

Article

A Comprehensive Assessment of the Ecological State of the Transboundary Irtysh River (Kazakhstan, Central Asia)

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Abstract: The diverse anthropogenic load on the transboundary Irtysh River necessitates an assessment of its ecological state, which was the goal of this work. We conducted this research in July 2023 in the upper and lower reaches of the Kazakh part of the Irtysh basin. We determined transparency; temperature; pH; salinity (TDS); oxygen, N-NO₃, N-NO₂, N-NH₄, PO₄, Mn, Fe, Si, Cd, Cu, Zn, Pb, Cr, Co, and Hg contents; permanganate index; and zooplankton variables at 27 stations. We assessed the ecological state of the river by comparing the contents of pollutants with their maximum permissible concentrations (MPC_{fw}), Classification Scales, and bioindications. An excess of MPC_{fw} was detected for N-NO₂, Cu, and Fe and locally for Cr and Zn. According to the Classification Scales, most analysed variables corresponded to slightly polluted waters; N-NO₂, Cr, and Zn corresponded to moderately and heavily polluted waters. Zooplankton was represented by 82 species, with an average abundance of 6728 individuals/m³, biomass of 2.81 mg/m³, Shannon index of 1.99–2.08 bit, Δ-Shannon of 0.09, and average individual mass of 0.0019 mg. The spatial distribution of abiotic and biotic variables indicated increased organic and toxic pollution downstream in the Irtysh. Potential sources of pollution of the Irtysh basin are discussed.

Keywords: pollution; zooplankton; bioindication; heavy metals; nutrients; water quality; transboundary basin



Citation: Krupa, E.; Romanova, S.; Serikova, A.; Shakhvorostova, L. A Comprehensive Assessment of the Ecological State of the Transboundary Irtysh River (Kazakhstan, Central Asia). *Water* **2024**, *16*, 973. <https://doi.org/10.3390/w16070973>

Academic Editors: Guilin Han, Jian Hu and Qian Zhang

Received: 23 February 2024

Revised: 19 March 2024

Accepted: 22 March 2024

Published: 27 March 2024



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1. Introduction

The most practical approach to objectively assessing the ecological state of aquatic ecosystems involves a combination of chemical and biological methods (bioindication) [1]. Bioindication is based on the response of biological communities to a set of external factors, which makes it possible to characterise the ecological well-being of a reservoir as a whole [2,3]. Using chemical variables for analysis aims to identify the potential causes of registered environmental problems.

Zooplankton is effectively used to assess the ecological state of lakes and reservoirs [4–9]. The bioindication of rivers is associated with methodological difficulties since the decisive factor in forming planktonic communities is the flow speed and constant removal of individuals by water masse [10]. The hydrological regime of a water body significantly impacts the species composition and quantitative variables of planktonic communities. In fast-flowing rivers, as a rule, rotifers dominate [11–15]. For planktonic crustaceans, favourable conditions develop in water bodies with slow water exchange (ponds, lakes, reservoirs, and slow-flowing rivers). Accordingly, at the same pollution level, the structure of zooplankton communities in rivers, lakes, and reservoirs can vary significantly. This must be considered when assessing the ecological state of rivers using bioindication methods mainly developed for lakes and reservoirs [4].

The transboundary Irtysh River flows through the territory of China, Kazakhstan, and Russia. Flow regulation and intensive use of water resources have given rise to many environmental and social problems throughout the Irtysh basin. The construction

of reservoirs [16] has led to the disruption of the floodplain watering regime and the degradation of floodplain ecosystems [17]. Irreversible water intake over the entire river basin area [18] led to the shallowing of the Irtysh. To ensure the safety of vessel traffic in the Pavlodar Irtysh region, dredging work is being carried out, which, together with sand extraction, causes a decrease in water transparency. The unsatisfactory water quality of the Irtysh River [19] is associated with the extraction and processing of minerals, water removal for agricultural and industrial purposes, and the discharge of poorly treated or untreated wastewater into the river and its tributaries [20–22].

Despite the close attention of scientists and the public to the environmental problems of the Irtysh River, a comprehensive assessment of its water resources has not been carried out to date. There are data (2010–2011) on the content of nutrients and some heavy metals in the water of the upper (Black Irtysh) and middle (in the zone of influence of the upper Irtysh cascade of reservoirs) reaches of the Irtysh River [22]. The same work assessed toxic pollution of the right tributaries of the middle reaches of the Irtysh (Ulba, Krasnoyarka, and others) using biotesting methods. An analysis of the long-term dynamics (1986–2011) of the pollutant contents in certain sections of the Irtysh River has been given [18]. The zooplankton of the upper Irtysh cascade of reservoirs has been relatively well studied [23–25], but only one work [26] has been devoted to river zooplankton.

The purpose of this study was to comprehensively assess the ecological state of the Kazakh part of the Irtysh River based on chemical variables and the structure of zooplankton communities. This work partially fills the existing gaps in the hydrochemical, toxicological, and hydrobiological description of the Irtysh River. In territorial terms, it covers the most poorly studied areas of the basin—its upper (Black Irtysh within Kazakhstan) and lower (Pavlodar region) reaches. This work demonstrates some methodological approaches that can be used to monitor water basin studies.

1.1. General Characteristics of the Irtysh River Basin

The Irtysh River begins on the western slopes of the Mongolian Altai in China, flows through Kazakhstan, and empties into the Ob River in Russia. The total length of the Irtysh River is 4248 km; in Kazakhstan, it is 1698 km. The nutrition of the Irtysh River is mixed: in the upper reaches, it is snow–glacial; in the lower reaches, it is snow, rain, and soil. The width of the riverbed reaches 0.2–0.9 km, with an average slope of 3–7 cm/km. The depth varies from 1 to 2 m on the rifts to 3 to 15 m on the reaches. The average current speed in low water is 2.5–3.5 km/h and up to 4.5–5.1 km/h in high water. The bottom is mostly pebble, sometimes sandy. The banks are composed of clay and overgrown with trees and shrubs.

In the upper reaches, from the source to the confluence with Zaisan Lake, the river is called the Black Irtysh (Figure 1). The length of this section in Kazakhstan is about 120 km. The riverbed is winding, breaks into branches, and forms an extensive delta before flowing into Lake Zaisan. The width of the floodplain is from 1.0 to 12.0 km. The Kalzhir River flows into the Black Irtysh (Figure 2a,b), originating in the mountain Markakol Lake at 1447 m above sea level. The left tributary Kenderlik (Figure 2c,d) originates on the northern slopes of the Sauyr ridge at an altitude of 3000–3200 m and flows into the mouth of the Black Irtysh.

Below Zaisan Lake, the Irtysh River is regulated by the Bukhtarminsky, Ust-Kamenogorsky, and Shulbinsky reservoirs (upper Irtysh cascade). Large right tributaries Bukhtarma, Kurchum, Ulba, Uba, and others flow into this section. Here are the cities of Altai, Serebryansk, Ust-Kamenogorsk, Semey, and Ridder. The length of this section of the river is about 820 km, with a height difference from 388 to 159 m above sea level.

There are no tributaries in the lower reaches of the Kazakhstani part of the Irtysh River (below the upper Irtysh cascade of reservoirs). The length of the section is about 760 km. The width of the floodplain varies from 5 to 15 km. The cities of Kurchatov, Aksu, and Pavlodar and numerous villages are located here.

