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TECHNICAL NOTE

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The Role of Natural and Anthropogenic Factors in the Distribution of Heavy Metals in the Water Bodies of Kazakhstan

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Abstract

The aims of present work were to analyze on the base of our data of 1997-2017 the changes in the content of heavy metals in 118 water bodies in Kazakhstan, determine the relationship between the content of heavy metals and the level of anthropogenic load, to reveal natural factors affecting the accumulation of heavy metals in the water. It was revealed that average Cd content was 0.01-7.7 µg dm^{-3}, Cu – 1.6-158.2, Zn – 1.5-44.1, Pb – 1.4-19.4, Cr – 0.05-14.6, Ni – 0.2-227.2 µg dm^{-3}. The level of toxic pollution of water bodies increased against the altitude gradient. The relationship between the content of heavy metals and the altitude of location of a water body was indirect, because was an accompanying change in the pH, temperature, and TDS of water. In water bodies with a TDS above 2000 mg dm-3, Pb, Cr, Cd and Cu were accumulating most intensively, whereas fresh waters contained higher amounts of Zn and Ni. Regression analysis revealed the leading role of pH in the accumulation of heavy metals in water bodies. An increase in anthropogenic load in the direction from mountainous areas to plains led to the additional enrichment of water bodies with heavy metals.

Introduction

Heavy metals (Cd, Cu, Zn, Pb, Ni and Cr) are among the priority pollutants of water bodies in the Central Asian region and Kazakhstan in particular (Barber *et al*., 2005; Kurakov & Tynybaeva, 2007; Tolymbekov, Kelamanov, Baisanov & Kaskin, 2008; Zhaoyong, Abuduwaili & Fengqing, 2015; Solodukhin *et al*., 2004; 2016). The content of heavy metals in natural aquatic ecosystems is determined by a complex of factors. Natural factors are represented by geological and zonal-climatic features of the territory (Shvartsev, 2008), including the nature of underlying rock and soils (Volkov, Zalicheva & Ganina, 1993), the degree of moisture in the catchment basin, the rate of water exchange, and the total dissolved solids (TDS) of water (Maksimovich, 1955).

Anthropogenic factors that affect the level of toxic pollution of water bodies differ significantly. The growth of industry, agriculture and production of pesticides and fertilizers, irrational water use, imperfections of treatment facilities – this wouldn't be a full list of factors that negatively affect the environment. Increases in heavy metal concentrations in air, ground, water bodies and aquatic biota occur in various regions of Asia and Europa (Zhumalipov, 2011; Huang, Amuzu-Sefordzi & Li, 2015; Burtseva & Konkova, 2016; Kaus *et al*., 2017; Niemiec, Szeląg-Sikora, Sikora, Cupiał, & Komorowska, 2018). Global air pollution leads to the redistribution of various chemicals between regions. With air currents, heavy metals can be transported over long distances and reach even remote mountain areas (Han, Jin, Cao, Posmentier, & An, 2007; Tornimbeni, Rogora, 2012; Abuduwailil, Zhaoyong, & Fengqing, 2015; Zhaoyong *et* *al*., 2015).

Kazakhstan has a large territory with diverse geological and climatic conditions. Wide temperature gradient and water TDS (Krupa, 2012), rich reserves of polymetallic ores (Mazurov, 2005), together with the uneven distribution of industrial and agricultural enterprises throughout the country – all this has a multidirectional impact on the level of toxic pollution of Kazakhstan's water bodies. However, published references provide information only on the absolute concentrations of heavy metals in the some water bodies of Kazakhstan (Amirgaliev, 2007; Burlibaev *et al.,* 2014; Burlibayeva, Burlibayev, Opp & Bao, 2016; Dostay & Tyumenev, 2009; Krupa & Barinova, 2016; Krupa, Romanova & Imentay, 2016; Krupa, Barinova, Amirgaliyev, Issenova & Kozhabayeva, 2017; Krupa, Barinova, Tsoy, Lopareva & Sadyrbaeva, 2017; Krupa *et al*., 2017c; Krupa, Barinova, Assylbekova & Isbekov, 2018; Slivinsky, Krupa & Akberdina, 2009; Slivinsky, Krupa, Lopatin, Mamilov & Prikhodko, 2010; Slivinsky, Krupa, Lopatin, Mamilov & Prikhodko, 2010a; Slivinsky, Krupa, Mamilov & Akhmetov, 2013; Savinkova, 2013; Slivinsky & Krupa, 2013; Zakarkina, Tskhai, Epifantseva & Akulova*,* 2011). The patterns of change of heavy metals content in the water bodies in relation to anthropogenic and natural factors were do not analyzed in the above-mentioned works.

