatures, or with a decrease in seasonal fluctuations in water discharge in the Dniester delta. A similar change was shown for different European rivers, while the warming trend associated with global climate change could affect zooplankton community structure, especially during the spring, allowing the “summer species” to start their development earlier [75,83,85].

Similarly, there are no significant correlations between the indicators of zooplankton and phytoplankton biomass, as well as any measured hydrophysical and hydrochemical parameters, except water temperature, for which the correlation with different zooplankton indicators ranged from 0.55 to 0.63. Thus, it is currently impossible to identify the main factor determining the development of zooplankton. To understand the processes taking place in the zooplankton community, it is necessary to analyse the complex influence of hydrological and hydrochemical factors.

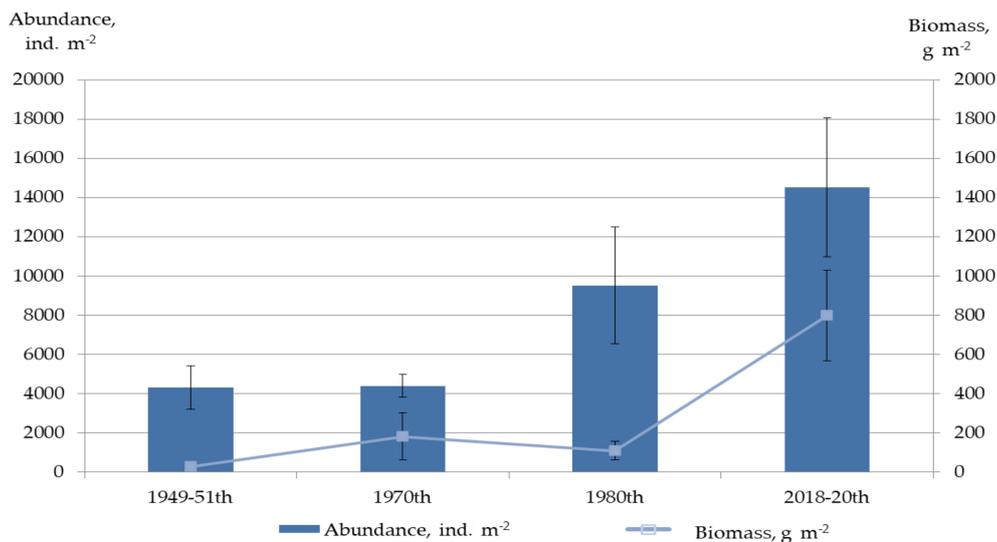


**Figure 17.** Long-term changes in the average  $\pm$  SE seasonal abundance of zooplankton (1949–1952 according to [7], 1976 according to [12], 2016–2020 according to [4,5] and project data).

Compared with the period of eutrophication, the saprobity calculated by zooplankton indicators on average was 1.83 (Supplementary Materials Figure S8), the value of the index being slightly better compared with the 1970s, when it was 1.88. Both values correspond to  $\beta$ -mesosaprobic zone (moderately polluted waters) [12,37,57]. This also indicates an improvement in the state of the zooplankton community in comparison with the 1970s [12]. A similar characteristic of saprobity (1.38–1.58 in 1962 and 1.74–2.01 in 2008) was given within the study of the Daugava river over the last 50 years [83]. Both examples show that zooplankton communities could keep relative stability for a long period.

The quality of historical data on macrozoobenthos of the Lower Dniester was different, and generally, the abundance and biomass were given only as characteristic of a big taxonomic group (family, order, etc.) and the species composition was given separately without qualitative characteristics [3,6,9–11]. Data from the period of natural conditions (before 1954) [3,9] contain figures available for calculation that made possible a detailed comparison with the modern situation using contemporary methods (Table 3). The  $\alpha$ -diversity was low (usually less than 15 species  $m^{-2}$ ) with a Shannon Index less than 1.5, typical for oligomixed communities. The main shifts in the taxonomic composition of the Lower Dniester took place after the start of Dubossary HPP and Dubossary reservoir exploitation [2,6]. In the 1950s, Yaroshenko F.M. [9] described six community types common for the Dniester river basing on substrates, but without distinguishing them by dominant species. According [3,9] *Viviparus viviparus*, *Lithoglyphus naticoides*, and *Polipedium spp.* were common for rock and aquatic plants biotopes, but currently, they are widely present on silts and sands. This shift in taxon composition and community structure were first described in the 1970s–1980s when the sedimentation characteristic change and the areas of silts increased and currently this tendency is still stable [6,10,11]. This illustrates the patch dynamics concept when species composition is stable, but the role and area of each species could change under an environmental or anthropogenic influence [86]. On the other hand, the role of species sensitive to water quality and common in the 1950s, such as *Unio crassus* (Philipsson, 1788) and *Palingenia longicauda* (Olivier, 1791) decreased. These formed their own communities, being extremely important as ecosystem engineers in the Lower Dniester and its delta, playing a significant role in ecosystem production processes [3,9]. A sharp decrease in the latter species in the 20th century is a pan-European trend [6,11,60]. It is shown that after the close extinction of this species in the 1970s, it recently appeared in the Moldavian Dniester and Prut [87,88]. We have not found EPT taxa regularly during 2018–2020, but have occasionally. During 2018–2020, only 4 species of crustaceans, mysids (*Katamysis warpachowskyi* G.O. Sars, 1893, *Limnomysis benedeni*