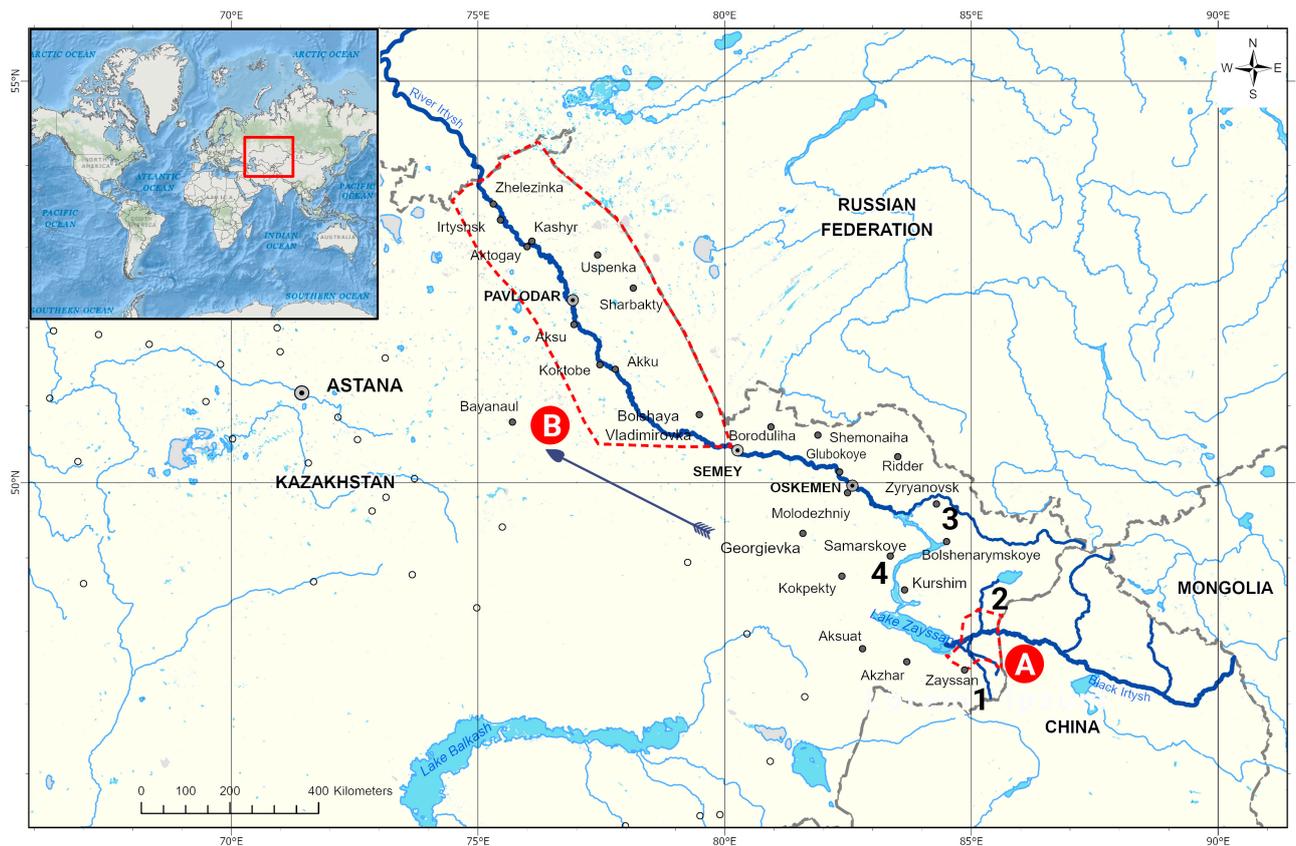


Figure 1. Map scheme of the location of the surveyed parts of the Irtysh River basin, July 2023. A—Black Irtysh River, B—Pavlodar Irtysh region. Arabic numerals: 1—left tributary Kenderlik, 2—right tributary Kalzhir, 3—right tributary Bukhtarma, 4—upper Irtysh cascade of reservoirs. The arrow shows the direction of flow of the Irtysh River, determining left-bank or right-bank tributaries from up to downstream (the river flow direction).



Figure 2. Tributaries of the Black Irtysh River, July 2023: (a) right tributary Kalzhir, mountainous part; (b) right tributary Kalzhir, before flowing into the Black Irtysh River; (c,d) left tributary Kenderlik. Photo by E. Krupa.

1.2. Potential Sources of Pollution of the Irtysh River

A significant part of the Irtysh basin is located in the zone of geochemical anomalies. There are deposits of gold [27] and polymetallic (Au, Ag, Mo, Cu, Fe, Pb, and Zn) ores [28]. In the Pavlodar region (lower reaches), 142 mineral deposits are known. Due to the geological features of the territory, the ratio of metals to water for the Irtysh basin is $Zn > Cu > Mn > Pb > Mo > Cr > Cd > Co$ [29,30]. Industrial enterprises in the middle and lower reaches of the Kazakh part of the Irtysh basin carry out ore processing. The total number of industrial enterprises in East Kazakhstan is 133 [31]. Most of them are concentrated in the cities of Ust-Kamenogorsk (61), Ridder (13), Glubokovsky (24), and Altai (14) (middle reaches). There are 185 industrial enterprises in the Pavlodar region (downstream), a significant part of which are located in the cities of Pavlodar (59), Aksu (23), and their surrounding areas (46) [32]. Near Pavlodar city, in the riverbed of the Irtysh River, non-metallic building materials (sands of various sizes and gravel–pebble deposits) are mined (Figure 3a).



Figure 3. The Irtysh River in the Pavlodar region, July 2023: (a) sand mining in the riverbed (below Pavlodar City); (b) wastewater discharge into the Irtysh River (Terenkol village); (c) water intake in the area of Zhelezinka village; (d) water intake in the area of Terenkol village. Photos by E. Krupa and A. Linnik.

Agriculture and livestock farming are widespread in the Irtysh basin. Within the Pavlodar region, the most significant areas sown with crops are concentrated in the lower part of the basin along both banks of the Irtysh River [32]. In the East Kazakhstan region, the most agriculturally developed territories are located at a considerable distance from the floodplain of the Black Irtysh River. The right bank part of the Black Irtysh drainage basin is represented by a foothill plain and mountainous areas unsuitable for agriculture. Directly adjacent to the left bank of the Black Irtysh floodplain are foothill sandy and alluvial–deltaic plains unsuitable for agriculture.

The environmental problems of the Irtysh basin are associated with the industrial and agricultural development of the region. The water of the Irtysh River is used for drinking water in populated areas (Figure 3c,d) as well as for agriculture, livestock farming, and industries. Wastewater is discharged into the river and tributaries, sometimes without

preliminary treatment (Figure 3b). In the Pavlodar region alone, there are 29 enterprises with 49 wastewater outlets [33]. The total wastewater discharge into the Irtysh River and its tributaries is almost 3000 million m³ annually [18].

2. Materials and Methods

Comprehensive studies of the Kazakh part of the Irtysh River were carried out in the East Kazakhstan and Pavlodar regions in four parts, which differ significantly in the intensity and nature of anthropogenic load (Table 1).

Table 1. Description of the surveyed parts of the Irtysh River, indicating potential sources of pollution.

Part Number	Description	Length, km	Number of Stations	Altitude above Sea Level	Potential Sources of Pollution
I	Black Irtysh River	120	5	390–419	Buran and Ordynka villages, transboundary flow from China
II	Above Pavlodar and Aksu cities	236	7	113–172	Kurchatov City, flow from the upper Irtysh cascade of reservoirs
III	Zone of influence of Pavlodar and Aksu cities	81	7	101–115	Pavlodar and Aksu cities, surface runoff
IV	Below Naberezhnoe village	316	8	79–102	Settlements, surface runoff

Part I includes the Black Irtysh River from the border with the People’s Republic of China to its confluence with Zaisan Lake (Figures 1 and 4a). It can be considered relatively unimpacted since the Black Irtysh River is located far from industrial centres and agricultural enterprises. Currently, there is only one relatively large village, Boran, with a population of 1506 (according to 2009 data). The second village of Ordynka (Zhideli) has only 327 residents.

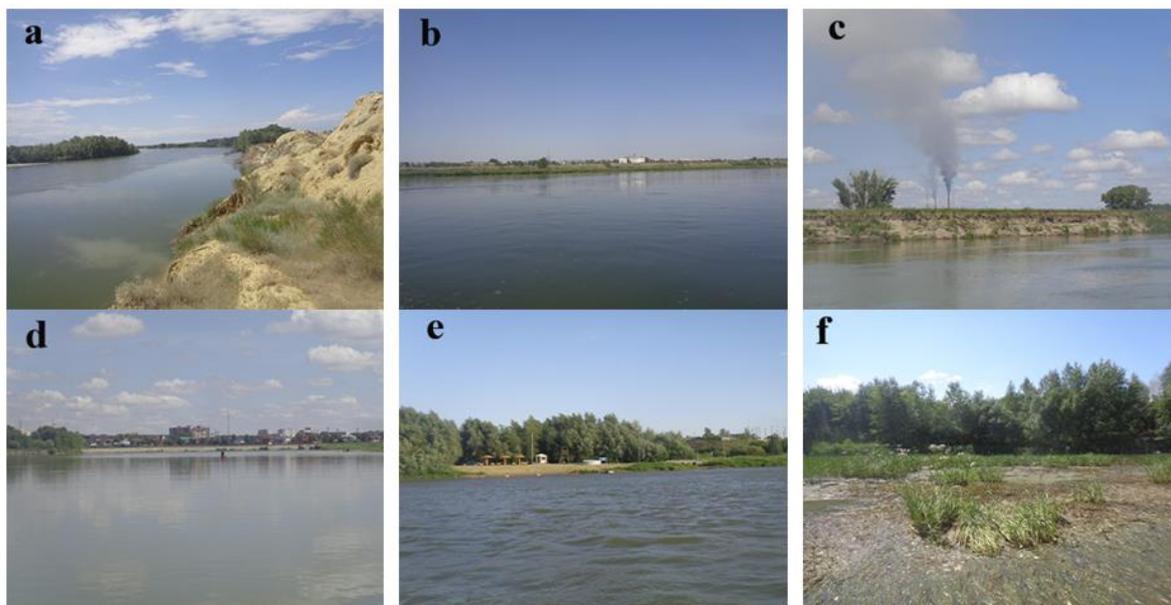


Figure 4. Surveyed parts of the Irtysh River, July 2023: (a) Part I (the Black Irtysh River); (b) Part II (the Irtysh River above Aksu city); (c) Part III (the Irtysh River in the zone of influence of Aksu city); (d) Part III (the Irtysh River in the zone of influence of Pavlodar city); (e) Part IV (the Irtysh River below Pavlodar city); (f) Part IV (the Irtysh River below Pavlodar city, 15 km from the border with Russia). Photos by E. Krupa.

