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Impact of Wastewater on Water Quality and Fish Community in the Tolych River, Perm Krai, Russia

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ABSTRACT

Boreal freshwater ecosystems are highly sensitive to pollution, but too little information is available on the use of both biotic and chemical indicators for estimation of the effect of wastewater on boreal rivers and streams. The purpose of this study was to assess the wastewater impact on the boreal river (Perm Krai, Russia). Physicochemical parameters of major ions and trace elements were detected with a field portable unit, capillary electrophoresis, and ICP-MS. Fish data was collected by gillnets. To evaluate the level of pollution from the Tolych River upstream to downstream, we calculated heavy metal evaluation index (HEI), ecological risk index (ERI), and index of biotic integrity (IBI). The anthropogenic impact from upstream to downstream showed the range from a very high to medium level of pollution by ERI and from a high to medium level by HEI values, where most of the studied major ions and trace elements often exceeded aquatic life limits. We found significant thermal pollution of the observed river with the decreasing temperature gradient from pollution source down to the river mouth due to hydromorphological factors. Observed thermal pollution leads to the absence of thermally sensitive cold-water fish species and the abundance of ecologically flexible fish species. The water quality assessed by biotic IBI index showed low and very low quality of lower reach of the studied river, which contradicts the results of assessment by HEI and ERI indices. The results show the importance of using aquatic organisms as bioindicators for assessing ecological water quality.

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INTRODUCTION

The discharge of treated and untreated wastewater from industrial sectors and urban areas of wastewater treatment plants into natural boreal water bodies causes serious ecological degradation in the surface water environment and biodiversity (Nikel et al., 2021; Preisner et al.,2020). A large amount of organic and inorganic pollutants in combination with thermal pollution significantly affects the quality of water for decades due to effluent wastewater (Michalec & Cupak, 2022; Koli et al., 2018 Rosen et al., 2015). Thermal pollution also highly infects aquatic biota due to the transformation of the biological, physical, and chemical processes including nutrient recycling in the river ecosystem (Malik et al., 2020; Gad et al., 2021). In the group of hydrobionts, fish comprise the largest number of species and the most abundant group of vertebrates in the world, which are located at the top of the food chain within aquatic

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ecosystems (Yang et al., 2021; Hamdhani et al., 2020). Fish are commonly used as an indicator of the ecological condition of river ecosystems (Ali et al., 2020; Schweizer et al., 2022; Dixit et al., 2021). With thermal pollution in the boreal climate, cold-water fish habitat may be reduced by 36% (Cassie, 2006).

The current state of knowledge on the responses of aquatic biodiversity across the boreal zone is challenged by increasing natural resource development and its interactions with other stressors, especially climate change (Cuss et al., 2019; Kreutzweiser et al., 2013; Vehanen et al., 2010). Temperature is one of the key abiotic factors affecting fish species distribution. For the bioassessment of pollution in boreal and northern temperate zones, cool- or cold-water fish species are often classified as intolerant species (grayling, brook trout, bullhead, brook lamprey, and brown trout) or intermediately tolerant (minnow and burbot). Warm-water-tolerant species can be classified as less sensitive to pollution (perch, roach, ninespine stickleback, and three-spined stickleback) or intermediately tolerant (northern pike and stone loach) (Sutela et al., 2021). Comparison of physicochemical parameters and fish species occurrence in small streams offered an opportunity for an ecological interpretation of the data and a promising basis for bioassessment (Sutela et al., 2020).

Berezniki-Solikamsk urban industrial agglomeration is a large industrial center in the northern part of Perm Krai (Russia) located in the boreal climate zone. The industry is mainly dominated by salt mining, chemical, pulp-and-paper, and oil refining plants. In this area, modern alluvial deposits of small rivers have been exposed to the permitted discharge of wastewater from the industrial sector for a long time. For instance, salt mining wastewater discharge into the Chernaya River (Solikamsk District) leads to a higher salinity up to 15 g/l. Potassium-sodium chloride compounds predominate in wastewater. Thermal pollution, high concentrations of trace elements such as Se, V, Mn, Mo, Cr, Ni, Cu, Sr, As, Co, Zn, Li are also identified. A prolonged intake of pollutants harms the quality of natural waters, which leads to their accumulation in bottom sediments. This is evidenced by the intensive accumulation of heavy metals in the Tolych River and the Chernaya River (Menshikova, 2016; Ushakova et al., 2020, Ushakova & Menshikova, 2021).

The key to the effective assessment of river pollution caused by wastewater discharges lies in the use of different surface water quality indices and analyses of the fish and invertebrate's species composition (Gad et al., 2022; Galib et al., 2018). The Water Quality Index (WQI), Modified Heavy Metal Pollution Index (m-HPI), Heavy Metal Evaluation Index (HEI), and Nemerow Index (NeI) are based on physicochemical parameters of water (Maskooni et al, 2020; Proshad et al., 2021; Son et al., 2020). Also, biotic indices are commonly applied to assess and classify water quality due to the importance of biodiversity assessment, which can show an ecosystem response to environmental transformations (Hooper et al., 2005; Aazami, 2015). Biotic indices quantify assemblage-wide tolerance to pollution based on known data on taxa-specific tolerance to environmental pollution (Hawkins & Carlisle, 2022). For bioindication purposes, fish, benthic macroinvertebrates, zooplankton, and phytoplankton species are referred to most frequently (Faquim et al., 2021; Lomartire et al., 2021). The most popular biotic indices are the regional pressure index (RPI), reservoir fish assemblage index (RFAI), macroinvertebrate-based index Indice Biotique Macroinvertébrés de Guyane (IBMG), the multimetric index (I2M2), the index of biotic integrity (IBI) and others (Huang et al, 2022).

In this study, the Tolych River in Berezniki was chosen as the study system due to the lack of published data on water quality assessment with biotic and physicochemical indices at boreal freshwater ecosystems. The purpose of this study was to assess the current condition of the Tolych River affected by wastewater discharges. The present study had the following aims: (a) to analyze the physicochemical pollution along the Tolych River; (b) to determine the spatial distribution of the major ions and trace elements in surface water along different reaches of the river; (c) to apply the Heavy Metal Evaluation Index (HEI), Ecological Risks of Heavy Metals in

Water (ERI), and index of biotic integrity (IBI) to evaluate and compare the Tolych River water quality estimated by difference indices. We expected a low quality of water estimated by both physicochemical characteristics and IBI index. The results of this study provided an input into understanding the pollution ecosystem effect on boreal freshwaters.