Czerniavsky, 1882) and gammarids (*Dikerogammarus haemobaphes* (Eichwald, 1841), and *Pontogammarus robustoides* (Sars, 1894)) were present regularly, but none of them became a community dominant [3,9,11]. The pulsation of the Ponto–Caspian species distribution is a long-term process associated with climate, in particular glacial changes, but this natural process is accelerated under the influence of flow regulation [89]. In 2018–2020, the taxa composition and the community structure was close to those of the Lower Dniester in the 1970s and 1980s, but the community biomass has increased significantly (KW-H(1;28) = 9.4828;  $p = 0.0021$ ) owing to Viviparidae [6,10,11] (Figure 18).



**Figure 18.** Long-term changes in the average  $\pm$  SE abundance and biomass macrozoobenthos, calculated based on historical [2,3,6,9–11] and project data.

Such production characteristics are common for polytrophic water bodies [19,63,66,90]. Hydropower dams could also affect the growth of Mollusca. The mussels immediately downstream from the dam grew faster than that of both up- and downstream populations, because of a substantial increase in water temperatures [75]. Our data are comparable with studies on the effects on macroinvertebrates, showing that hydropower dam construction can cause increases in biomass and decreases in taxon richness in downstream reaches [48,75,91]. Data from the period of natural conditions (before 1954) [3,9] contain figures available for calculation, making possible a detailed comparison with the current situation using contemporary methods (Table 3). Functional feeding groups and their compositions are common for big lowland rivers, with reestablishment of Gatherers/Collectors among the FFG. Conversely, the share of filter-feeders was relatively low in both periods. Consequently, the Potamon Type Index characterised the conditions as “bad” [63,66,90,92]. There was no significant difference between the mean LIFE index in 1950s and the modern period (Table 3), but the general range of the index has increased. No correlation with the discharge of the river and other chemical or physical factors was found. The Saprobity index has not shown the changes between the natural flow period and modern time, because of the prevalence of  $\beta$ -meso-saprobic indicator species within the community. Consequently, the water of the Lower Dniester is considered as “moderately polluted”; according to these criteria, the same figures were described for 1980s data [10,11].

#### 4.4. Biological Indicators of HPP Influence in the Lower Dniester

The effects of dam and HPP construction on biological communities have attracted the attention of researchers and environmental activists throughout the world [75]. HPP influences multiple aspects of the aquatic ecosystem, primarily changing the current velocity and decrease in general flow of the river, increasing the water temperature, shifting in sedimentation process, and migration of nutrients and other chemical elements. All

of these effects were observed within the study of the modern environmental state of the Lower Dniester during the 2018–2020 years. It is important to distinguish long- and short-term effects on the ecosystems' biological components, depending on the length of the life cycle of the organisms.

Dam construction led to the changes in microalgal communities both in reservoirs and in river reaches and estuaries below the dams [75,80,81]. During the study of the immediate effect of release from the Dubossary hydropower station in 2019 [55], it was shown that after the release, the concentration of dissolved silicates, and consequently, the proportion of diatoms, becomes higher. However, in the long term, precipitation of silicates in hydropower reservoirs led to the lack of dissolved silicates, and the dominant phytoplankton functional group shifted from diatoms (Bacillariophyta) to green algae (Chlorophyta) along the flow direction below the dam. The changes in proportion of Bacillariophyta and Chlorophyta may become a primary indicator of HPP impact. An increase of average diatom proportion in the spring may indicate the adaptation of the phytoplankton community in comparison with the first decades after hydropower construction. However, in the summer period, the proportion of Bacillariophyta decreased, together with increasing in cyanobacteria and dinoflagellates, which is characteristic of waters affected by upstream dams [75,80,81]. Nevertheless, the proportion of Bacillariophyta in total phytoplankton biomass in the 1970–72 and 2018–2020 remained the same.