The aim of the present work was to analyze distribution of Cd, Cu, Zn, Pb, Ni and Cr content in various types of water bodies of Kazakhstan depending on anthropogenic and natural environmental factors.

Materials and Methods

Study Area

We were investigated the level of toxic pollution of 118 water bodies in Kazakhstan during 1997-2007. The water bodies that were examined differed in the character of water-salt nutrition and were divided into two groups – fresh and mineralized. For the conditional boundary between these two groups of water bodies, the total dissolved solids (TDS) of water at 2000 mg dm^{-3} were taken.

Further, fresh and mineralized water bodies were divided into three categories depending on the intensity of the anthropogenic load: background water bodies, water bodies with a moderate level of anthropogenic impact, and water bodies with a strong level of anthropogenic impact (Figure 1).

Background water bodies are remote from sources of anthropogenic impact and have a minimal transformation or total integrity of the catchment areas. Background water bodies includes springs, wells, hot springs, mountain rivers, mountain lakes and reservoirs, and some water bodies of plains.

Water bodies with a moderate level of anthropogenic impact include rivers, lakes, reservoirs which are located on the plain. Reservoirs are used for irrigation purposes, which is associated with significant seasonal changes in the water level. Some large water reservoirs, in addition, are designed to generate electricity. Catchment basin areas of this type water

