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Heavy Metals in Fresh Waters of Kazakhstan and Methodological Approaches to Developing a Regional Water Quality Classification

Krupa E.[1*], Barinova S.[2], Romanova S.[3], Aubakirova M.[3], Ainabaeva N.[1]

[1] Republican State Enterprise (RSE) on the Right of Economic Management "Institute of Zoology", Science Committee of the Ministry of Education and Science, Kazakhstan, 050060, Almaty, Al-Farabi Ave., 93
[2] Institute of Evolution, University of Haifa, Mount Carmel, Israel, 3498838, Haifa, Abba Khoushi Ave., 199
[3] Al-Farabi Kazakh National University, Ministry of Education and Science, Kazakhstan, 050000, Almaty, Al-Farabi Ave., 93

* Corresponding author
E-mail: elena_krupa@mail.ru

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Abstract
The study aimed to define the classes in the Heavy Metals Section of the Regional Environmental Ranking System based on long-term data (1997-2017). When distinguishing water quality classes, the following factors were taken into account: background content of heavy metals, content of heavy metals in water bodies exposed to different levels and character of anthropogenic pollution, and response of biological communities to toxic pollution of their natural habitats. According to the proposed classification, the non-contaminated water of Class 1 contains the following: Cd<0.2, Cu<2.5, Zn<4, Pb<3, Cr<0.5, and Ni<0.5 μg dm^{-3}. Class 2 water is characterized by Cd<0.5, Cu<6, Zn<6, Pb<7, Cr<1, and Ni<2 μg dm^{-3} content. Moderately polluted water of Class 3 contains Cd<3, Cu<10, Cr<10, Ni<10, Zn<20, and Pb<20 μg dm^{-3}. Concentrations of all heavy metals increase proportionally and exceed 30-100 μg dm^{-3} in the most polluted water of Class 6. The proposed methodological approach assesses not only the local content of heavy metals in water bodies of Kazakhstan but also the degree of toxic pollution of their vast catchment basins. The proposed methods are applicable to other arid regions with similar physical and climatic conditions.

Key words: toxic pollution, fresh water bodies, classification criteria, catchment basin.

Paper type: Research article.

1. Introduction

Among multiple pollutants, it is heavy metals which pose the highest threat to nature and human health (Zhaoyong et al., 2015; Huang et al., 2015; Abuduwaili et al., 2015; Solodukhin et al., 2016). An objective assessment of toxic pollution of water bodies represents an essential task due to the annually increasing anthropogenic pressure on the environment. Usually, the content of toxic pollutants is compared with national water quality standards (Neamtu et al., 2009; Sappa et al., 2014; Ojekunle et al., 2016; Mottana et al., 2016; Bhutiani et al., 2017). In certain cases, integrated pollution indexes are calculated (Talalaj & Biedka, 2016) based on the content of several pollutants.

Unlike the methods mentioned above, the ecological classification of water quality is not based on absolute but ranked heavy metal concentrations (Romanenko et al., 1990). From an ecological point of view, the classification distinguishes six classes of water quality – from pure to extremely dirty. Each water quality class is assigned a range of concentration fluctuations (min and max values) of heavy metals. According to the European Water Framework Directive (2000), specific color coding is also utilized for classifying water quality. When applying this method for environmental monitoring purposes, the content of heavy metals established for a water body is compared to the corresponding water quality class (Barinova, 2017a). The next step of heavy metals content assessment includes visualizing and statistical mapping. The level of toxic pollution of individual sections of a catchment basin is color-coded according to the color code of the classification scale (Barinova, 2011; Barinova & Krassilov, 2012). As an applied tool for ecological classification, mapping allows evaluating the distribution of pollutants in various parts of the catchment area and establishing a connection with the primary sources of pollution. Besides, data visualization facilitates the perception of environmental information by decision-makers in water policy and integrated water resources management (Haddaway et al., 2016).

The basin approach serves the theoretical basis for the method, when any point on the watercourse is considered cumulative for the upstream catchment part collecting surface runoff from vast territories. Accordingly, the quality of water in a water body reflects the nature and intensity of its use by people and the degree of anthropogenic transformation and pollution of the catchment area. The priority of the basin approach in integrated water resources management is emphasized in numerous publications (European Water Framework Directive, 2000; Evers, 2016; Giakoumis & Voulvoulis, 2018).

The practical application of the classification mentioned above allows scaling under certain conditions. The starting point for highlighting the boundaries of water quality classes should be the determination of background concentrations of heavy metals performed based on statistical methods (Novikov & Draganov, 2017). The regional background content of heavy metals in continental waters depends on a combination of natural factors and varies significantly in different regions of the Earth (Shvartsev, 2008). As a result, the clean water class threshold may vary considerably, depending on the specific regional climatic conditions and geographical location of a relevant water body. In turn, the ability of water bodies to self-purify and adaptation of hydrocenoses to toxic pollution depend not only on the toxicity of heavy metals (Lee et al., 2015; Hoppe et al., 2015; Huang et al., 2017; Zhao et al., 2017) and species composition of communities (Matishev et al., 2003; Bulgakov, 2004; Krupa et al., 2016a) but likewise on a set of regional physicochemical factors (Caporale & Violante, 2016; Li et al., 2013). Therefore, the main internationally endorsed principle of integrated water resources management (Rijswick et al., 2010; Evers, 2016) can be effectively applied only based on considering the regional characteristics of abiotic and biotic components of aquatic ecosystems. This implies the need for ranking available data on pollutants and designing classification scales for each region with similar natural and climatic conditions.