MATERIALS AND METHODS

The study area located near the city of Berezniki (59°24′29″ N 56°48′19″ E), which is situated 160 km north of Perm, is an administrative center of Perm region located east of the European part of Russia (Fig. 1). At its middle course, the Tolych River receives waters from a tributary of the Zatolych River and then flows to the Kama River in the upper part of the Kama Reservoir. The Tolych River valley has an elevation between 106 and 234 meters a. s. l. From east to west, the Tolych River runs through the industrial area of the city Berezniki with large chemical and

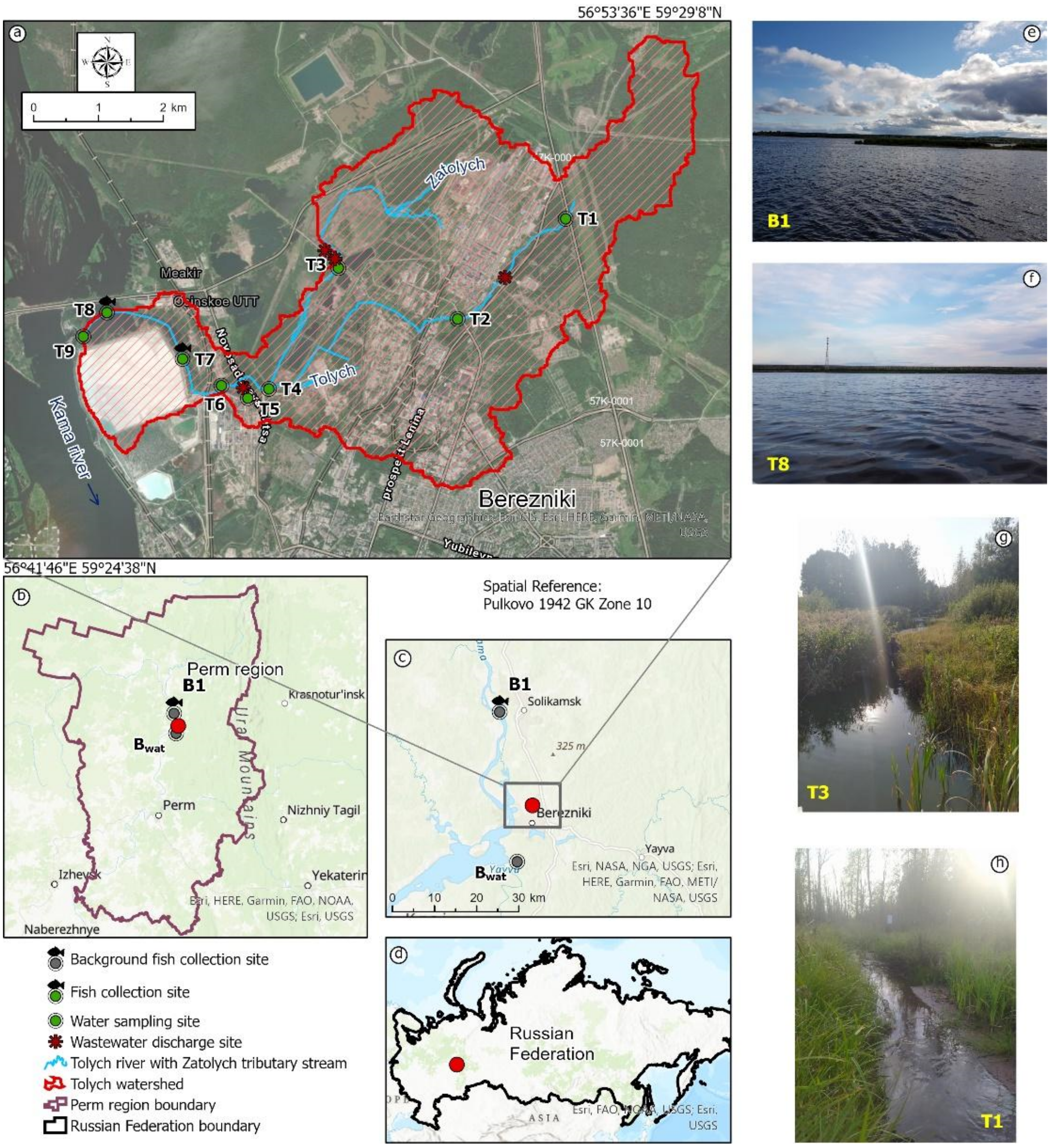

Fig. 1. Location of the Tolych River in Russia and positions of sampling sites

energy enterprises, settling tanks, and sludge reservoirs. The area is crossed by a network of roads and railroads. A significant proportion of the river catchment is covered with a hard waterproof surface.

The altitude of the study area gradually decreases from east to west (150-120 m). The climate of the area is continental, with moderately dry, long, snowy winters and moderately warm, short summers. The warmest month in the study area is July with an average monthly temperature of +17.9°C, the coldest is January with an average temperature of -14.9°C. The annual amplitude of the average monthly temperature is 32.8°C. The annual average air temperature is +1.7 ° C. The annual average precipitation is about 600 mm with approximately half of it as snow in winter.

Sampling locations and spatial distribution of groundwater quality indices throughout the study area were demarcated with ArcGIS software (10.3) (Esri, Redlands, CA, USA). Inverse distance weighting was applied for interpolation.

In the last days of July in 2021, we collected water samples at 9 sites of the Tolych River at various distances from the river mouth (T1-T9). The background (pre-industrial) sample of water ($B_{wat.}$) was collected at a river similar in its hydrological characteristics to the Tolych River (Fig. 1). We sampled the water materials during the summer low-water period, following the assumption that at this time the concentrations of trace elements in water from pollution sources is potentially the highest during the year, which can correspondingly affect water quality and fish community. Table 1 describes water and fish sampling locations. Water was sampled, transported, and stored under the technical standards GOST 31861-2012, 2014; R 52.24.353-2012, 2012. Water samples were collected at a depth of below 10 cm. Once collected, all water samples were acidified to pH < 2 with ultrapure HNO_3 and stored at 4°C in the refrigerator for sample conservation in the instrumental analytical laboratory.

Table 1. Location of sampling sites

Sampling site	Latitude (N)	Longitude (E)	Distance from the Tolych River mouth (km)
T1	59° 27' 30.35" N	056° 50' 48.56" E	10.6
T2	59° 26' 40.14" N	056° 49' 03.18" E	8.1
T3	59° 27' 05.40" N	056° 47' 06.41" E	6.2
T4	59° 26' 05.05" N	056° 45' 58.58" E	4.0
T5	59° 26' 00.33" N	056° 45' 38.18" E	3.6
T6	59° 26' 06.43" N	056° 45' 12.37" E	3.1
T7	59° 26' 19.74" N	056° 44' 33.98" E	2.1
T8	59° 26' 42.81" N	056° 43' 19.74" E	0.5
T9	59° 26' 30.78" N	056° 42' 56.93" E	0.0
B_{fish}	59° 38' 38.39" N	056° 39' 59.83" E	23.5*
B_{water}	59° 19' 31.69" N	056° 44' 34.70" E	13.1**

Note: * - fish reference sampling point, located at the Kama reservoir upstream from wastewater sources of Berezniki-Solikamsk urban industrial agglomeration; ** - water background-sampling sites located in a pre-industrial territory

To evaluate IBI index, fish community structure was analyzed at the segment of the Tolych River downstream last wastewater discharge and 2 km before the outflow into the Kama River. Fish were sampled at two locations on the Tolych River (T7, T8), as well as at a reference (B_{fish}) site on July 29-30, 2021 (Fig. 1). Reference data were collected in the bay of the left bank of the Kama reservoir, located upstream relative to the places of wastewater discharge from the Solikamsk-Berezniki industrial agglomeration (Fig. 1). Fish were sampled with a set of gill nets with a mesh size of 12, 14, 16, 25, and 40 mm which were deployed in the evening and collected the next morning. For each class of gill nets, the species composition of captured fish was estimated. To standardize the quantitative values of fish in catches, the CPUE was calculated as the number of captured fish divided by a standardized fishing effort. Fishing effort was calculated as follows: the length of the net multiplied by its height and the exposition value in hours. Then, the resulting value was divided by the value of the standard fishing effort. The standard fishing effort was assumed to be a net with the length of 37.5 m, the height of 2 m and an exposition of 24 hours. Water was sampled together with fish for chemical analysis. Also, water temperature, flow velocity, and bathymetric parameters were measured, and the type of the bottom substrate and aquatic vegetation were analyzed.