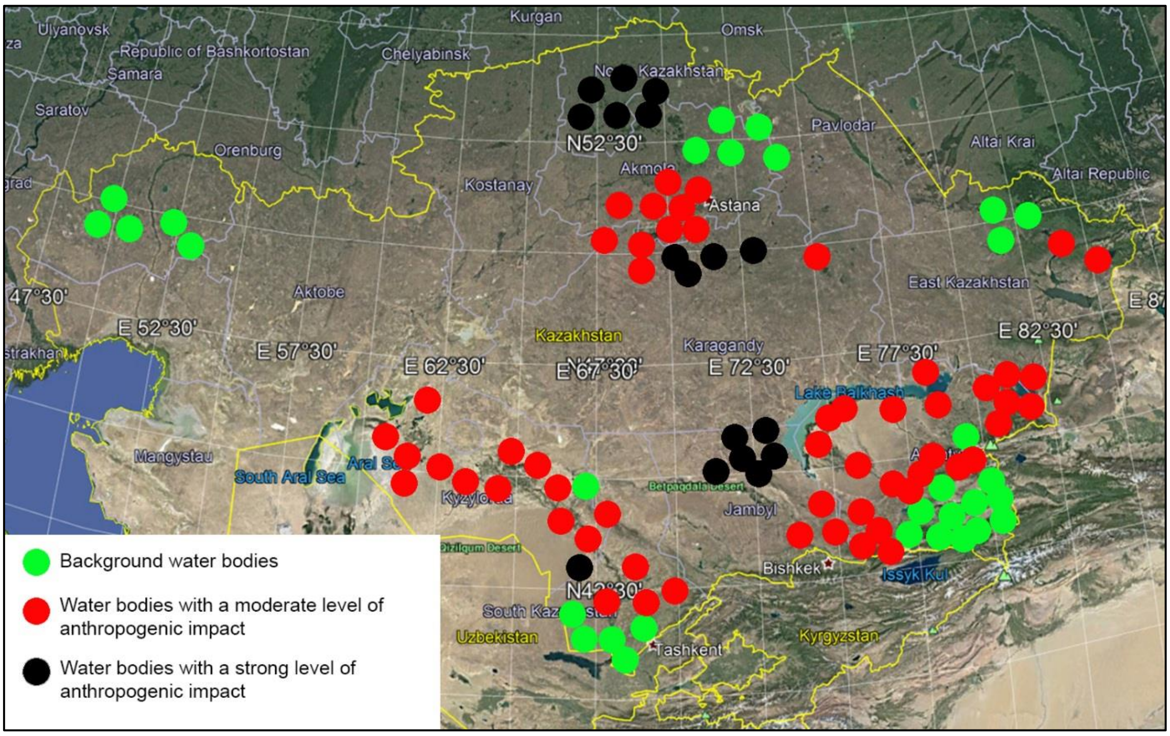

Figure 1. Location of water bodies of Kazakhstan that were surveyed.

bodies are generally used for agriculture and livestock husbandry, but the wastewater is not discharged directly into the water bodies. Pollution of water bodies occurs due to surface runoff and runoff from the inflowing rivers.

Water bodies with a strong level of anthropogenic impact are the storage facilities of pre-treated municipal and industrial effluents. That is, wastewater is discharged directly into these water bodies.

Sampling

Water samples were taken at each of 118 water bodies to determine the total dissolved solids (TDS) and heavy metal content. In small water bodies with an area of less than 1 km^2, three water samples were taken and then mixed. From this mixed sample, one integral subprobe was taken for the subsequent analysis. In large water bodies, water samples were selected from a grid of stations, evenly distributed throughout the water area. A total of 491 water samples were taken to determine the content of 6 heavy metals – Cd, Cu, Zn, Pb, Ni and Cr, and the same number of samples – for the determination of the TDS and chemical composition of water (Table 1). The samples for heavy metals were fixed in the field environment by adding nitric acid immediately after sampling. All collected samples were transported to the lab in an icebox. The measures the temperature and pH of the surface water layers were taken in the field environment by using Hanna HI 98129 instrument. Transparency of water was measured with Secchi disk. Coordinate referencing of the stations and altitude of each water body (a.s.l.) were done by Garmin eTrex GPS-navigator. The depth of each station and the maximum depth of a water body were determined by field conditions. In the Google Earth program, the area of each water body was determined on the basis of a coordinate reference. The maximum temperature of the surface layers of water was taken as the temperature recorded in the hottest month. For plain water bodies – this is the water temperature in July, for mountain water bodies – in August.

Methods of Chemical Analysis of Water and Determination of Heavy Metals

Conventional methods of chemical analysis of water were used (Semenova, 1977; Fomin, 1995). Water samples were analyzed in three – four replications. The error of estimate for major ions in the water was 0.5–5.0%, depending on the analysis.

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 [Interstate standard, 2013]. Heavy metal measuring was performed by mass spectrometry with inductively coupled plasma by using Agilent 7500 A manufactured by Agilent Technologies, USA (National Standard RK ISO 17294-2-2006). The device allows for the detection of the various chemical elements in complex matrices, including those in the sea and grey water and in the biological objects in micro-trace quantities. Concentrated nitric acid (based on 1 cm^3 of nitric acid per 200 cm^3 of water) was added to the analyzed water samples before the analysis. The water sample was heated in a current of inert gas (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}.

Table 1. The number of water samples and a brief characteristic of the studied water bodies in Kazakhstan