The next important step in developing regional classification scales is the determination of the upper margin of toxic pollution, in which aquatic ecosystems remain stable over a long time. It is most productive to create a combined classification scale accounting for both environmental variables and the response of biotic communities to a certain level of toxic pollution (Barinova, 2017b). The European Water Framework Directive (2000) and a broad range of publications stress the importance of utilizing biological indicators to assess the ecological state of water bodies (Aazami et al., 2015; Dembowska et al., 2018; Barinova & Krupa, 2017b; Krupa et al., 2018).

Kazakhstan features the climatic conditions and socio-economic problems common for other Central Asian states. As in other countries of this region, over 80% of Kazakhstan's population lack access to clean freshwater (Porkka et al., 2012). Low quality of water resources is conditioned by many factors, including their irrational use in an arid climate, high population density in certain regions, and the nature and intensity of economic activity (Karthe et al., 2017). Although the agricultural sector is mainly developed in the economies of Central Asian countries (Khamidov et al., 2016), heavy metals significantly contribute to the overall level of toxic environmental pollution. The ongoing climate change further exacerbates the existing water supply challenges in arid regions and the initial deficit of water resources (Barrett et al., 2017). The transboundary position of large regional rivers, such as the Irtysh, Syrdarya, Ural, and Ili, trigger interstate tensions over water use against the background of its scarcity (Guo et al., 2016). The above makes the basin principle essential for water quality assessment and integrated water resources management in the Central Asian region (Yu et al., 2018).

As in the neighboring countries (He et al., 2017), the assessment of toxic pollution of water bodies in Kazakhstan is mainly based on chemical (Slivinsky & Krupa, 2013; Romanova et al., 2012; Woszczyk et al., 2018; Krupa et al., 2017a, 2017b, 2017c; Burlibayeva et al., 2016) or biological variables (Barinova & Krupa, 2017a, 2017b; Barinova et al., 2018; Krupa et al., 2016b; Krupa et al., 2018). Despite the importance of the basin approach in water policy, it is currently difficult to apply it to water bodies in arid territories because an ecological classification of water quality (Romanenko et al., 1990) was initially designed for humid-zone European water bodies.

The study aimed to address the relevant challenges associated with assessing the toxic pollution of water bodies in arid zones based on the basin principle, i.e., to determine the range of classes under the all-regional classification of alkaline water quality for six heavy metals (Cd, Cu, Zn, Pb, Ni, and Cr) based on the long-term survey of water bodies in arid and semi-arid territories of Kazakhstan.

2. Study site

Kazakhstan is the largest country in Central Asia, with a total population of 18,356,890 people. The population density varies from 50 persons per 1 km^2 in areas with favorable climatic conditions to 0.5-1.0 persons per 1 km^2 in the arid central and western regions. The country has highly-developed farming and livestock husbandry (Khamidov et al., 2016), and it is rich in oil, gas (Bin, 2014), and polymetallic ores (Mazurov, 2005). There are only 3 major cities of republican and 14 cities of regional significance. About 58% of the population and large-scale industrial enterprises engaged in the extraction and processing of mineral resources are concentrated in urban localities (Woszczyk et al., 2018; Yin et al., 2012).

Kazakhstan ranks last among CIS countries (Commonwealth of Independent States) in water availability (Tyumenev, 2008). Surface water resources are distributed extremely unevenly throughout the territory of the country. Residents of central, western, and southwestern parts of the country face significant water shortages. The hydrographic network is better developed in the southeast, east, and north of the country. The largest rivers Irtysh, Syrdarya, Ural, and Ili originate on the territory of the neighboring states. The largest Kazakhstan's water body after the Caspian Sea is Lake Balkhash, located in the southeast. Whereas the lake's western part is fresh, its eastern part is brackish. The brackish Lake Alakol and the fresh lakes Sasykkol, Koshkarkol, and Zhalanashkol are located to the east of Balkhash. The largest artificial reservoirs include Bukhtarma, Kapshagai, and Shardara situated in the northeastern, southeastern, and southern parts of Kazakhstan, respectively.

The climate in most parts of the country is continental, arid, or semi-arid (Baidal, 1964), with cold winters and hot summers. The climatic features of the territory dictate high temperatures of waters (up to 26-32°C in summer), high Total Dissolved Solids (TDS) values (over 0.3-0.5 mg/dm^3), and low alkaline to alkaline water properties (Krupa, 2012). Relatively low content of organic substances and nutrients is typical for the majority of Kazakhstan's water bodies (Frumin & Krashanovskaya, 2014).

The anthropogenic pressure on water bodies is determined by the nature and intensity of their use and the degree of transformation and pollution of catchment areas. According to the level of anthropogenic exposure, Kazakhstan's water bodies are divided into three groups: 1) background, 2) moderate, and 3) high anthropogenic impact. The grouping principles applied to Kazakhstan's water bodies were described in earlier publications (Krupa et al., 2019).