The pH, water temperature (°C) and electrical conductivity (EC) were measured *in situ* by a portable multi-parameter water quality analyzer (AP-2000-D, Aquaread). Bicarbonate was determined by the titration method under GOST 31957–2012 (GOST 31957-2012, 2012). Water samples were filtered before the analysis. Other parameters such as K^+, Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, Cl^-, PO_4^{2-}, NO_3^-, NO_2^- were determined by capillary electrophoresis (Capel-104, Lumex). Additionally, the concentration of trace elements such as V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Ba, Hg, and Pb were measured by mass spectrometry ICP–MS (Aurora M90 ICP-MS spectrometer, Bruker). The blank samples and certified reference materials were used to calibrate the machine and verify the accuracy of the results. Trace elements were analyzed in three series; the results of the analysis were presented as an average value; the error didn't exceed 10%.

The concentrations of trace elements in the water samples of the Tolych River were compared against values of the Russian standards for fishery water bodies ($MPC_{fishery}$) and against the Russian drinking water quality standards ($MPC_{drinking}$) (Order, 2016; SanPIN 1.2.3685-21, 2021). Also, the chemical composition of water samples was compared against the average global concentrations of dissolved trace elements in river waters (Gordeev & Lisitzin, 2014).

The heavy metal evaluation index (HEI) provides an overview of the water quality of fishery water bodies with the focus on trace elements (Edet & Offiong, 2002). The index is calculated as follows:

$$HEI = \sum_{i=0}^{n} \frac{H_c}{H_{mac}},$$

where H_c is the trace concentration in the sampling site, and H_{mac} is the maximum admissible concentration of i^{th} trace elements (Issa & Alshatteri, 2021). This index is classified into three levels to demarcate water quality: low (HEI < 10), moderate (HEI = 10–20), and high (HEI > 20) (Moldovan et al., 2022).

To evaluate the potential ecological hazards associated with trace elements in water, we used the ecological risk index (ERI) (El Behairy et. al., 2021, Maskooni et al, 2020). The ecological risk index was determined as follows:

$$ERI = \sum_{i=1}^{n} [T_i \times (\frac{M_i}{I_i})],$$

where M_i is the measured value of element *i*, I_i is the reference value of element *i*, T_i is the toxic-response factor of element which reflects its toxicity levels and the sensitivity of biota to it (Fu et al., 2009). The toxic-response factor of heavy metals is given as: Hg=40; Cr=25; Ni=As=10; Cu=Pb= 5; Cr = 25; V=2; and Fe=Mn=Zn=Sr=Ba=1 (Li et al., 2019; Yu et al., 2021). The index classifies the water quality into four classes: low (ERI < 110), moderate (110 ≤ ERI < 200), considerable (200 ≤ ERI < 400), and very high (ERI ≥ 400) risk (Maskooni et al, 2020).

To assess the ecological quality of the Tolych River water, the biotic integrity index, or IBI (Index of Biotic Integrity) based on fish as indicator animals, was calculated (Karr, 1986). Index of Biotic Integrity based on fish biodiversity, as well as indicators of their abundance and ecology are mainly related to the trophic position or omnivory of different fish groups. The principle of the IBI index is that fish communities respond to anthropogenic disturbance in aquatic ecosystems in a predictable and measurable way (Wu et al., 2020; Semenchenko & Razlutsky, 2010). The IBI index is originally based on 12 metrics that were developed for the North American fish community. We have adjusted the metrics in accordance with the conditions of the Kama River basin in Perm Krai (Table 3). In our calculations, we assume that each of the metrics used can be characterized by three degrees: 1 – poor, 3 – moderate, and 5 – good. The number of points for each metric is calculated by dividing the metric value at the reference location by the metric value at the studied location and then evaluating the conditions (three degrees). Then, all calculated points are summed up, and the water quality is determined on the following scale: from 12 to 22 – "very low", from 28 to 34 – "low", from 40 to 44 – "moderate", from 48 to 52 – " considerable", from 58 to 60 – "very high" (Semenchenko & Razlutsky, 2010, Karr, 1986).

The calculated analytical results of ERI and HEI were imported to ArcGIS to demonstrate surface water quality parameters. The difference between limit values and chemical parameters of analyzed physicochemical parameters was processed by Microsoft Excel. Multivariate statistical analysis including Cluster Analysis (CA) was used to group water quality in sampling sites under Ward's method with Statistica app.

RESULTS AND DISCUSSION

Table 2 shows the physical and chemical parameters of water in the Tolych River, background fish and water sampling locations, and also the values of maximum permissible concentration for fishery and aquatic life ($MPC_{fishery}$) and for drinking water quality standards ($MPC_{drinking}$). The water temperature at the sampling sites along the Tolych River varied from 17.6 to 33.3°C.

Surface water pH values varied from 7.2 to 8.0, with a mean of 7.6. The TDS values for the collected samples ranged between 260.0 mg/L and 1936.0 mg/L, with a mean value of 826.5 mg/L. Ca^{2+} and Mg^{2+} concentrations in water samples ranged from 35.0 to 428.0 mg/L and from 6.2 to 36 mg/L, respectively. Na^{+} and K^{+} levels in water were found to be from 43.0 to 160.0 mg/L for sodium and from 5.2 to 60.0 mg/L for potassium. HCO_3^{-} ranged from 54.0 to 293.0 mg/L. Cl^{-} level in water samples varied from 99.0 to 1178.0 mg/L. The concentration of SO_4^{2-} ranged from 15.2 to 170.0 mg/L. Nitrates and nitrites were insignificantly identified all through the river from 0.3 to 4.6 mg/L and from 1.1 to 2.4 mg/L, respectively. Phosphate (PO_4^{3-}) was not detected in the studied samples (<0.025 mg/L). The highest concentrations of most of the pollutants were detected in T1 located in the Tolych River headwaters.

The majority of the elements were significantly higher concentrated in the Tolych River and reference sampling sites than the average global concentrations of dissolved trace elements in river water, except for the concentrations of Pb, Zn, and Mn. Such a comparison for samples of water from the Tolych River demonstrates a significant excess of Ni, Sr, Hg, Cr (Fig. 2). Mn was found to exceed 19 times at the sampling site T1.

At the T1, T8, and T9 sampling points, the Cl^{-}concentrations of the analyzed ions in water exceeds the values of $MPC_{fishery}$ and $MPC_{drinking}$ in Russia (Fig. 3). The highest level of chlorides, which exceeded 3 times, was found at the sampling site T1.