The reduction in river discharge and consequent current velocity resulted in a change from lotic (rheophilic) communities to lentic (limnophilic) ones. Upper and middle parts of rivers are usually more sensitive to such impacts, based on the River Continuum Concept [63,66,75], but in lower reaches, this effect is also visible in long-term studies both in the zooplankton and macrozoobenthos. In the case of the Lower Dniester, the start of Dubossary HPP and Dubossary reservoir exploitation in the 1950s caused the shifts in structure and functioning of invertebrate communities. Since the 1950s, there has been a tendency to decrease the role of running water Rotifera taxa in the zooplankton community and a concomitant increase in that of Copepoda, which may provide an indicator of HPP impact [63,75–77]. These structural changes may be a result of increases in average seasonal temperatures, as well as a smoothing in seasonal water fluctuations in the Dniester delta after HPP construction. The last assumption is supported by the work of Naberezhny A.I., who noted a change in the ratio towards rotifers in high-water years [12]. However, we have observed no clear correlation between the proportion of rotifers and discharge volumes [16,57].

The decrease of role of Ponto–Caspian species complexes and reduction of macrozoobenthos community types covering the river bed was observed during the 1970s and 1980s, in comparison with the natural flow period [6,10,11]. Due to the changes in sedimentation regime, the area of soft-bottom sediments and water plants increased, favouring Gastropoda, specially *Viviparus ater*, *Viviparus contectus*, and *Viviparus viviparus*. This resulted in a significant increase of community biomass, but without a general shift in FFG composition, with a predominance of gatherers in the community, confirming a coincidence with the combined concept of river ecosystem functioning of Bogatov V.V. [66,86,93]. It should be noted that no changes of Potamon Type index values in the natural flow and modern period was observed, which may be related to the influence of Dniester Estuary on the Lower Dniester, slightly mitigating the HPP effect. The value of the index characterised the environmental state as “bad” on both occasions, however, perhaps related to regional fauna differences [63]. On the other hand, the fast growth of the mussel population both in up- and downstream from the dam also could be related, not only with sedimentation loads, but with rises in annual water temperatures [75]. Therefore, the loss of benthic community types and their unification within the water area with the increase of Gastropoda biomass, can be considered as indicators of HPP impact.

## 5. Conclusions

A decrease in the maximum flow rates during floods, due to the transforming and smoothing effect of the Dniester and the Dubossary reservoirs, leads to a significant deterioration in the “washing” of the riverbed and cleansing of silt deposits, especially in the lower part of the river. This negative phenomenon is especially manifested in years of medium and low water levels. The problem of a decrease in discharge in the Middle and Lower Dniester, which manifested itself after the construction of the Dniester reservoir, is not only the result of evaporation and infiltration into the groundwater horizons that do not discharge into the river channel, but also irreversible losses due to water management needs. Predominantly, this is due to a significant decrease in inflow from the Dniester tributaries flowing into the main river below the Mohyliv-Podilskiy HGS. The decrease of precipitation and increase in average annual air temperature has already led to a decrease in the total water content of the Dniester River, which for almost 10 years has not been able to reach the value of the statistical “norm”. To date, the norm or long-term average value of the total annual runoff of the Dniester, with different assessment methods, is taken to be from 9.2 to 10.2 km<sup>3</sup>.

The concentrations of various forms of nutrients are characterised by multidirectional seasonal dynamics and depend on the temperature, runoff value, and autotrophic production/decomposition of organic matter. In the last 20 years, the stabilization of concentrations took place. These concentrations are lower than at the peak of eutrophication in the 1970s–1980s, but higher than in the 1950s. The construction of reservoirs leads to a long-term decline in silica concentrations.

In terms of the concentration of heavy metals and metalloids in water and bottom sediments, the lower part of the Dniester River generally corresponds to the ecological status of “Moderate”. Exceeding the environmental quality standard EQS of the most toxic heavy metals such as mercury, lead, and cadmium, was observed only in isolated cases. To a large extent, with an excess of EQS, there is copper pollution in the lower reaches of the Dniester, which belongs to the II (second) hazard class. On the section of the Dniester river between Palanca (51 km) and Maiaky in bottom sediments, a decrease in the concentration, on average by 10%, of all studied heavy metals and metalloids was observed.