3. Materials and methods

3.1 Sampling

The study entailed surveying 90 freshwater water bodies across Kazakhstan, including background underground water sources, mountain rivers, lakes, reservoirs, natural water bodies of plains, as well as other water bodies of plains polluted by runoff from catchment basins and receiving municipal and industrial wastewater (Table I). Water samples from each surveyed water body were collected to determine heavy metal concentrations in the summertime during 1997-2017. Three water samples were collected from small water bodies below 1 km^2 area. Then samples were mixed into one integral sample from which one subsample for subsequent analysis was taken. Water samples from large water bodies were taken over a grid of stations evenly spread throughout the water area. A total of 347 samples were collected to determine the content of Cd, Cu, Zn, Pb, Ni, and Cr. For preservation, nitric acid was added to the samples immediately after sampling. All samples were transported to the laboratory in an icebox. Temperature and pH measurements of surface water layers were executed during field trips using Hanna HI 98129 instruments. Water transparency was measured with the Secchi disk.

Table I. Physical and chemical variables of the surveyed fresh water bodies in Kazakhstan.

Level of anthropogenic impact	Type of water body	Altitude, m ASL	*TDS, mg/dm^{-3}	Temperature, °C	Number of water bodies (number of samples)
Background	Underground and ground waters	680-1,469	26.6-574.8	10.7-37.0	11 (13)
	Mountain rivers	1,078-1,986	99.0-468.1	10.1-18.0	15 (18)
	Mountain lakes and reservoirs	1,069-3,170	26.6-574.8	12.1-24.1	11 (12)
	Plains water bodies	33-529	211.5-862.9	14.9-28.0	12 (33)
Moderate	Plains water bodies polluted by runoff from catchment basins	44-975	161.8-1,981.9	14.4-30.7	34 (200)
High	Receivers of municipal and industrial wastewater	448-619	312.3-1,319.3	24.0-30.0	7 (71)

**TDS – according to: Krupa et al., 2019.*

3.2 Methods of determining heavy metals content

The analysis of water samples for heavy metals was carried out in the analytical laboratory "KAZEKOANALIZ" (accreditation certificate No. KZ.I.02.1017) according to the Interstate Standard (2013). Heavy metals measurements were performed by mass spectrometry with inductively coupled plasma using Agilent 7500 A Series ICP-MS Water Analyzer manufactured by Agilent Technologies, Santa Clara, CA 95051, United States (National Standard of the RK ISO 17294-2-2006). The device allows detecting various chemical elements in complex matrices, including these in sea and greywater, and biological objects in micro-trace quantities. Concentrated nitric acid (1 cm^3 of nitric acid per 200 cm^3 of water) was added to the analyzed water samples before the analysis. Each water sample was heated in a current of argon according to a program including drying, ashing, atomization, and annealing of the furnace. Abundance Sensitivity of Agilent 7500 A: Low Mass<5×10^{-7}, High Mass<1×10^{-7}.

3.3 Statistical analysis

For descriptive statistics purposes, the obtained data were distributed based on the Distribution Fitting function, and Box-Whiskers graphs were plotted using the Statistica 10.0 application. In addition to mean values and standard deviations, median values and the 75th percentile were used to describe the data (Glantz, 1999). The grade differences in mean and median values were assessed by nonparametric methods as per the Kruskal-Wallis criterion.

4. Results

4.1 Brief description of the examined fresh water bodies

The surveyed water bodies are located in different regions of Kazakhstan (Fig. 1.) at altitudes from 44 to 3,170 m above sea level (Table I). Most of the background water bodies are situated in inaccessible mountainous areas, including the territory of nature reserves and natural parks. All background water bodies – both mountain and plain – have undisturbed catchment areas. Some reservoirs of plains with a moderate level of anthropogenic impact are used for irrigation and power generation. Catchment basins of these water bodies are generally used for agriculture and livestock farming, but the wastewater is not discharged directly into them. Pollution of water bodies occurs due to surface runoff and runoff from inflowing rivers. Water bodies exposed to severe anthropogenic impact include storage facilities of pre-treated municipal and industrial effluents, e.g., direct receivers of sewage. The areas of the studied water bodies vary from 0.02 to 10,556 km^2, with the maximum depths of 0.1-44.0 m. Water transparency during sampling averaged 0.1-9.0 m. The pH values varied from 7.0 to 9.5. Water temperatures during summer varied widely and showed maximum values in hot underground springs.

4.2 Characteristics of toxic pollution of fresh water bodies in Kazakhstan

On average, the Cd content reached 3.5, Cu –14.8, Zn – 32.8, Pb – 12.9, Cr – 3.3, and Ni – 87.9 $\mu g/dm^{-3}$ for all the studied fresh water bodies. The minimum mean concentrations of all heavy metals were registered in background water bodies (Fig. 2.). The most substantial amounts of Cd, Cr, and Ni were detected in the water bodies under high anthropogenic impact. At the same time, Cu, Zn, and Pb were present at higher average concentrations in water bodies exposed to a moderate anthropogenic load.