In terms of SO_4^{2-}, the quality status of the Tolych River in sampling site T4 was determined to be 1.7 times higher than the values of $MPC_{fishery}$. Other samples did not show excessive sulfates.

At sampling points T1, T8 and T9, Na^{+} exceeded from 1.3 to 1.1 $MPC_{fishery}$. The highest level of sodium was detected at the sampling site T9. The concentrations of Ca^{2+} and K^{+} in sampling site T1 were above detection limits for $MPC_{fishery}$ by 2.4 and 1.2 times, respectively.

In all water samples, concentration of Mg^{2+} was recorded below the permissible limit set for the $MPC_{fishery}$ and $MPC_{drinking}$. The highest level of magnesium ions was detected at sampling sites T1 and T4.

Manganese in the analyzed water samples exceeded the allowable concentration for guidelines for aquatic-life (10 μg/L) and drinking water (100 μg/L) only in the studied site T1

Table 2. Water quality parameters of the Tolych River and reference sites

Parameters	Unit	Min	Max	Mean	B_{fish}	B_{water}	$MPC_{fishery}$	$MPC_{drinking}$
Temp	°C	17.6	33.3	23.3	18.0	11.0	-	-
pH	pH unit	7.2	8.0	7.6	7.6	8.0	*	6.0-9.0
EC	µS/cm	440	2034	1080	-	-	-	-
TDS	mg/L	260.0	1936.0	826.5	160.0	178	-	1500
Ca^{2+}		35.0	428.0	152.5	28.1	42.0	180	-
Mg^{2+}		6.2	36.0	13.9	5.7	1.40	40	50
Na^{+}		43.0	160.0	104.4	19.4	3.8	120	200
K^{+}		5.2	60.0	20.7	1.06	1.2	50	-
HCO_3^-		54.0	293.0	120.0	79.0	110	-	-
CO_3^-		-	6	-	-	-	-	-
Cl^-		99.0	1178.0	388.0	26.2	< 10	300	350
SO_4^{2-}		15.2	170.0	46.7	15.8	30.4	100	500
PO_4^{2-}		<0.025	-	-	-	-	0.2	-
NO_3^-		0.3	4.6	2.1	0.47	2.4	40	45
NO_2^-		1.1	2.4	1.6	<0.2	0.026	0.08	3.0
V	µg/L	0.52	1.30	0.61	0.75	6	1	100
Cr		2.00	4.74	3.17	2.97	23.12	20	50
Mn		3.01	194.16	27.65	2.88	2.43	10	100
Fe		117.46	852.96	319.50	64.77	350.0	100	300
Ni		6.29	31.34	17.59	15.81	12.13	10	200
Cu		2.90	7.76	7.58	6.61	5.51	1	1000
Zn		3.45	7.08	5.02	4.82	1.35	10	5000
As		0.12	4.29	1.07	0.59	0.585	50	10
Sr		238.15	880.87	479.55	187.28	110.54	400	7000
Ba		25.76	235.58	112.89	13.27	33.886	740	700
Hg		0.01	0.05	0.03	0.02	0.0054	0.01	0.5
Pb		0.04	0.43	0.20	0.16	0.125	6	10

* the background value of the indicator for the water in fishery water bodies

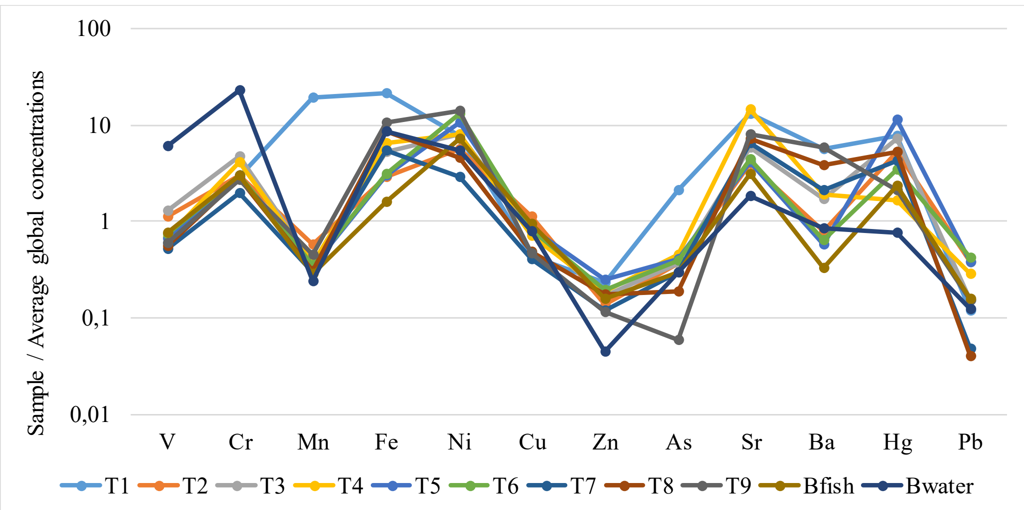

Fig. 2. Multi-element plot showing river water quality normalized to the average global

and reached 194.16 µg/L. The concentration of iron water at all sampling sites was over the $MPC_{fishery}$ permissible limit of 100 µg/L except for the background sampling site B_{fish}. Compared to $MPC_{drinking}$, a level of iron was higher by 2.8 times at the sampling sites T1, while T8, T9 and B_{water} showed a level limit permissible for drinking (Fig. 4).

Copper was 3-7 times higher against $MPC_{fishery}$ in all sampling sites in the Tolych River. The highest excess was recorded in T2; further concentration gradually decreases, while the copper level drops by half at the mouth part of the river.

Nickel was found to be higher against $MPC_{fishery}$ at all sampling points except for T7 and T8. After effluent discharge at sampling site T6, nickel level increased, where it exceeded $MPC_{fishery}$ by 2 times, which is due to the influence of effluent discharge (T5). In the mouth of the river (T9), the level of nickel was the highest, thus exceeding $MPC_{fishery}$ by 3 times.

One-time exceedance of $MPC_{fishery}$ in strontium was detected at sampling sites T1, T4, T8, and T9 from 2 to 1 times. The largest exceedance was recorded in T4. After wastewater discharge (T5), the level of strontium content significantly decreased, and further downstream to the mouth, it recovered to the $MPC_{fishery}$ level again.