The following three parts (II–IV, Pavlodar Irtysh region) are located below the upper Irtysh cascade of reservoirs, from the eastern border of the Pavlodar region to the border with Russia (Figure 4b–f). The section of the river above the Pavlodar and Aksu cities (Part II) experiences residual pollution coming from the upper reservoirs of the upper Irtysh cascade. Part III is located in the zone of influence of industrial and utility enterprises in the Pavlodar and Aksu cities. The lowest section of the Irtysh River (Part IV) experiences residual pollution from the upstream sections of the river. There are no large cities or industrial enterprises there. Numerous settlements and agricultural fields make an additional contribution to the overall level of pollution in the lower reaches of the Kazakh part of the Irtysh River.

The selection of sites allows us to assess the water quality of the transboundary Irtysh River at the inlet (receipt from the territory of China), the entry of pollutants into the territory of Kazakhstan, and their further transboundary transfer to the Russian part of the basin.

2.1. Field Methods

Sampling was conducted in the Irtysh River at 27 stations in July 2023 (Figure 5).

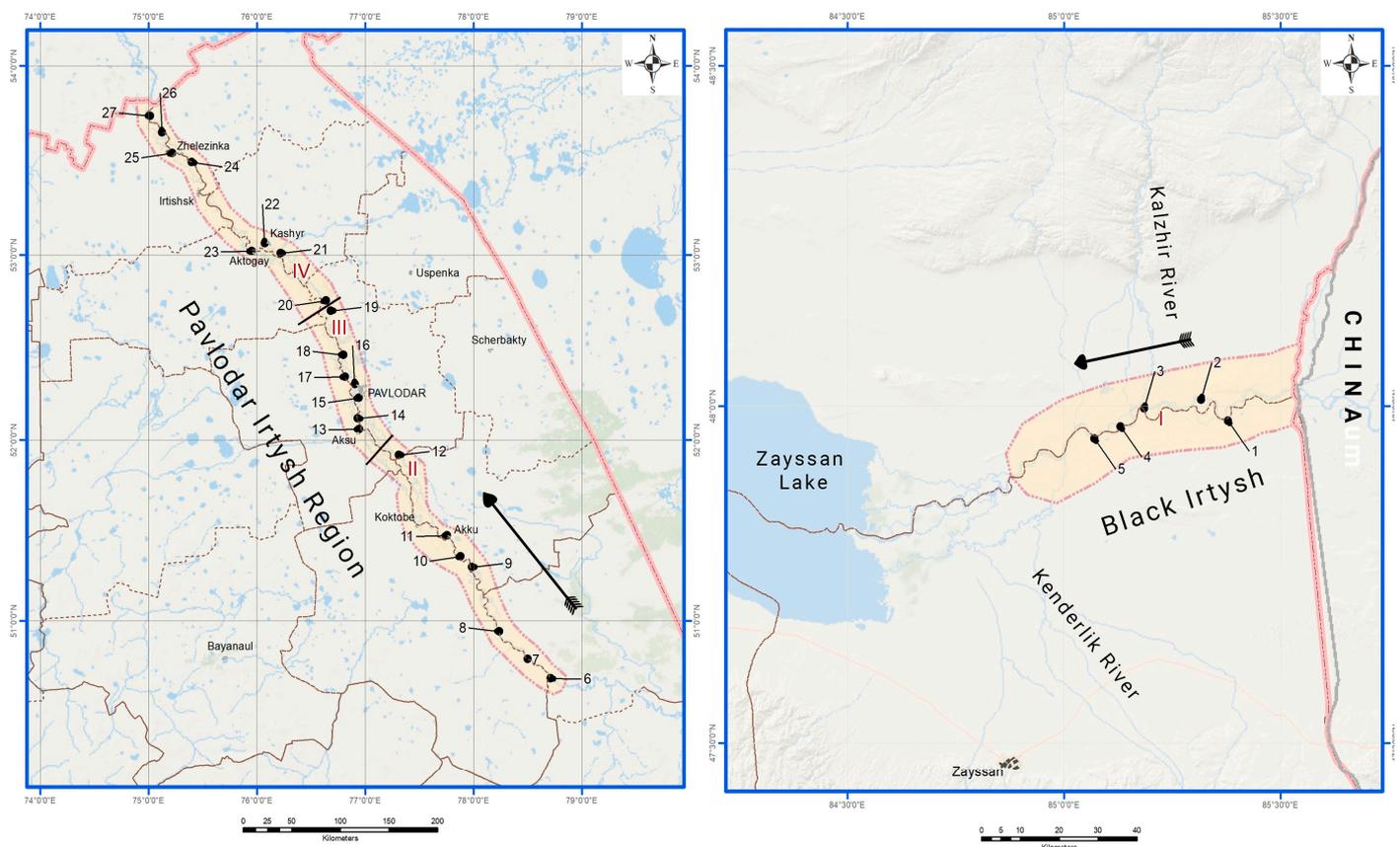


Figure 5. Material sampling stations in the Black Irtysh (Part I) and Pavlodar Irtysh (Parts II–IV) regions, July 2023. Roman numerals indicate the numbers of surveyed parts of the Irtysh River basin. Arabic numerals indicate station numbers. Arrows indicate the direction of flow.

Station coordinates were determined using a Garmin eTrex GPS navigator. Transparency, water temperature, and pH values were determined at each station. The pH value was measured using an AMTAST digital pH meter. Water samples were taken to determine dissolved oxygen, mineralisation (TDS), nitrates (N-NO₃), nitrites (N-NO₂), ammonium nitrogen (N-NH₄), phosphates (PO₄), manganese (Mn), total iron (Fe), silicon (Si), and easily oxidised organic substances (permanganate index PI). Water samples were also taken to determine the content of seven heavy metals, cadmium (Cd), copper (Cu), zinc (Zn), lead

(Pb), chromium (Cr), cobalt (Co), and mercury (Hg), as the most dangerous toxic pollutants in the Irtysh water basin. Samples for the determination of nutrients were fixed with chloroform for the determination of heavy metals with concentrated nitric acid and easily oxidised organic substances with sulphuric acid at a dilution of 1:3. The determination of dissolved oxygen was carried out in field conditions using the Winkler method [34]. This method is based on the ability of manganese hydroxide to oxidise into a compound of higher valency in an alkaline environment. Manganese hydroxide quantitatively binds oxygen dissolved in water and then, in an acidic environment, it is again converted into divalent compounds while oxidising an equivalent amount of iodine. The released iodine was determined by titration with thiosulfate. Zooplankton samples were collected by filtering 50–100 L of water through Apstein’s plankton net [35] and fixed with 40% formaldehyde to a final concentration of 4%.

2.2. Laboratory Analysis Methods

The determination of the ionic composition of water, TDS, and contents of Mn, Fe, Si, nitrites, nitrates, ammonium, and phosphates was carried out by the following methods [34,36]. First, the content of ions (Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , HCO_3^- , CO_3^{2-} , and $\text{Na}^+ + \text{K}^+$) was determined using traditional hydrochemical methods to calculate TDS further. Hydrocarbonate and carbonate ions were determined by volumetric direct titration. Calcium and magnesium ions and total hardness values were determined by the complexometric method with indicators chrome black murexide ET-00. Sulphates were determined by the gravimetric method. The volumetric argentometric method was used to determine chlorides. The total content of sodium and potassium ions was calculated as the difference between the sum of anions and cations. Finally, we summed the content of all anions and cations to calculate the total mineralisation or TDS. The content of nutrients and manganese was determined by the photolorimetric method (method sensitivity 0.02 mg/dm^3 , error $\pm 2\text{--}4\%$). Depending on the element being determined, we used various indicators: for ammonium ions—Nessler’s reagent, for nitrite and nitrate ions—Griess’s reagent, for phosphates—ascorbic acid, for iron—sulfosalicylic acid, for silicon—ammonium molybdate, for manganese—formaloxime.

The determination of heavy metals was carried out at the Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan (Almaty, Kazakhstan) by mass spectrometry with inductively coupled plasma on an ELAN 9000 device (Perkin Elmer SCIEX, Shelton, CT, USA) according to Interstate Standard 31 870-2012 [37] with an accuracy of $0.00006\text{--}0.0002 \text{ }\mu\text{g/dm}^3$.