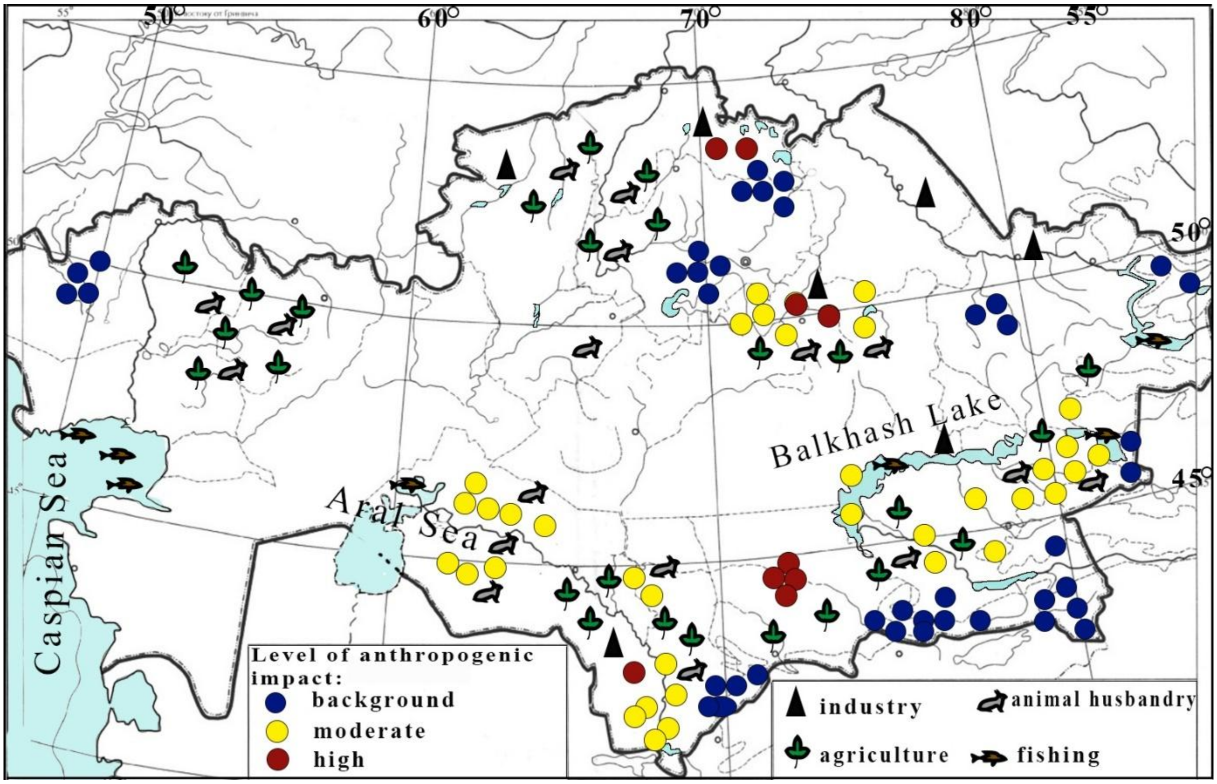

Figure 1. Map of surveyed fresh water bodies and distribution of key economic sectors in Kazakhstan.

Variation coefficient values indicated an extensive range of heavy metal concentrations recorded for water bodies with different anthropogenic loads (Table II). The comparison of data according to the Kruskal-Wallis test showed that mean concentrations of all heavy metals, except Cu, were statistically significantly lower in background water bodies than in water bodies of other categories. The average Cu content in background water bodies was considerably lower than in water bodies under the moderate anthropogenic impact. It did not differ from the average Cu content in water bodies with the high anthropogenic load. Statistically, water bodies exposed to moderate and high anthropogenic pressure differed significantly in the average content of Cd, Cu, and Cr. However, they demonstrated no differences in the average concentrations of Zn, Pb, and Ni.