The level of mercury at all sampling sites exceeds the concentration for guidelines for aquatic-life (0.01 µg/L). The highest excess in relation to MPC was found in sampling sites T1 (the upper part of the river) and T5 (wastewater discharge). At the same time, the mercury concentration is significantly reduced to the mouth part, where the excess is 1.7 times. However, mercury

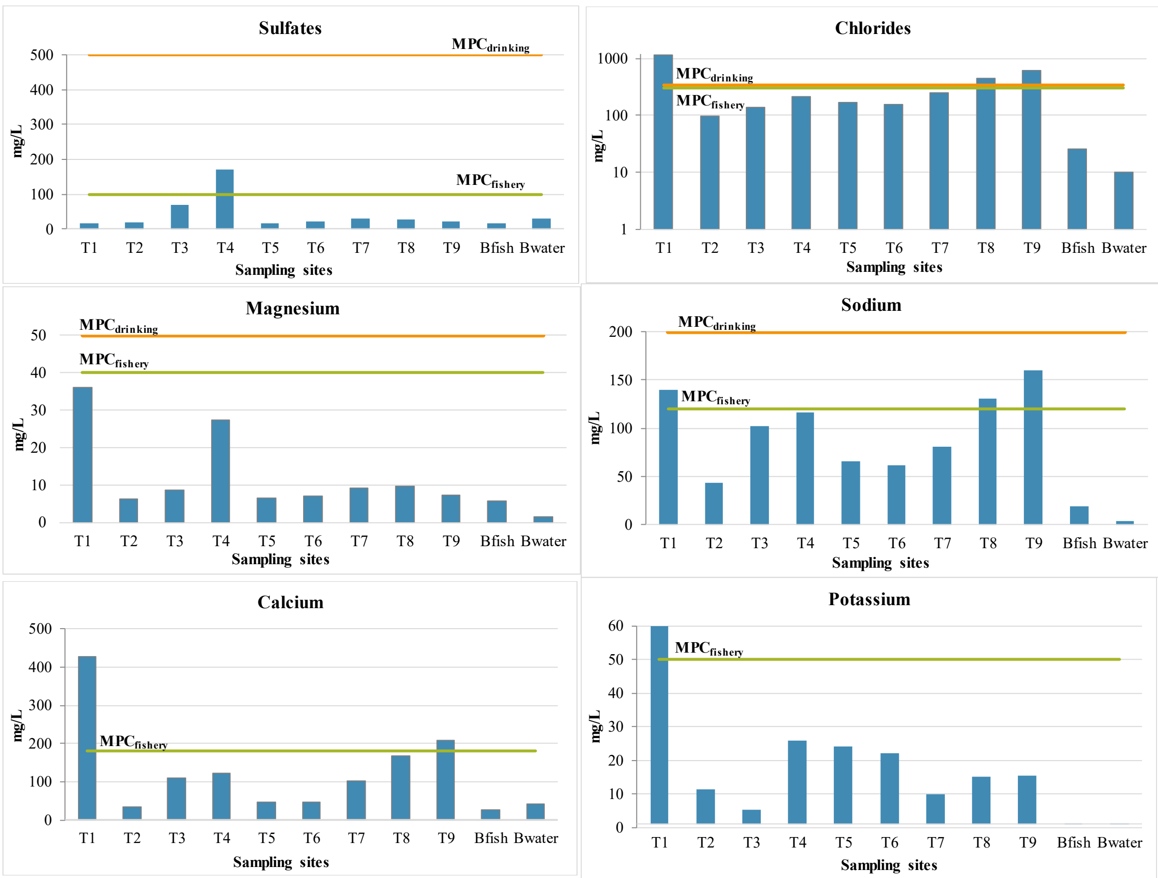

Fig. 3. The levels of major ions in all water samples compared against the requirements in the Russian water quality control guidelines

concentrations at all sampling sites correspond to drinking water and do not exceed 0.5 µg/L.

Fig. 5 gives the calculated HEI values for each site and the standards for the Russian values of $MPC_{fishery}$. The HEI values ranged from 11.2 to 41.9 with a mean of 18.0. Relatively to $MPC_{fishery}$, HEI values for site T1 demonstrated the high level of pollution in this part of the Tolych River and also T5 (wastewater discharge). The sampling sites (T2, T3, T4, T6, T8, and T9) fall within the medium pollution category (10>HEI<20), which may be due to anthropogenic impact in these sites. At the low reach of the Tolych River (site T9), as well as at the reference B_{fish} and B_{water} sites, the HEI value corresponds to the moderate level of pollution. However, unlike the Russian drinking water quality standards ($MPC_{drinking}$), the HEI for all studied locations indicated low contamination of water with respect to the trace elements.

The ERI values ranged from 152 to 654 or from a moderate level to a very high level of pollution with a mean of 331 (a considerable level). The highest ERI values in the Tolych River were recorded at the sampling site T1 and T3. In the middle stream of the Tolych River to the point of sampling T4, pollution decreases to its moderate level. Also, T5 (wastewater discharge) demonstrated the highest level of pollution. In water samples T1 and T5, the dominant pollutant was Hg with its contributions of 67% and 89%, respectively. After the discharge of wastewater over a 2 km distance up to the point of withdrawal T8, the level of pollution was recorded as considerable. And only in the mouth part (T9), pollution by ERI decreased to its moderate level.

At the lower reach of the Tolych River in the 2.1 km distance from the river mouth (point T7,