We identified the species of planktonic invertebrates using the MCX-300 Orchid LED microscope (MICROS, Hunnenbrunn, Austria) according to the identification keys and figures given in the monographs [38–40]. We processed zooplankton samples according to the methods described by Kiselev [35], with our additions. First, a sample was brought to a particular volume ($150\text{--}500 \text{ cm}^3$). After thorough mixing, three sub-samples were taken from the sample using a 1 mL stamp pipette. In this sub-sample, all encountered individuals and age stages of certain species (the most numerous) were counted in Bogorov’s cell. The sample was concentrated to $125\text{--}150 \text{ cm}^3$ in the next step. Three sub-samples were retaken from it, where less abundant age stages or species were counted. The whole procedure was repeated once more while the sample was concentrated to a volume of 50 cm^3 . In the end, the sample, with its volume of $20\text{--}25 \text{ cm}^3$, was viewed in its entirety for counting large and rare species of planktonic invertebrates. The results of counting individuals of all species and age stages were recalculated per one m^3 using the below formula (separately for each sample dilution):

$$N = \frac{n \times (V1/V2)}{V3} \quad (1)$$

where N—abundance (specimens/ m^3), n—number of individuals (specimens) in a portion, V1—dilution volume (cm^3), V2—subsample volume (cm^3), and V3—filtered water volume (m^3). The filtered volume of water (50–100 L) was recalculated per m^3 ($0.05\text{--}0.10 \text{ m}^3$).

We calculated an individual's mass (including different age stages of planktonic invertebrates) according to formulas specific to each species [41]. The formulas were based on the relationship between an individual's mass and length. We calculated each species' total abundance and biomass by summing the abundance and biomass of their individual age and size stages. Ultimately, we determined zooplankton's total abundance and biomass (per m³) by summing up the abundance and biomass of all species in the sample.

For each sample, we calculated the Shannon index by abundance (Shannon Ab) and biomass (Shannon Bi) [42], the Δ -Shannon index [43], and the average individual mass of a specimen [4]. Shannon index values were calculated in the Primer 6 programme. Δ -Shannon values were found as the arithmetic difference between two versions of the Shannon index, Shannon Ab and Shannon Bi [43]. The average individual mass of a specimen was found by dividing the total biomass by the total abundance of zooplankton [4].

The calculation of species similarity was performed as the network analysis in JASP 0.9.0.0 (Jeffrey's Amazing Statistics Program, University of Amsterdam, Amsterdam, The Netherlands) with the botnet package in R-Statistica 4.1.1 (R Core Team, Vienna, Austria). JASP plot analysis was created as a calculation result of the 50% similarity; the level was significant only when $p < 0.05$ [44].

2.3. Environmental Assessment

We assessed the ecological state of the Irtysh River by comparing the recorded concentrations of pollutants with (a) their maximum permissible content for water bodies of fishery importance (MPC_{fw}) [45]; (b) the Ecological Classification Scale in the section "Nutrients" [46]; and (c) the Regional Classification Scale in the section "Heavy metals" [47].

Bioindication of the ecological state of the Irtysh River was carried out based on the analysis of the abundance of zooplankton, the composition of dominant species and their environmental preferences, values of the Δ -Shannon index [43], the average individual mass of a specimen [4], and the presence of specimens with morphological deviations in copepod populations [48]. The Δ -Shannon index is a numerical analogue of the graphical index of Clarke's W-statistic [49] and characterises the structure of species dominance in communities. In undisturbed communities, large species dominate, especially in terms of biomass, so Shannon Ab is more than Shannon Bi. As a result, Δ -Shannon values are positive [43]. At eutrophication, the increased dominance of small species in abundance and biomass reflects the inverse ratio of these variables and negative Δ -Shannon values.

3. Results and Discussion

3.1. Hydrophysical, Hydrochemical, and Toxicological Characteristics

The banks of the Irtysh River are composed mainly of clays (Figure 3). Woody vegetation is widespread in the floodplain of the Black Irtysh River. Significant areas in the Pavlodar Irtysh region are characterised by sparse vegetation cover. In the coastal zone, especially in the lower reaches (sections II–IV), common reed *Phragmites australis* Cav. Trin. ex Steud. is widespread (Figure 6d). In shallow waters, the umbrella plant *Butomus umbellatus* L. (Figure 6b) and several species of pondweeds, including *Potamogeton perfoliatus* L. (Figure 6c), are widespread. Filamentous algae develop on mass (Figure 6a). Bottom sediments are represented mainly by pebbles and sand in places with a thin layer of silt.

During the research period, the water temperature reached 23.0–25.2 °C. The transparency of the water was low and did not exceed 5–7 cm. The large number of particles suspended in the water was due to several factors: in the upper reach, these factors were a relatively high flow speed and the destruction of clayey banks; in the lower reach, these factors were the destruction of clayey banks (locally) and dredging and sand mining in the river bed (Figure 2a). The dissolved oxygen content was at a high level (Table 2).



Figure 6. Higher aquatic and semi-aquatic vegetation in the lower reaches of the Irtysh River, July 2023: (a) filamentous algae; (b) umbrella pine *Butomus umbellatus* L.; (c) pondweed *Potamogeton perfoliatus* L.; (d) common reed *Phragmites australis* (Cav.) Trin. ex Steud. Photos by E. Krupa.

Table 2. Hydrophysical, hydrochemical, and toxicological characteristics of the surveyed parts of the Irtysh River, July 2023 (mean and standard error).

Variable	¹ The Part of the Irtysh River			
	I	II	III	IV
Temperature, °C	23.00 ± 0.17	24.90 ± 0.26	24.40 ± 0.38	25.20 ± 0.13
pH	7.20 ± 0.06	7.90 ± 0.06	7.60 ± 0.03	7.70 ± 0.05
Oxygen, mg/dm ³	9.04 ± 0.06	8.44 ± 0.40	8.39 ± 0.29	10.07 ± 0.06
TDS, mg/dm ³	100.7 ± 3.4	176.2 ± 3.0	177.7 ± 2.3	175.5 ± 3.2
Hardness, mg.eq./dm ³	1.03 ± 0.04	1.70 ± 0.01	1.72 ± 0.01	1.75 ± 0.01
PI, mgO/dm ³	5.21 ± 0.75	5.59 ± 0.84	3.98 ± 0.14	3.94 ± 0.15
N-NO ₃ , mg/dm ³	0.319 ± 0.169	0.009 ± 0.007	0.018 ± 0.018	0.007 ± 0.004
N-NO ₂ , mg/dm ³	0.027 ± 0.004	0.046 ± 0.005	0.063 ± 0.008	0.043 ± 0.007
N-NH ₄ , mg/dm ³	0.193 ± 0.124	0.384 ± 0.026	0.525 ± 0.058	0.482 ± 0.035
Total N, mg/dm ³	0.539 ± 0.166	0.440 ± 0.026	0.606 ± 0.080	0.532 ± 0.035
PO ₄ , mg/dm ³	0.034 ± 0.010	0.023 ± 0.004	0.021 ± 0.006	0.028 ± 0.002
Si, mg/dm ³	4.02 ± 0.58	3.87 ± 0.46	4.01 ± 0.39	3.97 ± 0.25
Fe, mg/dm ³	0.58 ± 0.07	0.14 ± 0.01	0.28 ± 0.08	0.31 ± 0.04
Mn, µg/dm ³	30.0 ± 3.7	78.6 ± 13.6	85.1 ± 17.2	116.0 ± 11.6
Cd, µg/dm ³	0.05 ± 0.00	0.05 ± 0.00	0.06 ± 0.01	0.06 ± 0.01
Co, µg/dm ³	0.06 ± 0.01	0.16 ± 0.04	0.11 ± 0.03	2.60 ± 2.86
Cr, µg/dm ³	0.93 ± 0.33	2.24 ± 0.03	2.67 ± 0.34	38.00 ± 34.57

Table 2. Cont.

Variable	¹ The Part of the Irtysh River			
	I	II	III	IV
Cu, µg/dm ³	0.61 ± 0.21	2.22 ± 0.10	1.80 ± 0.08	3.90 ± 2.30
Pb, µg/dm ³	0.07 ± 0.03	0.04 ± 0.0	0.08 ± 0.04	0.04 ± 0.00
Zn, µg/dm ³	1.00 ± 0.00	15.61 ± 9.61	7.59 ± 4.02	28.61 ± 25.24
Hg, µg/dm ³	below detection limit			

Note: ¹ Descriptions of the surveyed parts of the river are given in Table 1.

According to the results of chemical analysis (Table 2), the Irtysh water was an alkaline, fresh, soft, hydrocarbonate class of the calcium group [45]. The contents of easily oxidised organic substances (PI), phosphates, silicon, nitrate, ammonium nitrogen, and heavy metals were low. Mercury was not detected in any water samples. Similarly, low levels of heavy metals, including mercury, were recorded in the river water in 2010–2011 [18]. A comparison of the results obtained with the data of the work cited above showed a slight decrease in the copper content in transboundary runoff from 2010–2011 to 2023.

The water of the Black Irtysh River (Part I) was characterised by lower temperatures, pH values, TDS, and hardness and higher contents of N-NO₃, PO₄, and Fe compared to the lower parts of the river (II–IV, the Pavlodar Irtysh region). In the direction from the upper to the lower reaches of the river, the amount of easily oxidised organic substances (PI) decreased slightly, and the contents of Mn, Co, Cu, Cr, and Zn in the water increased. The distribution of Si, Cd, and Pb along the longitudinal profile of the river was relatively uniform.