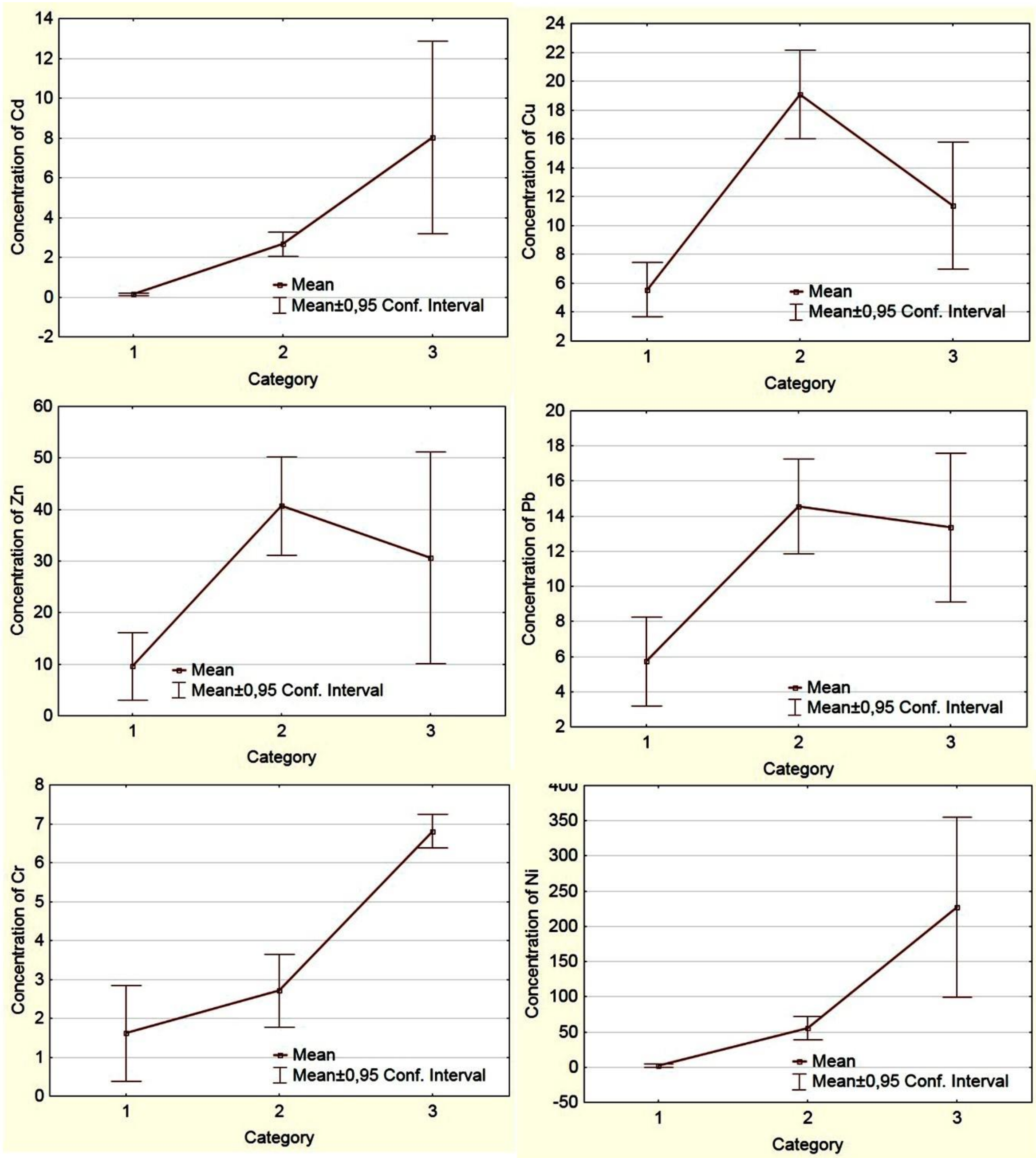

Figure 2. Mean values and confidence intervals for heavy metals (μg/dm^{-3}) in Kazakhstan's background water bodies (Category 1), water bodies under moderate (Category 2) and high level of anthropogenic impact (Category 3).

The evaluation of primary data using the Distribution Fitting function and the data in Table II. showed that the distribution of heavy metal concentrations in all water bodies diverged from normal. Thus, to describe the level of toxic pollution of the surveyed water bodies, median values of heavy metal concentrations were used.

Table II. Heavy metal concentrations in Kazakhstan's fresh water bodies with different level of anthropogenic impact (descriptive statistics).

Heavy Metal	Valid N	Average concentration, μg/dm^{-3}	Standard error	Median	Min.	Max.	75th Percentile	Standard deviation	Coefficient of variation
1. Background									
Cd	35	0.14	0.03	0.00	0.00	0.60	0.20	0.18	130.18
Cu	64	5.55	0.94	2.40	0.00	36.00	6.10	7.54	135.96
Zn	57	9.56	3.29	3.60	0.00	176.00	6.30	24.86	260.04
Pb	46	5.74	1.26	2.65	0.00	47.30	6.70	8.53	148.62
Cr	37	1.61	0.61	0.50	0.00	19.90	0.90	3.71	230.30
Ni	36	2.51	1.08	0.15	0.00	35.90	1.75	6.47	258.24
2. Under moderate anthropogenic impact									
Cd	187	2.66	0.30	1.70	0.00	33.00	3.28	4.14	155.95
Cu	192	19.09	1.55	11.95	0.00	142.00	24.00	21.47	112.48
Zn	189	40.67	4.85	16.50	0.00	564.90	48.90	66.65	163.87
Pb	183	14.56	1.38	10.00	0.00	186.70	20.50	18.65	128.11
Cr	15	2.71	0.44	2.50	0.40	6.40	3.60	1.69	62.24
Ni	60	55.33	8.14	36.95	0.00	194.00	61.89	63.04	113.93
3. Under high anthropogenic impact									
Cd	62	8.02	2.42	3.15	0.00	89.00	5.80	19.02	237.30
Cu	64	11.39	2.21	4.50	0.10	84.30	11.93	17.66	154.94
Zn	64	30.69	10.28	19.74	0.10	664.90	29.00	82.22	267.94
Pb	62	13.36	2.12	5.84	0.10	82.00	23.00	16.71	125.11
Cr	20	6.81	0.21	6.95	4.50	8.50	7.30	0.93	13.61
Ni	36	227.16	63.08	6.25	3.60	1,310.00	191.00	378.47	166.61

Median values of heavy metal concentrations were lower than average values, although they changed in water bodies the same way (Fig. 3.) the average values did (Fig. 2.). According to the Kruskal-Wallis test, median concentrations of all heavy metals in background water bodies were statistically significantly lower than in water bodies under the moderate and severe anthropogenic impact. Background concentrations of Pb were lower in water bodies under the moderate anthropogenic impact. They did not differ from the median concentrations of this metal in water bodies with the high anthropogenic load. There were no statistically significant differences in the median concentrations of Cd, Zn, Pb, and Ni in water bodies under moderate and high anthropogenic impact.