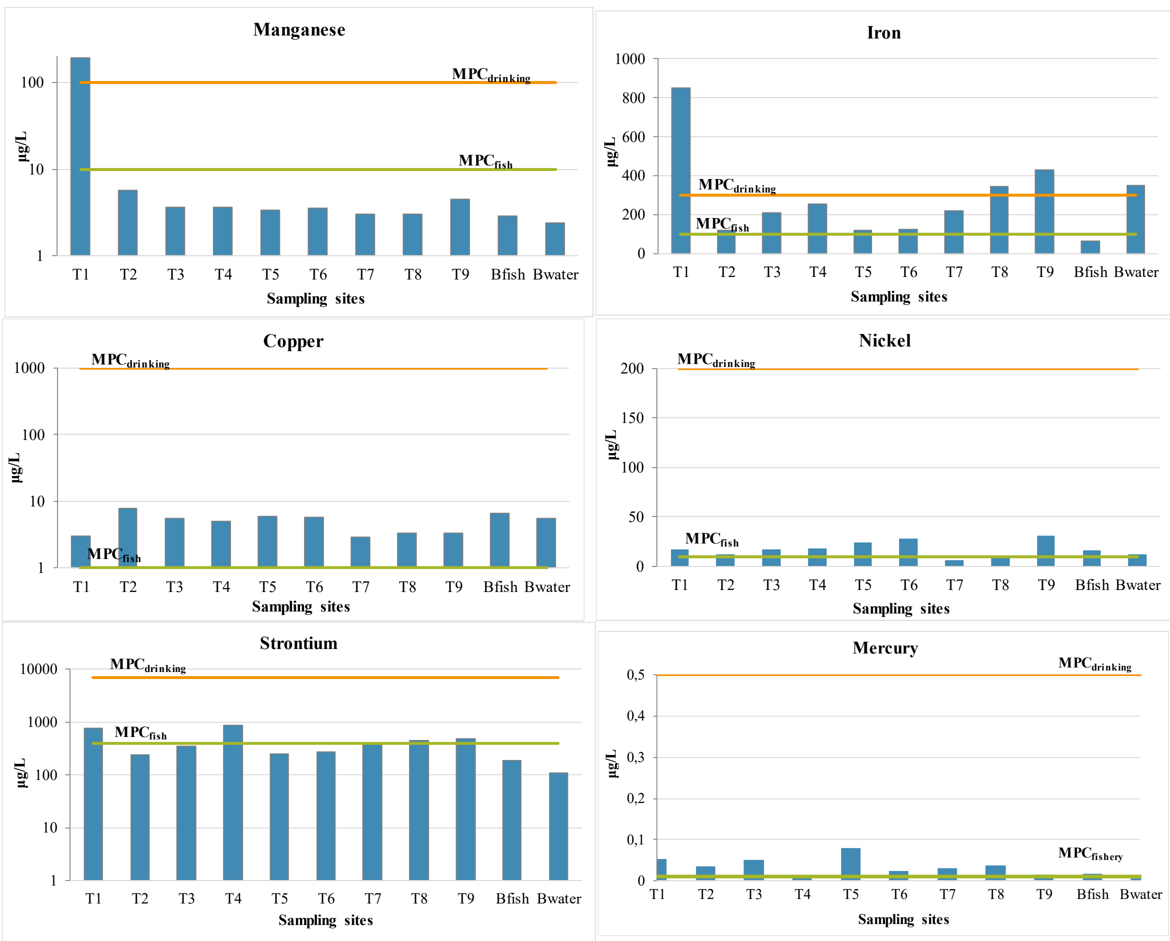

Fig. 4. The levels of trace elements in all water samples compared against the requirements in the Russian water quality control guidelines

Fig. 5), the water temperature was equal to 25°C during fish sampling. At this location, there was a section with a flow velocity of 0.3-0.5 m/s. Depths of 1-1.5 m were most common. The site is also characterized by areas with slow currents and backwaters. The bottom was muddy and sandy. The coastline is known for its vegetation such as *Typha* sp., *Scirpus* sp., and *Phragmites australis*. The gill nets which were set at the slow flow area captured 7 species of fish: roach *Rutilus rutilus*, bream *Abramis brama*, perch *Perca fluviatilis,* silver bream *Blicca bjoerkna*, ide *Leuciscus idus*, bleak *Alburnus alburnus*, asp *Aspius aspius*. Benthofages (roach) and polyzoophages (perch, ide) dominated in quantity with one species of piscivores (asp). The catch per unit effort (CPUE) as an average number of fish per fishing effort was 152 individuals per standard gillnet-day. The water quality at this location, based on the calculated value of the IBI index, was estimated as low (Table 3).

At the lake-shaped extension of the Tolych River at a 0.5 km distance from the river mouth (point T8, Fig. 4), the water temperature was 20°C; depths of 1.4-1.6 m prevailed; the flow was absent. The shoreline and littoral habitats were covered by macrophytes such as *Potamogeton* sp., *Niphar* sp., *Typha* sp., *Scirpus* sp., and *Phragmites australis*. Apart from the coastline, the rest of the water area was not covered by aquatic vegetation. During the survey, the water level in the lake-shaped extension of the Tolych River was higher than in the Kama reservoir, and mixing of the water from the reservoir and the Tolych River was not observed. The gill nets which were set up in the central part of the lake-shape extension of the river and near the shoreline along the edge of aquatic vegetation, caught 5 species of fish: ruffie *Gymnocephalus cernuus*, crucian carp *Carassius carassius*, roach, bream, perch. Quantitatively, polyzoophages (perch) prevailed. The CPUE was 66 fish individuals per standardized fishing effort. The value of the IBI index was 22 (a very low quality of the water).

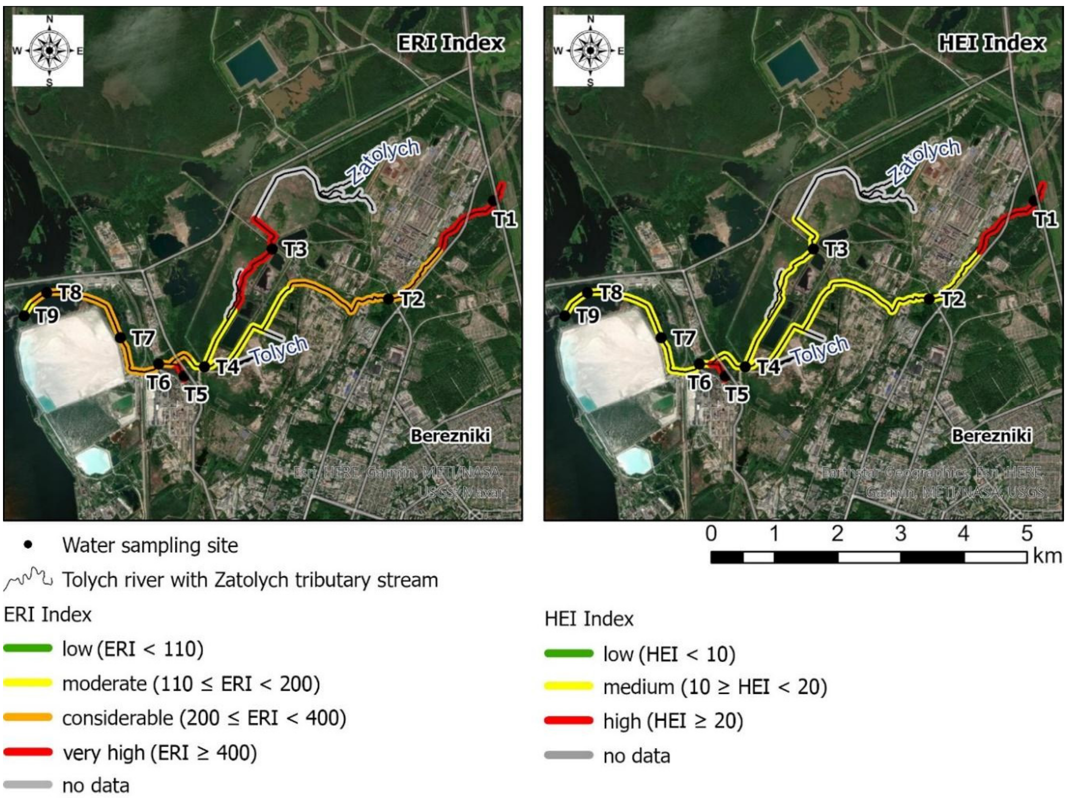

Fig 5. Water quality classification of the Tolych River by ERI and HEI indices

The background location (site B_{fish}, Fig. 1) was characterized by the following conditions: the water temperature was equal to 18 °C; the maximum depth was 2.5 m; the bottom was composed of a silty substrate; no water flow was observed. There were no zones with developed aquatic vegetation. As a result of gill net sampling in the central part of the studied bay of the Kama reservoir, 7 species of fish were captured including roach, bream, perch, walleye *Stizostedion lucioperca*, sabre carp *Pelecus cultratus*, bluefish *Abramis ballerus*, Black-Kaspian Sea sprat *Clupeonella cultriventris*. Benthophagous fish such as roach and bream dominated quantitatively. The zooplanktivores such as sabre carp, bluefish and sprat were subdominants by

Table 3. The number of points for the IBI index used to assess the Tolych River water quality