Nonparametric correlation analysis showed that changes in temperature; water hardness; and N-NH₄, Mn, Cr, Fe, and PI contents along the longitudinal profile of the river were statistically significant (Table 3). Negative statistically significant relationships between Fe and Co, Fe and Cu, and Fe and TDS reflected the asynchronous nature of the spatial variability of these variables across the surveyed areas. Positive connections between Cu and Co, Cu and Zn, and Cr and Mn may indicate a single source of their entry into the river.

Table 3. Spearman correlation coefficients (R) between environmental variables of the Irtysh River, July 2023, at $p < 0.05$.

Pair of Variables	R	Pair of Variables	R	Pair of Variables	R
Altitude–Temperature	−0.490	Altitude–Cr	−0.731	Cu–Co	0.731
Altitude–Hardness	−0.664	Fe–pH	−0.625	Cu–Zn	0.674
Altitude–PI	0.664	Temperature–TDS	0.584	Cu–pH	0.632
Altitude–N-NH ₄	−0.586	Fe–Co	−0.607	Cr–Mn	0.693
Altitude–Mn	−0.585	Fe–Cu	−0.595	TDS–Fe	−0.594

3.2. Zooplankton

Eighty-two species were identified among the zooplankton, including 60 rotifers, 12 cladocerans, and 10 copepods (Table 4). The species richness of zooplankton communities linearly doubled from up to downstream. The species composition of zooplankton had a low similarity between sampling stations (Figure 7a). In total, the low similarity in the species composition of planktonic invertebrates was between Parts II and IV of the river (Figure 7b) and high similarity was found for Parts I (the Black Irtysh River) and III (the Irtysh River in the zone of influence of the Pavlodar and Aksu cities). Rotifers *Brachionus angularis*, *Bdelloida* gen. sp., *Keratella cochlearis*, and *Euchlanis oropha* were found everywhere. Rotifers *Brachionus quadridentatus*, *Cephalodella* sp., *Filinia longiseta*, *Synchaeta stylata*, cladocerans *Alona affinis*, *Bosmina* (*Bosmina*) *longirostris*, *Bosminopsis deitersi*,

Macrothrix hirsuticornis, and *Pleuroxus trigonellus* were relatively widespread, mainly in the lower reaches of the river (Parts II, III, IV).

Table 4. Species composition and frequency of occurrence of planktonic invertebrates in the Irtysh River, July 2023.

Taxon Name	Part of the Irtysh River			
	I	II	III	IV
Rotifera				
<i>Asplanchna henrietta</i> (Langhans)	0	0	13	57
<i>Asplanchna intermedia</i> (Hudson)	20	0	13	0
<i>Asplanchna priodonta</i> (Gosse)	0	0	13	0
<i>Asplanchna sieboldi</i> (Leydig)	0	0	0	14
Bdelloida gen. sp.	60	29	63	100
<i>Brachionus angularis</i> (Gosse)	40	29	88	100
<i>Brachionus bennini</i> (Leissling)	20	0	75	71
<i>Brachionus budapestiensis</i> (Daday)	0	0	13	0
<i>Brachionus calyciflorus</i> (Pallas)	0	0	0	29
<i>Brachionus calyciflorus anuraeiformis</i> (Brehm)	0	0	0	29
<i>Brachionus calyciflorus dorcas</i> (Gosse)	0	0	13	57
<i>Brachionus diversicornis</i> (Daday)	0	0	25	71
<i>Brachionus diversicornis homoceros</i> (Wierzejski)	0	0	0	14
<i>Brachionus plicatilis</i> (Muller)	0	0	0	14
<i>Brachionus quadridentatus</i> (Hermann)	40	0	13	29
<i>Brachionus quadridentatus zernovi</i> (Voronkov)	0	29	13	14
<i>Brachionus quadridentatus ancylognathus</i> (Schmarda)	0	0	0	29
<i>Brachionus quadridentatus brevispinus</i> (Ehrenberg)	0	0	13	43
<i>Brachionus variabilis</i> (Hempel)	20	0	0	71
<i>Keratella cochlearis</i> (Gosse)	40	43	50	86
<i>Keratella cochlearis tecta</i> (Gosse)	0	14	0	29
<i>Keratella quadrata</i> (Muller)	20	0	0	0
<i>Keratella quadrata dispersa</i> (Carlin)	40	0	0	0
<i>Cephalodella gibba</i> (Ehrenberg)	0	14	0	0
<i>Cephalodella</i> sp.	20	0	13	14
<i>Euchlanis calpidia</i> (Myers)	0	14	0	0
<i>Euchlanis deflexa</i> (Gosse)	0	14	0	0
<i>Euchlanis lyra</i> (Hudson)	0	14	0	0
<i>Euchlanis oropha</i> (Gosse)	40	43	13	14
<i>Euchlanis</i> sp.	40	29	0	0
<i>Filinia longiseta</i> (Ehrenberg)	40	0	13	100
<i>Hexarthra mira</i> (Hudson)	0	0	0	14
<i>Hexarthra intermedia</i> (Wiszniewski)	0	0	0	14
<i>Lecane (Monostyla) bulla</i> (Gosse)	20	0	0	0
<i>Lecane (Monostyla)</i> sp.	0	14	0	0
<i>Lecane (s.str.) flexilis</i> (Gosse)	0	14	0	0

Table 4. Cont.

Taxon Name	Part of the Irtysh River			
	I	II	III	IV
Rotifera				
<i>Notholca acuminata</i> (Ehrenberg)	20	0	0	0
Notommatidae gen. sp.	0	0	13	0
<i>Platyias patulus</i> (Muller)	0	0	13	0
<i>Polyarthra dolichoptera</i> (Idelson)	20	0	0	29
<i>Polyarthra luminosa</i> (Kutikova)	0	0	0	14
<i>Polyarthra major</i> (Burchhardt)	0	0	25	14
<i>Polyarthra minor</i> (Voigt)	0	0	0	57
<i>Polyarthra remata</i> (Skorikov)	0	0	0	14
<i>Polyarthra vulgaris</i> (Carlin)	0	0	0	14
<i>Pompholyx sulcata</i> (Hudson)	0	0	0	57
<i>Postclausa hyptopus</i> (Ehrenberg)	60	0	0	0
<i>Synchaeta pectinata</i> (Ehrenberg)	40	0	0	0
<i>Synchaeta stylata</i> (Wierzejski)	40	0	25	71
<i>Testudinella patina</i> (Hermann)	0	14	0	0
<i>Trichocerca</i> (<i>Diurella</i>) <i>bidens</i> (Lucks)	0	0	0	14
<i>Trichocerca</i> (<i>Diurella</i>) sp.	0	0	0	14
<i>Trichocerca</i> (<i>Diurella</i>) <i>myersi</i> (Hauer)	0	0	0	43
<i>Trichocerca</i> (s.str.) <i>cylindrica</i> (Imhof)	0	0	0	57
<i>Trichocerca longiseta</i> (Schrank)	0	0	0	14
<i>Trichocerca</i> sp.	0	0	0	14
<i>Trichotria pocillum</i> (Muller)	0	14	13	0
<i>Trichotria tetractis</i> (Ehrenberg)	0	0	13	0
<i>Trichotria truncata</i> (Whitel.)	0	0	0	43
Rotifera gen. sp.	0	0	0	14
Total Rotifera	19	15	22	39
Cladocera				
<i>Alona affinis</i> (Leydig)	20	14	13	0
<i>Alona rectangula</i> (Sars)	0	0	13	0
<i>Bosmina</i> (<i>Bosmina</i>) <i>kessleri</i> (Uljanin)	0	0	0	14
<i>Bosmina</i> (<i>Bosmina</i>) <i>longirostris</i> (O.F. Muller)	80	0	13	86
<i>Bosminopsis deitersi</i> (Richard)	0	14	50	100
<i>Ceriodaphnia pulchella</i> (Sars)	0	0	0	14
<i>Diaphanosoma</i> sp.	0	14	0	43
<i>Ilyocryptus acutifrons</i> (Sars)	0	0	13	0
<i>Pleuroxus trigonellus</i> (O.F.Muller)	0	14	50	29
<i>Scapholeberis mucronata</i> (O.F.Muller)	0	14	0	0
<i>Sida crystallina</i> (O.F.Muller)	0	0	13	0
<i>Macrothrix hirsuticornis</i> (Norman et Brady)	0	14	13	14
Total Cladocera	2	6	8	7

Table 4. Cont.

Taxon Name	Part of the Irtysh River			
	I	II	III	IV
Copepoda				
<i>Acanthocyclops robustus</i> (Sars)	0	0	0	14
<i>Ectocyclops phaleratus</i> (Koch)	0	14	13	0
<i>Eucyclops serrulatus</i> (Lilljeborg)	20	0	0	0
Eucyclopinæ gen.sp.	60	29	38	14
<i>Mesocyclops leuckarti</i> (Claus)	100	43	75	100
<i>Microcyclops afghanicus</i> (Lindberg)	0	29	0	0
<i>Paracyclops affinis</i> (Sars)	0	0	13	0
<i>Thermocyclops crassus</i> (Fischer)	0	0	50	43
Cyclopoida gen.sp.	0	29	0	0
Harpacticoida gen.sp.	20	14	38	0
Total Copepoda	4	6	6	4
Total species	25	27	36	50

Notes: I—the Black Irtysh River from the border with China to the confluence with Lake Zaisan, II—the Irtysh River above Pavlodar city, III—the Irtysh River in the zone of influence of the Pavlodar and Aksu cities, IV—the lower part of the Irtysh River to the border with Russia.