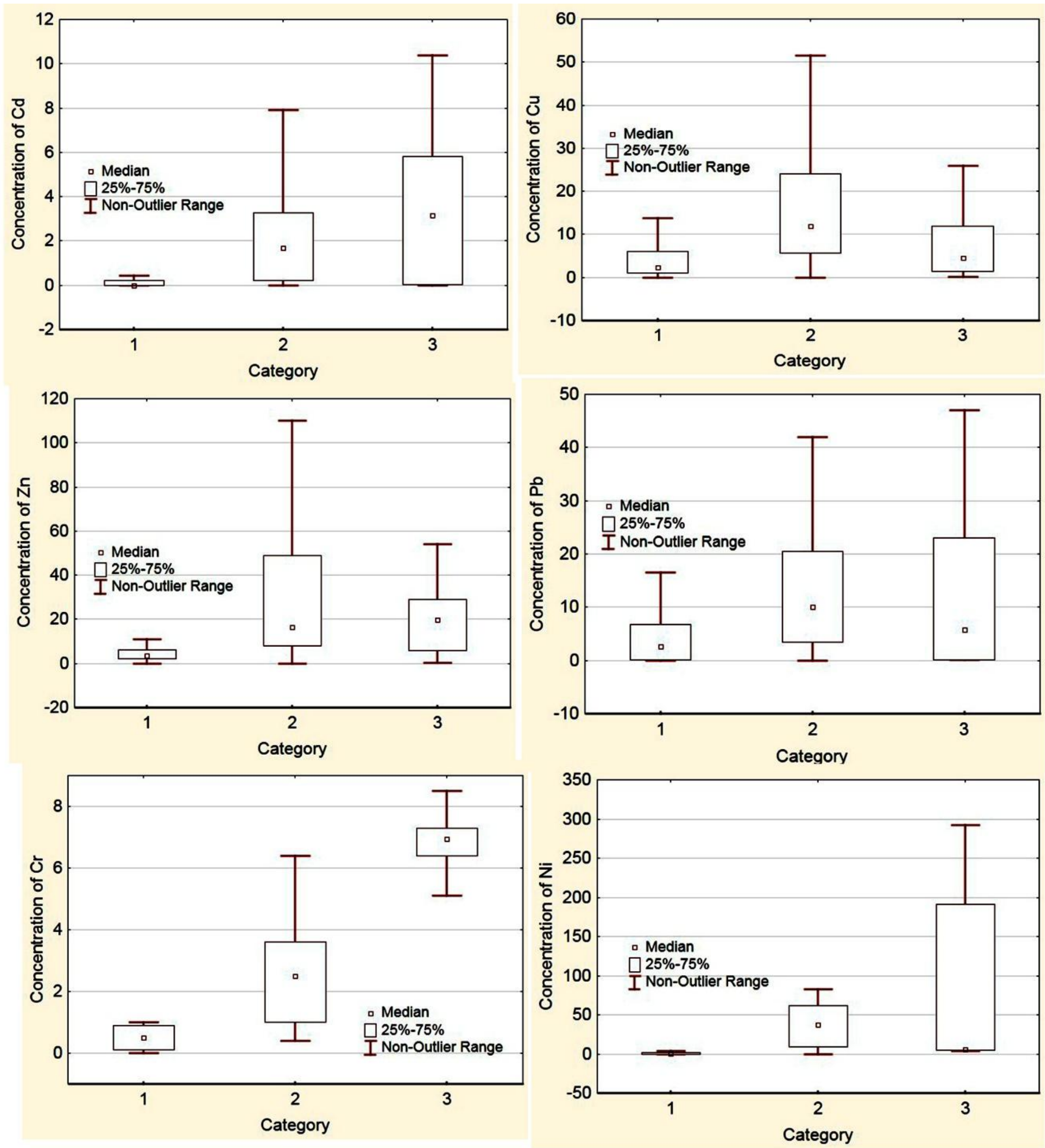

Figure 3. Median values and values of 25th to 75th percentile of heavy metal concentrations (μg/dm^3) in Kazakhstan's background water bodies (1), water bodies under moderate (2), and high anthropogenic impact (3).

Considering that data distribution differs from normal, the median values of heavy metal concentrations and 75th percentile values served as the basis for the regional water quality classification.

4.3 Regional ecological classification of water quality in Kazakhstan's fresh water bodies

The proposed regional classification for assessing the ecological state of Kazakhstan's water bodies in the Heavy Metal Section includes six water quality classes (Table III). Class 1 (uncontaminated water) corresponds to water containing heavy metals at the level of median values registered in background water bodies. The Cd content corresponds to the 75th percentile since the median concentration values of this metal in background water bodies equal zero. Class 2 (slightly contaminated water) is characterized by heavy metal content at the 75th percentile also registered in background water bodies. When distinguishing the boundaries of Water Quality Classes 3-6, the range of heavy metal content in the most polluted water bodies of Kazakhstan and the response of biological communities in their natural habitats – described in detail in the discussion section – were taken into account.

Table III. Regional ecological classification of the water quality in Kazakhstan water bodies (1) in the "Heavy Metals" Section compared to the ecological classification of the surface lotic waters of Europe (2) using own color codes.