NO	Metrics	Sampling sites		
		T7	T8	B_{fish}
1	the number of fish species	5	3	5
2	the number of benthic species preferring habitats with flow	1	1	1
3	the number of species preferring backwaters and still water	1	3	3
4	the number of pelagic species	3	1	5
5	the number of species intolerant to pollution	1	1	3
6	percentage of individuals of intolerant fish species	1	1	3
7	percentage of individuals not related to omnivorous species	3	3	5
8	percentage of individuals of zooplanktivores	1	1	3
9	percentage of individuals of benthophages	3	1	5
10	percentage of individuals of obligatory piscivores	3	1	3
11	average number of fish per standardized fishing effort	5	1	3
12	percentage of individuals with diseases, parasites and other anomalies	5	5	5
	TOTAL	32	22	44

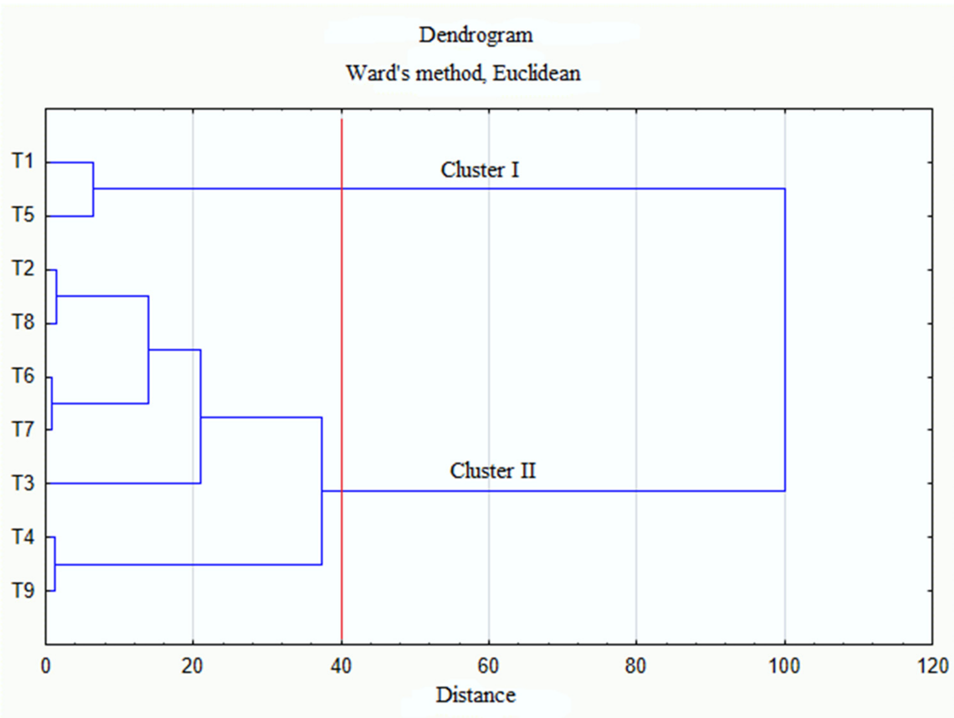

Fig. 6. Clustering surface water quality in the Tolych River

abundance at this location. Also, one species of obligatory piscivores (pike perch) was registered. The average number of fish per standardized fishing effort was 120 individuals. The value of the IBI index, based on the use of fish as an indicator group, was equal to 44, which corresponds to a moderate quality of the water.

The highest concentrations of major ions and trace elements were found in the upper reaches of the Tolych River (T1). Also, the temperature was equal to 24.6 °C which is much higher than the one at the background sampling site. According to the remote sensing data, the upper flow of the Tolych River begins within the forest area, and there is no infrastructure which poses a challenge for further research to identify the anthropogenic or natural source of pollution in the upstream river basin. One hypothesis of changes in the chemical composition of water in the river headwaters may be associated with a natural highly mineralized spring discharge (TDS=2-5 g/l) which flows from terrigenous-carbonate and salt-mergel sediments of the Lower Permian located in the Verkhnekamskoye salt deposit and complicated by the Durinsk fault (Belkin, 2020; Khayrulina et al., 2022). At T1 sampling point, the water temperature is by 6.6 degrees higher than background pre-industrial values. This excess can be explained by the fact that the sampling point B_{water} is located in the upper part of the watershed, where cold springs are unloaded to give birth to the water flow. There is no information about unloading of high-temperature springs in the study area. The simplest explanation is that during sampling, the air temperature reached 30 °C, which could lead to overheating of river headwaters.

At sampling site T4, the temperature in the Tolych River drops to 17.6 °C, despite the discharge of wastewater from non-ferrous metallurgy and power plants located above sampling sites T2 and T3. Site T5 is located at the chemical plant's wastewater discharge 3.6 km before the mouth of the Tolych River, with the average annual volume of wastewater discharge equal to 42,578 thousand m^3. The highest value of water temperature (34.4°C) was measured for wastewater discharging from the chemical plant. At sampling site T6, the temperature gradient decreased by 1.1 degrees 500 meters after the effluent discharge (T5). The temperature at sampling point T6 was 33.3°C. At sampling site T9 in the mouth of the River Tolych, the temperature decreased to 20 °C, indicating that the temperature regime was normalized. A survey of the watercourse detected a cascade of small artificial waterfalls above sampling point T7, which contribute to water cooling.

The decrease in the temperature gradient to the mouth may occur due to the large area and shallowness of the lake extension before its confluence with the Kama River. There is a high temperature gradient in the Tolych River water, which can cause direct adverse effects on fish according to the CCME for aquatic organisms (CCME, 2007). The results of temperature changes after wastewater discharges in the Tolych River indicate the restoration of the temperature regime, which corresponds to water quality standards in fishery water bodies. According to this standard, anthropogenic activities should not increase water temperatures higher than 28°C in summer in waters which are inhabited by cold-living fish (Order, 2016). The effects of temperature gradient change on freshwater ecosystems due to both wastewater impact and climate change will probably be the most unpredictable in the boreal region in Perm Krai (Voutilainen et al., 2014).

Conductivity was found to range from 440 to 2034 μS/cm. Such values may result not only from leaching rock components (in a combination of geological structure and amount of precipitation) but also from anthropogenic activities (Aleksander-Kwaterczak & Plenzler, 2019).

The comparison results of major ions and trace elements of the Tolych River against reference values has shown increased concentrations of Mn, Ni, Sr, and Hg. Rivers in Perm Krai flow through sandstones of the Permian period with the highest concentration of Cu and Fe (Tchaikovsky et al., 2018). This leads to high concentrations of copper and iron in the water of the rivers in Perm Krai, and also iron is the most common element in the environment in humic rivers (Miroshnichenko, 2011; Kopylov, 2012; Heikkinen et al., 2022). In addition to the natural source of iron, about 16 tons of iron enter the Tolych River waters annually due to wastewater discharges, which explains the high iron concentrations at the sampling points. The highest copper concentrations recorded at sampling site T2 occur due to the influence of wastewater discharges from a non-ferrous metallurgy enterprise. Thus, the results we obtained on the concentration of copper and iron in different sampling locations can be explained by natural and anthropogenic influence on the river flow, except for the upper reaches of the river Tolych, where the concentration of iron was significantly higher than in the control site.