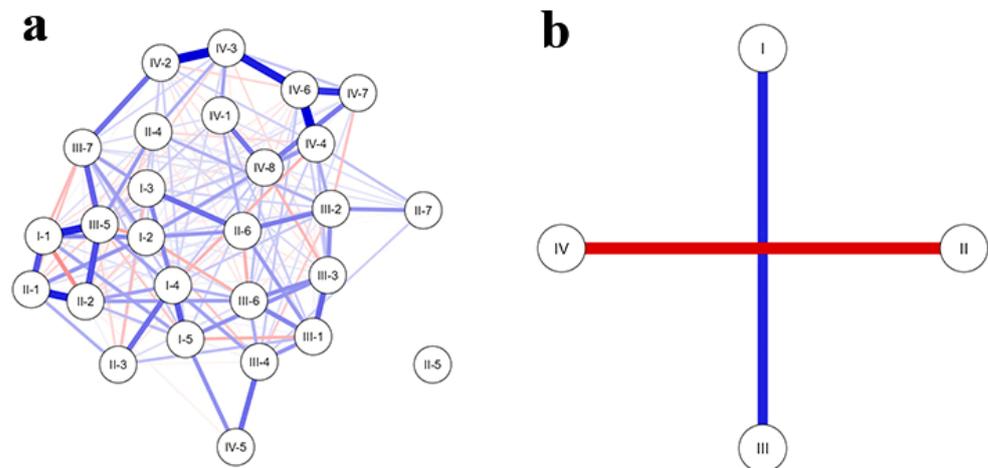


Figure 7. The similarity of the species composition of planktonic invertebrates in the Irtysh River according to JASP analysis, July 2023: (a) comparison between individual stations; (b) comparison across selected parts of the Irtysh River, where I—the Black Irtysh River from the border with China to its confluence with the Zaisan Lake, II—the Irtysh River above Pavlodar city, III—the Irtysh River in the zone of influence of the Pavlodar and Aksu cities, IV—the lower part of the Irtysh River to the border with Russia. Arabic numerals indicate the numbers of stations within each of the surveyed parts. The colour and line width between points reflect the correlation: blue—positive, red—negative, and the colour saturation—correlation strength.

Quantitative zooplankton variables were very low, except for downstream of the Irtysh River (Table 5). Rotifers dominated. Copepods were subdominant. In the total quantitative variables of zooplankton, the share of rotifers increased from 45.1–52.5% in Part I to 97.6% in Part IV. In the zooplankton of the Black Irtysh River (Part I), the dominant complex was represented by the rotifers *Bdelloida* gen. sp. and the crustaceans *Bosmina longirostris*, *Eucyclops serrulatus*, and *Mesocyclops leuckarti* (Table 6). The role of the first three species in zooplankton decreased almost linearly downstream, while the share of the rotifer

Brachionus angularis, on the contrary, increased sharply. The cyclops *Mesocyclops leuckarti* and *Thermocyclops crassus* played a significant role in zooplankton locally.

Table 5. Quantitative variables of zooplankton in the Irtysh River (mean with standard error), July 2023.

Part of the Irtysh River	Rotifera	Cladocera	Copepoda	Total
Abundance, specimen/m ³				
I	147 ± 75	16 ± 7	161 ± 92	326 ± 164
II	276 ± 123	109 ± 98	135 ± 69	526 ± 206
III	455 ± 137	91 ± 26	361 ± 80	906 ± 198
IV	23,582 ± 6388	181 ± 20	395 ± 46	24,158 ± 6362
Average abundance	6347 ± 2538	105 ± 28	274 ± 41	6728 ± 2553
Biomass, mg/m ³				
I	0.22 ± 0.09	0.12 ± 0.04	0.27 ± 0.11	0.62 ± 0.18
II	0.35 ± 0.20	1.00 ± 0.94	0.16 ± 0.09	1.54 ± 1.23
III	0.41 ± 0.09	0.66 ± 0.18	0.50 ± 0.19	1.57 ± 0.17
IV	5.04 ± 1.17	0.98 ± 0.25	1.03 ± 0.20	7.05 ± 1.40
Average biomass	1.56 ± 0.50	0.73 ± 0.25	0.51 ± 0.10	2.81 ± 0.68

Table 6. Composition of dominant species in the zooplankton of the Irtysh River, July 2023.

Taxon Name	Part of the Irtysh River							
	I	II	III	IV	I	II	III	IV
	Abundance, %				Biomass, %			
<i>Bdelloida</i> gen. sp.	21.7	4.8	5.1	0.7	19.3	13.5	11.8	3.2
<i>Brachionus angularis</i>	1.2	1.4	31.5	71.9	0.1	0.1	2.4	43.5
<i>Euchlanis oropha</i>	2.5	19.9	0.4	0.02	1.6	4.6	0.1	0.02
<i>Eucyclops serrulatus</i>	27.4	6.2	1.0	4.4	17.0	0.7	0.3	0.1
<i>Scapholeberis mucronata</i>	0.0	2.5	0.0	0.0	0.0	20.9	0.0	0.0
<i>Bosmina longirostris</i>	4.3	0.0	0.7	0.2	15.7	0.0	3.2	3.0
<i>Mesocyclops leuckarti</i>	21.5	1.7	23.1	1.4	27.2	2.0	11.8	11.8
<i>Thermocyclops crassus</i>	0.0	0.0	14.7	0.2	0.0	0.0	17.4	2.5

The average abundance of zooplankton varied widely and reached a maximum in the lower reaches of the Irtysh River (Part IV) (Table 7). According to the Shannon index values, the diversity of zooplankton communities varied from low to medium levels [4]. The spatial dynamics of the Shannon and Δ-Shannon indices indicated a change in zooplankton structure, which was most pronounced downstream (Part IV). Low values of the average individual mass of a specimen were associated with the dominance of small rotifers in zooplankton communities.

According to the Spearman correlation coefficient values, from the upper to the lower reaches, the abundance of rotifers, cladocerans, and copepods; the number of species; and the Shannon Bi index (negative relationship with “Altitude”) increased statistically significantly; the average individual mass of a specimen (positive relationship with “Altitude”) decreased (Table 8). For rotifers, a negative relationship with PI and positive relationships with oxygen, Cr, N-NH₄, and water hardness were recorded. The abundance of cladocerans and copepods increased slightly with increasing ammonium nitrogen content. The relationship between the abundance of Cladocera and Cr was negative. The values of the

average individual mass of a specimen decreased statistically significantly with increasing water temperature and Cr concentrations.

Table 7. Structural variables of zooplankton in the Irtysh River (mean with standard error), July 2023.

Part of the Irtysh River	Average Species Number	Shannon Ab	Shannon Bi	Δ -Shannon	Average Individual Mass, mg
I	9.6 ± 1.9	2.48 ± 0.24	1.91 ± 0.35	0.57 ± 0.24	0.0031 ± 0.0010
II	5.7 ± 1.7	1.82 ± 0.43	1.23 ± 0.36	0.59 ± 0.15	0.0016 ± 0.0010
III	9.5 ± 0.9	2.40 ± 0.14	2.10 ± 0.14	0.35 ± 0.18	0.0028 ± 0.0008
IV	19.7 ± 1.4	1.67 ± 0.11	2.69 ± 0.13	−0.88 ± 0.20	0.0004 ± 0.0001
Average	11.2 ± 1.2	2.08 ± 0.14	1.99 ± 0.16	0.08 ± 0.15	0.0019 ± 0.0004

Table 8. Spearman correlation coefficients (R) between biological and environmental variables of the Irtysh River in July 2023, $p < 0.05$.

Pair Variables	R	Pair Variables	R
Altitude–Rotifera Ab	−0.795	Rotifera Ab–Cr	0.603
Altitude–Cladocera Ab	−0.720	Rotifera Ab–N-NH ₄	0.565
Altitude–Copepoda Ab	−0.642	Rotifera Ab–Hardness	0.603
Altitude–Total Ab	−0.852	Cladocera Ab–PI	−0.620
Altitude–Species Number	−0.657	Cladocera Ab–Cr	−0.620
Altitude–Shannon Bi	−0.563	Cladocera Ab–N-NH ₄	0.468
Altitude–Average Mass	0.596	Copepoda Ab–N-NH ₄	0.446
Rotifera Ab–PI	−0.471	Average Mass–Temperature	−0.580
Rotifera Ab–Oxygen	0.544	Average Mass–Cr	−0.614

Thus, the species richness of the zooplankton of the Irtysh River was generally assessed as high, especially considering a single sampling of material in July 2023. For comparison, 104 taxa were recorded in the zooplankton of the Northern Dvina River over eight years (2012–2019) [13]. The predominance of rotifers in the Irtysh zooplankton is generally typical for rivers [11,50], but depends on local conditions. Rotifers dominated the riverbed zone of the regulated Missouri River (USA) [10] and crustaceans dominated in areas between reservoirs. In the Syrdarya River (Southern Kazakhstan) below the Shardara reservoir, the total species richness of crustaceans (34) was higher than that of rotifers (21) [51]. Above the reservoir and in the mouth zone, before the Syr Darya flows into the Aral Sea, rotifers dominated (58–73% of the total species richness) [52].