Water Quality Class	Quality of natural water	Source	Color	Concentration, µg/dm^{-3}					
				Cd	Cu	Zn	Pb	Cr	Ni
1	Uncontaminated	1	blue	<0.2	<2.5	<4	<3	<0.5	<0.5
		2*		<3	<20	<200	<10	<20	<20
2	Low polluted	1	green	0.2-0.5	2-6	4-6	3-7	0.5-1	0.5-2
		2*		5	50	1000	20	50	50
3	Moderate polluted	1	yellow	0.5-3	6-10	6-20	7-20	1.0-10	2.0-10.0
		2*		10	100	2000	50	100	100
4	Heavy polluted	1	orange	3-10	10-30	20-50	20-50	20-50	10-50
		2*		20	200	5000	100	200	200
5	Very heavy polluted	1	red	10-30	30-80	50-100	50-100	50-100	50-100
		2*		30	500	10000	200	500	500
6	Ecological catastrophe	1	brown	>30	>80	>100	>100	>100	>100
		2*		>30	>500	>10000	>200	>500	>500
** according to: Romanenko et al., 1990*									

5. Discussion

The proposed separate classification scale for freshwaters takes into account the pronounced effect of TDS on the accumulation of heavy metals in Kazakhstan's water bodies (Krupa et al. 2019), as well as the importance of fresh water quality for the population and the economy. For the upper boundary of fresh water classification, TDS values of 2,000 mg/m^{-3} were applied, since the chemical composition of water metamorphoses at a higher value of this variable (Krupa et al., 2017a). Chemical analysis data and biological variables of the surveyed Kazakhstan's water bodies were compared for the first time to determine the boundaries of freshwater quality classes (Krupa & Barinova, 2016; Krupa et al., 2008;Krupa et al., 2016b, Slivinsky & Krupa, 2013; Krupa, 1998, 2005, 2008, 2011, 2012, 2014).

The proposed regional classification of freshwater quality (Heavy Metals Section) includes six water quality classes – from unpolluted down to extremely polluted by heavy metals. The background concentration of heavy metals serves as the starting point for the proposed classification. The background content of heavy metals varies considerably depending on specific local physical and geographical conditions (Volkov et al., 1993; Shvartsev, 2008) and, thus, it should be taken into account when designing criteria for assessing the ecological status of water bodies (Chernova & Beketskaya, 2011). The background content of heavy metals was estimated based on median and 75th percentile values, which allowed excluding the outlier effect (Glantz, 1999). The importance of applying adequate statistical procedures is highlighted in other studies on background heavy metal concentrations estimations (Novikov & Draganov, 2017).

According to average and median values, the content of all heavy metals – except Cu – in Kazakhstan’s background water bodies was extremely low and did not exceed the maximum permissible concentrations for fishery water bodies (MPC_{fw}) (Guseva, 2002). The background concentrations of Cu exceeded their MPC by 5.5 (average values) and 2.4 times (median values) for all the surveyed water bodies (Table II).

In addition to median values, the boundaries of Class 1 water quality were defined by the reaction of regional aquatic fauna and flora to the toxic background pollution of cold-water oligotrophic lakes. Earlier it was found that in such lakes with a low amount of nutrients, the multiplication of planktonic algae was suppressed when Cu content in the water exceeded 2.5 $\mu g/dm^{-3}$ (Krupa & Barinova, 2016; Krupa et al., 2016b). Therefore, this value can be deemed the upper threshold of Class 1 of the regional classification (Table III), and it substantially coincides with the median Cu concentration established for background water bodies of Kazakhstan.

For Class 2 of the regional classification (Table III), it is proposed to use the content of heavy metals at a background level below the 75th percentile (Table II). Background concentrations of certain heavy metals above the 75th percentile were registered locally, predominantly in small mountain rivers and groundwater sources, and were associated with geochemical anomalies (Mazurov, 2005). Thus, the concentrations of all heavy metals except Cu that were selected for the upper boundary of Class 2 (slightly polluted waters) do not reach the MPC_{fw} level, and Cu content is 2.5-6.0 times higher than MPC_{fw}. Such concentrations of Cu do not affect planktonic invertebrates in Kazakhstan’s oligotrophic cold water bodies but can suppress the development of planktonic algae (Krupa & Barinova, 2016; Krupa et al., 2016b). It should be noted that no influence of Cu content of about 2.5 $\mu g/dm^{-3}$ was detected on the algal flora and the hydrofauna of warm mesotrophic water bodies (Slivinsky & Krupa, 2013; Krupa, 2011, 2014). Heavy metals in the concentrations selected for Class 2 do not exert a mutagenic effect on biota even with long-term presence and high summer water temperatures in water bodies of plains (Krupa, 2012).

The boundaries of Classes 3 and 4 in the regional classification (Table II) were determined based on median values and the range of heavy metals concentrations in water bodies with moderate and high anthropogenic impact (Table III). According to statistical analysis, the water bodies under moderate and high anthropogenic impact significantly differed in the mean content of Cd, Cu, Cr, and median concentrations of Cu and Cr. Higher Cu content in water bodies of plains under moderate anthropogenic load can be attributed to the general inflow of salts of this metal with surface runoff due to the agricultural use of fertilizers and pesticides containing Cu (Gorbunova & Stulin, 2016). Accordingly, higher concentrations of Cr in wastewater storage facilities indicate that metal comes mainly from industrial wastewater. Thus, the toxic pollution of water bodies with moderate and high anthropogenic impact levels is primarily due to separate metals, depending on the composition of the discharged wastewater.