In some sampling sites, T1, T8, and T9, the concentrations of Fe exceeded the guideline limits for $MPC_{fishery}$ and $MPC_{drinking}$ of water quality. However, the effect of iron on aquatic organisms is mainly indirect (Abdel-Satar et al., 2017). The concentrations of Cu, Ni, and Hg in almost all the samples were above the guideline limits for $MPC_{fishery}$. The maximum concentration of Sr was higher than the maximum permitted concentrations established by $MPC_{fishery}$ at sites T4 and T1. The decrease in concentrations of major ions and trace elements in T4 relative to upstream sampling points is probably associated with self-purification of water and is an important indicator for river health (Tian et al., 2011). A high concentration of trace elements in sampling sites may lead to the accumulation of trace elements in the sediment and plant tissues. The water quality of the Tolych River in terms of major ions is determined by anthropogenic effluents, which are also highly affected by both snowmelt and rainfall conditions.

The distribution of major ions after the wastewater discharge in the Tolych River at point T6 indicates dilution of the wastewater. However, concentrations of trace elements such as nickel and mercury increase after wastewater discharge, which is associated with the intake from the wastewater discharge. At the same time, this wastewater discharge is the source of thermal pollution of the river. Starting from T6 point up to T9 point, concentrations of major ions and trace elements increase, which may be caused by the migration of the main flows of pollution associated with filtration discharges from operating and mothballed sludge storage and storage of liquid and solid waste, located in the left bank part of the Tolych River (Lepikhin et al., 2020).

The spatial distribution of ERI and HEI indices indicates generally similar results, with high levels of pollution in the upper part of the watershed and sampling point T5 (wastewater discharge). After wastewater discharge, the level of pollution is significant in ERI and average in HEI at sampling points T8 and T9. And in the mouth part of the Tolych River before flowing into the Kama river, the level of pollution by ERI and HEI was estimated as medium.

Figure 6 shows classification of sampling sites by ERI and HEI indices. At Euclidean distance of 40, water quality in the area was grouped into 2 clusters. Cluster 1 includes 2 locations (T1 and T5); cluster 2 includes 7 locations (T2, T8, T6, T7, T3, T4 and T9).

The results showed that the water quality in cluster 1 had average values of ERI=626.5 and HEI=30.9 signaling bad water quality, and water quality in cluster 2 had average values of ERI=269.7 and HEI=15.0 indicating moderately polluted water. Water quality in cluster 1 was characterized by high temperature and high Hg, Mn Fe, Cl, Na, Ca, K, and Mg, in contrast to Cluster 2.

Unlike the reference background site, the water quality of the lower reach of the Tolych River estimated by the IBI index is lower. Water quality between points T7 and T8 differs in both concentrations of chemical contaminants and habitat conditions. This may be explained by the fact that habitat diversity within wide catchments makes it difficult to use the index within large lotic systems. This, in its turn, may affect the standardization of the data and the interpretation of the results (Oberdorff & Hughes, 1992). Thus, during the study, it was found that habitat characteristics of T8 were closer to the point we selected as a reference site. Therefore, the differences in water quality estimated by the IBI index between the reference and T8 sites are mostly determined by the level of pollution. In the T7 location, the environment was highly heterogeneous. There were both areas with a high flow rate and still backwater zones. In rivers, such zones with low flow velocity located near the riffles usually have increased density of fish

(McCabe, 2011). This can affect our findings in high fish abundance in terms of CPUE in T7 location, which determined the large values of the IBI index, compared with T8 point.

The water quality determined by the HEI, ERI and IBI indices in the lower reaches of the Tolych River differs. This may relate to the use of different approaches for the assessment of the pollution level. The HEI and ERI indices we used are based on the reference values of the chemical parameters of the water of the baseline sampling points or the standard values of the MPC. However, IBI's index water quality is assessed by the composition of the fish community. This reflects not only the number of tolerant and intolerant fish species, but also the abundance of diverse ecological groups of fish which is determined by conditions at previous ecosystem levels. For example, despite proper habitat conditions preferable for rheophilic fish species and the presence of asp, obligate piscivore species at T7 location, rheophilic benthic species which are also sensitive to environmental pollution, were not observed there (Schinegger et al., 2013). In addition, there were no intolerant species in both locations, but there was a high number of omnivorous species and low occurrence of zooplanktivorous fish. All that determined low water quality assessed by the IBI index and showed the degradation of biota on lower trophic of zooplankton and macrozoobenthos. These results correspond to the published evidence on higher sensitivity of biotic indices compared to the chemical ones (Ghani et al., 2018). Also, there are no published studies where IBI index is used to assess water quality of boreal streams, although some studies analyze fish data (Chu et al., 2003; Murdoch et al., 2020; Ilmast, Sterligova, 2020; Sutela et al., 2021). This can demonstrate the novelty of current study.

It should be noted that the shallow depths within the surveyed locations of the lower reaches of the Tolych River may indicate that the most observed fish species inhabit the river temporarily. It is most likely that the fish observed in the Tolych River are individuals who came from the Kama reservoir in spring to spawn. Subsequently, these fish can stay in the river for summer feeding mostly due to higher temperatures in the lower reaches of the Tolych River, which are preferable for both feeding and growth (Jeppesen et al., 2010). Then, at low-water level in winter with higher concentrations of pollutants (Whitehead et al., 2009), fish are highly likely to migrate into the Kama reservoir. The crucian carp is the only species that can inhabit year-round within T8 location, but its abundance, according to results of the gill net sampling, was extremely low. The predominantly transit composition of the fish community within the areas of waters affected by pollution is also mentioned in literature (Schinegger et al., 2016; Jurajda et al., 2021). Anyway, additional research is required to confirm the hypothesis arising from the current study.

CONCLUSION

The results of this study confirmed the importance of combining abiotic and biotic indicators in the assessment of ecosystem health of freshwater boreal rivers. The baseline information concerning the levels of water quality, assessment and comparison of abiotic indices in small boreal stream of Perm Krai (Russia) showed that the allowable limits for SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, K^+, Mn, Fe, Cu, Ni, Sr and Hg exceeded mainly the values of the Russian fishery standards ($MPC_{fishery}$). The major pollutants are SO_4^{2-}, Cl^-, Fe, Ni, Cu, Hg, and these parameters can be used as contamination indicators for future monitoring. In different parts of the river, the values of the HEI and ERI water quality indices demonstrated moderate to very high levels of pollution. Downstream from the main wastewater sources, the level of pollution decreases from high to moderate. Thermal pollution is also registered and negatively affects aquatic life of the observed boreal river, which is confirmed by IBI index values. At the lower reaches of the Tolych River, no intolerant fish species were recorded with a high number of omnivorous species and low occurrence of zooplanktivorous fish. This demonstrates low water quality assessed by the IBI index and shows the degradation of biota at lower trophic levels. A comparison between biotic and abiotic indices demonstrates that fish can be used as a more sensitive indicator of water pollution. The analysis of the occurrence of fish species with different pollution tolerances can help in predicting fish community response to adverse effects from both effluent discharge and temperature pollution. Further studies based on various biotic indices should be conducted to estimate anthropogenic impact on boreal freshwater ecosystems.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy have been completely observed by the authors.

LIFE SCIENCE REPORTING

The present field study was approved by the Federal Agency for Fisheries of the Russian Federation and Perm State University Animal Care and Use Committee.

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