The spatial dynamics of species composition and quantitative and structural variables of zooplankton reflected the variability of external conditions in the Irtysh River. One of the reasons for the increase in the abundance of planktonic invertebrates was the decrease in the speed of the Irtysh flow in the Pavlodar region. A similar increase in the abundance of planktonic invertebrates was recorded in the lower reaches of the Northern Dvina [13] and Nakdong [53] Rivers. The increase in the abundance of zooplankton communities can also be associated with increased organic pollution in the lower reaches of the Irtysh River, which was confirmed by chemical analysis data (Table 2).

3.3. Assessment of the Ecological State of the Irtysh River by Chemical Data

3.3.1. Assessment of Organic Pollution

Comparison with Global Values

In river ecosystems around the globe, the content of ammonium nitrogen varies from 0.005 to 0.04 mg/dm³ (median 0.015), nitrate nitrogen varies from 0.05 to 0.2 (median 0.10), and phosphates vary from 0.002 to 0.025 (median 0.01) mg/dm³ [54]. According to the

results, in the Irtysh River, the amount of ammonium nitrogen was 12.9–35.2 times and phosphates were 2.1–3.4 times (Table 2) higher than the global median values for rivers. In Part I (Black Irtysh River), the content of nitrate nitrogen exceeded the global median values by 31.9 times; in Part II, it exceeded global values by 1.8 times; in other parts, it was below global values.

Comparison with MPC_{fw}

In the Irtysh River, a widespread excess of MPC_{fw} was detected only for nitrite nitrogen, with a maximum in the zone of influence of the Pavlodar and Aksu cities (Part III) (Table 9). A slight excess of MPC_{fw} for ammonia nitrogen was recorded at the same site. An analysis of published data showed that an excess of MPC_{fw} for nitrite nitrogen was observed in the Irtysh River earlier, in the period from 1990 to 1999 [18]. In July 2023, the average nitrite nitrogen content in the Pavlodar Irtysh region was 1.4 times lower compared to data from previous years.

Table 9. Assessment of the level of pollution of the surveyed parts of the Irtysh River by chemical variables, July 2023.

Variable	I	II	III	IV	¹ MPC _{fw} (mg/dm ³)	Water Quality Classes			
	Multiplicity of Exceeding MPC _{fw}					I	II	III	IV
² PI	–	–	–	–	–	2b	2b	2a	2a
² N-NO ₃	0.04	0.001	0.002	0.0008	9.10	2b	1	1	1
² N-NO ₂	1.35	2.3	3.15	2.15	0.02	4a	4a	4b	4a
² N-NH ₄	0.39	0.77	1.05	0.96	0.50	2b	3b	4a	3b
² PO ₄	0.68	0.46	0.42	0.56	0.05	3a	2b	2b	2b
Fe	5.8	1.4	2.8	3.1	0.10	–	–	–	–
Mn	3.0	7.9	8.5	11.6	0.01	–	–	–	–
³ Cd	0.10	0.10	0.12	0.12	0.0005	1	1	1	1
³ Co	0.006	0.016	0.011	0.26	0.01	1	1	1	1
³ Cr	0.2	0.4	0.5	7.6	0.005	1	1	1	4
³ Cu	0.6	2.2	1.8	3.9	0.001	1	2	2	2
³ Pb	0.007	0.004	0.008	0.004	0.01	1	1	1	1
³ Zn	0.1	1.5	0.8	2.8	0.01	1	3	1	4
³ Hg	Below detection limit				0.0001	1	1	1	1

Notes: I–IV—parts of the Irtysh River. ¹ MPC_{fw} according to Guseva [45]; ² ranks and classes of water quality according to Romanenko et al. [46]: 1—unpolluted water, 2a—very clean, 2b—quite clean, 3a—fairly clean, 3b—slightly polluted, 4a—moderately polluted, 4b—heavily polluted; ³ water quality classes according to the regional scale developed by Krupa et al. [47]: 1—clean water, 2—slightly polluted, 3—moderately polluted, 4—highly polluted.

Comparison with Classification Scales

Classification Scales [46] make it possible to assess water quality from the point of view of its use for various purposes. Based on the content of easily oxidised organic substances (PI) and nitrate nitrogen, the Irtysh water was assessed as pure of the second quality class (Table 9). The phosphate content was at the level of quite clean (second class) and fairly clean (third class) water. The content of ammonia nitrogen varied from the level of completely clean waters in the Black Irtysh River to slightly and moderately polluted waters in the Pavlodar Irtysh region. To the greatest extent, the Irtysh River was polluted with nitrite nitrogen at the level of quality class 4 (moderate and severe pollution). Deterioration in water quality in terms of nitrite and ammonium nitrogen content was recorded in Part III in the zone of influence of the Pavlodar and Aksu cities.

Assessment Based on the Ratio of Forms of Nitrogen Compounds

Nutrient compounds enter natural ecosystems mainly in the form of ammonium ions, which are oxidised to unstable nitrite ions and then to nitrates [55]. The ratio of the forms of nitrogen compounds allows us to estimate the approximate time of their entry into the aquatic ecosystem [56]. Table 10 shows that persistent nitrate ions predominated in the Black Irtysh (Part I) water, indicating predominantly “old” pollution. As mentioned above, there are currently only two small villages in the Kazakh part of the Black Irtysh floodplain, and their influence on the river ecosystem can be assessed as weak. At the same time, the Chinese part of the Black Irtysh basin is densely populated; industry and agriculture are developed here [57]. Thus, the water quality of this section of the Irtysh River is determined mainly by the transboundary transport of pollutants from the territory of the People’s Republic of China. A significant predominance of ammonium ions (an indicator of recent pollution) in the lower reaches of the Irtysh River indicated a constant influx of pollutants into the Pavlodar Irtysh region. Potential sources of nitrogen compounds are the discharge of municipal wastewater (Figure 2b) from the Pavlodar and Aksu cities and numerous villages in the Irtysh River’s coastal zone.

Table 10. The ratio of nitrogen forms (percentage of the total amount) in the water of the surveyed parts of the Irtysh River, July 2023 (mean with standard error).

Variable	Part of the Irtysh River			
	I	II	III	IV
N-NO ₃	45.0 ± 18.7	2.1 ± 1.6	1.7 ± 1.7	0.3 ± 0.6
N-NO ₂	16.7 ± 12.5	10.6 ± 0.9	10.5 ± 0.6	8.3 ± 1.2
N-NH ₄	38.3 ± 15.4	87.3 ± 2.3	87.8 ± 1.9	90.4 ± 1.2

3.3.2. Assessment of Toxic Pollution

Comparison with MPC_{fw}

A widespread excess of MPC_{fw} was detected for Fe, Mn, and Cu (for Cu, except for the Black Irtysh River) and locally for Cr and Zn (Table 9). The maximum excess of MPC_{fw} for Fe was recorded in the upper reaches of the river (Part I, Black Irtysh River). The excess of MPC_{fw} for Mn, Cr, and Zn increased almost linearly from the upper to lower sections of the Irtysh River.

Comparison with the Regional Classification Scale

Earlier, we developed the Regional Classification Scale based on the determination of background concentrations of heavy metals and statistical analyses of their distribution in ecologically diverse water bodies of Kazakhstan [47,58]. Rich reserves of ore minerals [59] lead to naturally elevated levels of some heavy metals, especially copper, in water bodies, which was considered when developing a regional water quality classification [47]. For example, the average background copper content in unpolluted lakes of Kazakhstan is 0.0052 mg/dm³, and in unpolluted rivers, it is 0.0106 mg/dm³ [60], which is 5.2–10.6 times higher than MPC_{fw} [44].

According to the Regional Classification Scale, Cd, Hg, and Pb content in the Irtysh River was at the level of extremely clean waters of the first quality class. Despite exceeding the MPC_{fw} for copper by 2.2–3.9 times (Table 9), we classified its content in the Irtysh River at the level of clean (quality class 1) and slightly polluted (quality class 2) waters [47]. Regarding Cr and Zn content, the quality of the Irtysh water deteriorated from quality class 1 in the upper reaches (unpolluted waters) to quality class 4 (heavy pollution) in the lower reaches.

Thus, in July 2023, the content of heavy metals in the water of the Irtysh River was generally at a low level, with their spatial distribution being heterogeneous. The low content of all heavy metals (except Fe) in the Black Irtysh River indicated an insignificant

contribution of natural factors (leaching of metals from rocks) [59] and transboundary transfer from China to the overall level of toxic pollution of the Kazakh part of the river. As before [18], in 2023, an increased iron content was recorded in the water of the Black Irtysh River.