In addition to the chemical analysis data, the limits of Classes 3 and 4 were also determined by the response of biological communities to a certain toxic pollution rate. The mutagenic effect of heavy metals (Reutova, 2015) should be considered as an indicator of water bodies' toxic pollution. Different aberrant forms were described for various taxonomic groups of aquatic fauna and flora under the toxic impact (Oliveira, 1999 Bhattacharyay et al., 2005; Al-Shami et al., 2011; Barinova, 2017c). According to own data (Krupa, 1998, 2005, 2008), planktonic invertebrates with teratological abnormalities are always present in Kazakhstan's warm water bodies with Cd content exceeding 3, Cu – exceeding 10, Pb – exceeding 20 $\mu g/dm^{-3}$. Therefore, water with the content of heavy metals below these values is classified as moderately polluted (Class 3) and above these values – as heavily polluted (Class 4). Apart from the presence of individuals with morphological abnormalities, toxic pollution of water bodies at the level of Class 3 and 4 causes various changes in the structure of hydrocenoses, including the death of the most sensitive species, sharp changes in the diversity and quantitative variables of communities (Krupa, 2015; Krupa et al., 2006, 2018; Barinova & Krupa, 2017a).

The boundaries of Classes 5 and 6 (Table III) were determined based on the maximum concentrations of heavy metals registered for the most polluted water bodies of Kazakhstan (Table II). It stands to mention that the thresholds of water quality classes for Cr and Ni are preliminary, and further investigation is necessary to expand the set of water bodies with registered concentrations of these metals.

Generally, waters of Classes 4 to 6 are characterized by mixed pollution. Organic and nutrient substances in heavily polluted water bodies alleviate the negative impact of heavy metals on living organisms (Serra et al., 2010). The most damaging effect on aquatic biota is caused by a sharp increase in heavy metal concentration when the amount of biogenic elements and nutrients remains disproportionately low. For instance, a sharp drop in the abundance of planktonic crustacean populations in Lake Balkhash (South-Eastern Kazakhstan) was observed under the influence of polluted runoff of the Ili River when concentrations of Zn in water increased from 20 to 264 μg/dm^{-3} (Krupa et al., 2008). This gradient of Zn concentration is within the limits of Classes 4-6 of the proposed water quality classification.

The new regional ecological classification describes six classes of water quality in the natural environment in the "Heavy metals" Section (Table III). The absolute values of all heavy metal concentrations for each class of water quality in the classification are several orders of magnitude lower against the ecological grades for European humid zone water bodies (Romanenko et al., 1990; Barinova, 2017d). The most considerable discrepancy between the classifications is associated with the content of Zn, which is due to multiple factors, including geological, climatic, and hydrochemical features of humid and arid territories (Mazurov, 2005). Additionally, it can be assumed that the atomic absorption spectrometry – applied to determine heavy metal concentrations – renders more accurate results than the previously used analytical methods (Romanenko et al., 1990).

The data presented above describe only some examples of the reactions of biological communities to a particular level of heavy metal content in their natural habitats. Biological field data are crucial since laboratory experiments assess the toxicity of heavy metals for test-objects (Bácsi et al., 2015; Zeng et al., 2015) and cannot be fully applied to complex natural ecosystems for several reasons. Besides, the use of biological data to determine the boundaries of water quality classes should be based on the understanding of nonlinear variability in the structure of communities within the gradient of external factors (Krupa, 2015; Krupa & Barinova, 2017). Earlier, an empirical model was proposed demonstrating a nonlinear coupling between diversity, the structure of algal communities, rate of organic pollution of continental water bodies, as well the assessment of water quality using different taxonomic levels organisms in a trophic pyramid (Barinova, 2017b; Protasov et al., 2019). The proposed Heavy Metals Section of the regional classification of water quality can be refined based on a more comprehensive range of biological data, which may become the task of extensive research in the future. Nevertheless, the proposed methodological approach expands the possibilities of assessing the level of toxic pollution of Kazakhstan's water bodies compared to traditional methods based on MPC_{fw} as it considers both chemical data and biological variables.

6. Conclusion

The regional ecological classification of fresh water quality in the Heavy Metals Section is proposed for the first time based on the long-term surveying of Kazakhstan's water bodies for toxic pollution. It includes six classes of water quality, from clean to heavily polluted water. The basis for determining the boundaries of water quality classes include the background content of heavy metals, the specifics of accumulation of heavy metals in water bodies of Kazakhstan with different levels and character of anthropogenic pollution, and the response of biological communities to toxic pollution in their natural habitats. Absolute values of all heavy metals' concentrations for each class of water quality in the regional classification are several orders of magnitude lower than in the ecological grades established for European humid region water bodies. The proposed methodological approach expands the possibilities for assessing the level of toxic pollution of Kazakhstan's water bodies compared to conventional methods. It is comprehensive since it takes into account not only chemical data but also biological variables. The proposed regional classification of water quality in the heavy metals section can be applied to other arid areas/countries with similar physical, geographical, and climatic conditions.

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