During the period of study, 264 taxa of microalgae that belong to 11 classes were found. Diatoms, green algae, and cyanobacteria dominated by species number and by abundance, but from year to year, the share of separate phyla varied significantly. Comparing with the previous studies of the regulated period (1970–1972 and 1986), we noticed an evident decrease of phytoplankton biomass. However, for most of the year, phytoplankton biomass was higher than in the pre-regulated period. Almost all year round, diatoms are dominated in the biomass. Comparing with 1970–1972, the role of Cyanobacteria in total phytoplankton biomass of the Lower Dniester in the autumn and winter period had decreased, and in summer period increased, and the share of Bacillariophyta in spring increased, and in summer decreased. No constant difference in quantitative characteristics between surface and bottom layers and between sites was shown, but in the summer period, the proportion of diatoms in the bottom layer was higher.

During the period of study, 47 taxa of planktonic invertebrates, Cladocera, and Rotifera were widely represented by species number, but Copepoda dominated in abundance and biomass of the community over all seasons. The role of Rotifera in the community decreased, but there was no evident correlation with the Dniester discharge. Because of changes in water temperature, the maximum abundance shifted from summer to spring, abundance and biomass over the autumn and winter were lower than the natural flow period.

Macrozoobenthos communities could be characterised as oligomixed ones (Shannon index did not exceed 1.5), but  $\beta$ -diversity was relatively high and comparable with the historical data. A number of 108 taxa were identified to the lowest possible rank; among them were Diptera (23), Gastropoda (22), and Oligochaeta (18). Compared to the period before the regulation of the Dniester flow, there is a decrease in the role of macrozoobenthos

species in the communities of the Ponto-Caspian species and the rare occurrence of sensitive groups—Ephemeroptera and Trichoptera. *Viviparus* spp. with different co-dominants covered all the biotopes. Average values of abundance of  $14,500 \pm 3500$  ind.  $m^{-2}$  and biomass of  $0.8 \pm 0.2$  kg  $m^{-2}$  for the community are common for polytrophic water bodies.

Saprobity index calculated both for zooplankton (1.83) and macrozoobenthos ( $2.25 \pm 0.06$ ) characterised the Lower Dniester waters as moderately polluted waters during 2018–2020. Comparing benthic biotic indexes (BMWP, BBI and PTI) computed on natural flow period and modern period, described the environmental state as low on both occasions. The range of the LIFE index increased, but it was not significantly different from the 1950s and was comparable with low current velocity ecosystems. DSFI is not applicable for the Low Dniester because of the lack of indicator groups both in modern and historical data and suggests an adaptation for big lowland rivers of the Black Sea basin.

Biological communities react to HPP impact both in short and long-term aspects. Hydropower dams change nutrient bioavailability downstream, which in the long-term causes changes in the phytoplankton community, especially the decrease of diatoms due to the lack of silicates because of deposition in reservoirs. However, in the short-term, after the release from the HPP dam, the concentration of silicates and the proportion of Bacillariophyta increases. Long-term changes also include decreasing of Rotifera proportion and increase in the proportion of Copepoda in the total abundance of zooplankton. In addition, this matches with the zoobenthos community with an increase Gastropoda biomass within the water body. All can be considered as indicators of the HPP impact.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/app11219900/s1>. Figure S1: Dynamics of monthly runoff values and amount of total suspended solids, Figure S2: The ratio of the average seasonal concentrations of heavy metals and metalloids to their environmental quality standards (EQS) in the waters of the Lower Dniester near the village of Maiaky, Figure S3: The ratio of average and extreme concentrations of heavy metals and metalloids to their environmental quality standards (EQS) in bottom sediments of the Lower Dniester, Figure S4: Taxonomic structure of phytoplankton of the Lower Dniester (2018–2020), Figure S5: Correlations between phytoplankton biomass and hydrochemical indicators (2018–2020), Figure S6: Changes of (a) total phytoplankton biomass and (b) the contribution of different classes in the surface (S) and bottom (B) layer of Lower Dniester (2020), Figure S7: Taxonomic diversity of zooplankton in the Lower Dniester during 2016–2020, Table S1: Inter-annual variation of zooplankton abundance and biomass (Average  $\pm$  SE) in the Lower Dniester in 2016–2020, Figure S8: Saprobity level for zooplankton in the Lower Dniester during 2016–2020 according to [4,5] and project data, Figure S9: Correlations between zooplankton statistics and hydrochemical indicators, Figure S10: Combined hydrograph of the annual runoff volumes for the 1946–1981 period within selected HGS, Figure S11: Combined hydrograph of the annual runoff volumes for the 1987–2020 period within selected HGS, Table S2: Long-term variations of nutrients in the Lower Dniester (above the line—average values; below the line—range of variation), Figure S12: The contribution of different phyla of microalgae in the total phytoplankton biomass (a) total biomass per year; (b) seasonal changes of biomass; 1970–1972 according to [15], 2018–2020—our data.

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