The deterioration of water quality for almost all variables in the Pavlodar Irtysh region may be due to the influx of wastewater from the cities of Pavlodar and Aksu and numerous villages, polluted surface runoff, and the transit transfer of pollutants from the upstream sections of the river (the middle reaches of the Kazakhstan part). As already mentioned, the Altai, Ust-Kamenogorsk, Semey, Ridder, and Zyryanovsk cities with large industrial enterprises are in the middle reaches. In 2010–2011, in the zone of influence of the city of Ust-Kamenogorsk, the average content of Cu in the river water reached 2.2 MPC_{fw}, Zn 2.4 MPC_{fw} [18]. Downstream, near Semey city, the Cu content varied from 0.9 to 5.9 MPC_{fw}, with a low Zn content.

3.4. Bioindication

3.4.1. Assessment of Organic Pollution

The biological assessment of aquatic ecosystems is based on the nonlinear relationship between the level of organic pollution and the structure of biological communities [4]. With increasing organic pollution (eutrophication), communities become enriched in species, the total abundance of zooplankton increases as well as the dominance of small species, the average individual mass of a specimen decreases [4], and the Δ -Shannon index becomes negative [43]. Eurytopic species, which tolerate high organic matter in the ecosystems, dominate the communities. For example, rotifers of the genus *Brachionus* and *Pompholyx sulcata* and the crustaceans *Bosmina longirostris* and *Thermocyclops crassus* [4] usually inhabit eutrophic waters. In Kazakhstan, *Brachionus angularis* prefers heavily polluted and extremely dirty waters of the 4 and 5 quality classes [48,61]. According to our data [60], with increasing organic pollution of fresh lakes and reservoirs in Kazakhstan, the average individual mass of a specimen decreases from 0.0157–0.0354 to 0.0036–0.0057 mg.

An indicator of increased organic pollution in the Irtysh River was a twofold increase in the total species richness of zooplankton downstream (Table 4). The number of rotifer species increased from 19 in the Black Irtysh River to 39 in the lower reaches, and cladocerans increased from 2 to 7–8. The species richness of rotifers of the genus *Brachionus* increased significantly from 4 to 13. Signs of eutrophication of the river ecosystem in the lower reaches were the appearance of the small-sized rotifer *Pompholyx sulcata* in the zooplankton (Table 4), increased dominance of *Brachionus angularis* and the cyclops *Thermocyclops crassus* (Table 6), negative Δ -Shannon index values, and decreases in the average individual mass of a specimen (Table 7).

There are Classification Scales for lakes and reservoirs [46,60,62,63] that have ranked values of quantitative biological variables for waters of different quality classes. There are no Classification Scales for river ecosystems. River zooplankton communities are predominantly influenced by flow speed and the amount of suspended matter. Substances suspended in water create unfavourable conditions for crustaceans, particularly clogging cladoceran filtration apparatus [64]. The flow velocity and, as a rule, the amount of suspended substances decrease from the upper to the lower sections of rivers, which is one of the reasons for the increase in zooplankton abundance [13,53].

This trend is also true for the rivers of Kazakhstan. We compared the abundance of zooplankton in the transboundary and regulated rivers Irtysh (East Kazakhstan), Syrdarya (South Kazakhstan), and Ili (Southeast Kazakhstan). A comparative analysis showed that in the Irtysh River, the abundance of zooplankton (0.3–24.2 thousand specimens/m³) was approximately at the same level as in the Ili River (0.5–25.3 thousand specimens/m³) [52] but lower than in the Syrdarya River (0.8–85.2 thousand specimens/m³) [51]. In all cases, the abundance of planktonic invertebrates increased from the upper to the lower sections of the rivers. In the Ili and Syrdarya Rivers, an increase in the abundance of zooplankton occurred against the background of an increase in water transparency (from 0.005–0.010 m

before reservoirs to 0.3–0.4 m below reservoirs). Considering approximately the same water transparency (0.03–0.04 m) in the Irtysh River, the increase in the abundance of zooplankton in the lower reaches (section IV) by more than 25 times (Table 5) against the background of the changes in its structure can be associated with anthropogenic pollution. This assumption is confirmed by the results of the chemical (Table 2) and statistical analysis (Tables 3 and 8).

3.4.2. Toxic Contamination Assessment

To assess the level of toxic pollution of aquatic ecosystems using zooplankton, a reliable indicator is the presence of copepods with deviations in morphology [60]. In the zooplankton communities of the Irtysh River, only the cyclops *Mesocyclops leuckarti* was widespread. The absence of individuals with deviations in morphology in their populations generally confirmed the low level of toxic pollution of the river water.

Thus, chemical analysis data and the structure of zooplankton communities indicated increased organic pollution and a low level of toxic pollution in the Irtysh River in July 2023. Regarding the content of nitrogen compounds, the most noticeable deterioration in water quality occurred in the zone of influence of the Aksu and Pavlodar cities (Part III). The most pronounced changes in the structure of zooplankton communities downstream (Part IV) indicated a delayed response of planktonic invertebrates to increased organic pollution of the river ecosystem. Local deterioration of water quality in terms of chromium and zinc content downstream (Part IV) did not hurt the structure of zooplankton communities.

With the intense anthropogenic load on the entire Irtysh basin, the low content of heavy metals in the water may be due to their sorption on the surface of suspended particles, bottom sediments, and plant accumulation. Clays can sorbate up to 80% of nickel, zinc, lead, cobalt, aluminium, and iron ions [65,66]. Among the *Potamogeton* species, the highest amounts of heavy metals were recorded in *Potamogeton perfoliatus* (1.88 µg/g for Cd; 13.14 µg/g for Cu; 13.32 µg/g for Pb; 57.96 µg/g for Zn) [67]. *Butomus umbellatus* accumulated chromium in the highest concentrations; pondweed accumulated zinc and chromium [68]. Such results indicate the high self-purifying ability of the Irtysh River ecosystem.

4. Conclusions

A comprehensive assessment of the ecological state of the Kazakh part of the Irtysh River in its upper (Black Irtysh River) and lower (Pavlodar region) reaches was given. The maximum content of easily oxidised organic substances, phosphates, and nitrate nitrogen in the Irtysh River did not exceed the level of completely clean or slightly polluted waters. The maximum content of ammonia nitrogen did not exceed the level of moderately polluted waters. The nitrite nitrogen content was most often at the level of moderately polluted waters; in the zone of influence of the cities of Pavlodar and Aksu, it increased to the level of highly polluted waters. The ratio of the forms of nitrogen compounds indicated a constant influx of fresh pollution into the Irtysh River in the Pavlodar region. Of the nine heavy metals (Fe, Mn, Cd, Co, Cr, Cu, Pb, Zn, Hg), widespread excess of MPC_{fw} was recorded only for Fe, Cu, and Mn and locally for Zn and Cr. Based on the content of heavy metals, the water of the Irtysh River was predominantly assessed as clean and slightly polluted, with a local deterioration in the quality of water in the lower reaches to the level of highly polluted waters. The structure of zooplankton communities also indicated increased organic pollution and a low level of toxic pollution in the Irtysh River. The spatial distribution of biotic and abiotic indicators allows us to draw the following conclusions: (a) in terms of the content of organic substances and heavy metals, water from the territory of the People's Republic of China is of satisfactory quality; (b) the constantly increased iron content in the Black Irtysh River may be due to natural factors, namely, its leaching from underlying rocks; (c) in the lower reaches of the Kazakhstan part of the Irtysh basin, there is a deterioration in water quality in terms of the content of ammonium and nitrite nitrogen, total nitrogen, and manganese; (d) the main contribution to the deterioration of river water

quality comes from the discharge of industrial and municipal wastewater in the middle and lower reaches of the Kazakhstan part of the basin; (e) at a high level of anthropogenic load on the Irtysh basin, the distribution of the analysed variables indicated intensive processes of self-purification of the water; (f) self-purification of the water column occurs due to high flow speed and favourable oxygen conditions; sorption of heavy metals by particles and clays suspended in water, which make up the banks of the Irtysh; and absorption of nutritional compounds and heavy metals by aquatic and semi-aquatic vegetation.

Author Contributions: Conceptualisation, methodology, writing, editing, E.K.; investigation, E.K., S.R. and A.S.; research management, E.K. and L.S.; editing, L.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan, the Scientific Program “Assessment of biological resources of the Kazakh part of the transboundary Irtysh basin in the context of climate change (BR18574062)”.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We are grateful to V.A. Kamkin (Pavlodar State University, named after Toraigrov, Pavlodar, Kazakhstan), who determined species of semi-aquatic and aquatic plants, and D.V. Malakhov (Institute of Zoology, Almaty, Kazakhstan), who made the schematic maps.

Conflicts of Interest: The companies Institute of Zoology and Kazakh Agency employed Author Elena Krupa for Applied Ecology. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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