Level of anthropogenic load	Type of water body	Altitude above sea level, m	TDS, mg dm^{-3}	Water temperature, °C	Number of water bodies (number of samples)
fresh, TDS less than 2000 mg dm^{-3}					
background	1. underground and ground waters	680-1469	26.6-574.8	10.7-37.0	11(13)
	2. mountain rivers	1078-1986	99.0-468.1	10.1-18.0	15(18)
	3. mountain lakes and reservoirs	1069-3170	26.6-574.8	12.1-24.1	11 (12)
	4.water bodies of plains	33-529	211.5-862.9	14.9-28.0	12 (33)
moderate	5.water bodies of plains	44-975	161.8-1981.9	14.4-30.7	34(200)
strong	6.storage facilities of pre-treated municipal and industrial effluents	448-619	312.3-1319.3	24.0-30.0	7(71)
mineralized, TDS more than 2000 mg dm^{-3}					
background	7.underground and ground waters	600-1925	9785.8-24788.2	14.0-40.7	2(2)
	8.water bodies of plains and mountains	21-1967	2904.0-133410.0	17.1-20.0	6(6)
moderate	9.water bodies of plains	45-347	2192.3-9251.0	17.0-28.0	14(130)
strong	10.storage facilities of pre-treated municipal and industrial effluents	191-192	2400-5000	22.0-24.0	6(6)

Statistical Analysis

The statistical processing of data on the content of heavy metals in water was carried out in the Excel and Statistica 10 programs. Average values and standard deviations are given for all analyzed parameters. The differences in average values were determined by the Student's *t*-test (Glantz, 1999). Scattering diagrams were constructed in Statistica 10 program. In the same program, a stepwise regression analysis (Lukyanova, 1999) was performed in order to identify the main factors that affect the accumulation of heavy metals in water bodies.

Results

Brief Characteristics of Studied Water Bodies

The studied water bodies are located at various altitudes (Table 1). The areas of the water bodies vary from 0.02 to 10556 km^2. Maximum depths reach 0.1-44.0 m. Transparency of water is 0.1-9.0 m. Small shallow fresh water bodies are characterized by varying degrees of development of macrophytes – from 10 to 100%. In large water bodies, macrophytes are prevalent mainly in the coastal zone. In background deep-sea and cold-water lakes, macrophytes are mostly absent. The degree of presence of macrophytes in background shallow-water lakes also varies largely.

The pH in all water bodies varies within relatively small ranges – from 7.0 to 9.5, that is, at the level of mildly alkaline and alkaline waters. The temperature gradient of water in surface water bodies is more pronounced – from 10.1 to 32.0°C, which is due to their location at various altitudes. Fresh and mineral hot springs were characterized by the maximum water temperatures – 37.0-40.7°C.

The Content of Heavy Metals in the Water Bodies of Selected Categories

According to the average values, the content of heavy metals in our water samples varied widely (Table 2). The average Cd content varied from 0.01 to 7.7 µg dm^{-3}, Cu – from 1.6 to 158.2, Zn – from 1.5 to 44.1, Pb – from 1.4 to 19.4, Cr – from 0.05 to 14.6, Ni – from 0.2 to 227.2 µg dm^{-3}.

In order of decrease in the absolute average values, heavy metals formed the following series:

TDS less 2000 mg dm^{-3}

1. background underground and ground waters – Zn>Cr>Cu>Pb>Ni>Cd
2. background mountainous rivers – Zn>Pb>Cu>Cr>Ni>Cd

Table 2. The average concentrations of heavy metals in Kazakhstan water bodies in comparison with the maximum permissible concentration in water bodies' intent for fishery (MPC)

Level of anthropogenic load	Type of water body	Content of heavy metals, µg dm^{-3} Cd	Cu	Zn	Pb	Cr	Ni
fresh, TDS less than 2000 mg dm^{-3}							
background	1.underground and ground waters	0.06±0.06	1.6±0.6	18.6±15.8	1.2±0.3	2.3±2.0	0.2±0.2
	2. mountain rivers	0.06±0.03	4.5±1.3	9.9±4.2	9.0±3.4	1.4±0.7	0.4±0.3
	3. mountain lakes and reservoirs	0.2±0.07	4.1±1.1	6.9±4.2	2.7±0.7	1.3±0.6	1.2±0.4
	4.water bodies of plains	0.01±0.001	6.5±1.6	3.7±0.7	11.3±2.3	no data	13.7±5.9
average for background water bodies		0.1±0.03	5.0±0.8	8.3±2.9	5.6±1.2	1.6±0.6	2.5±1.1
moderate	5.water bodies of plains	2.6±0.3	20.2±1.6	44.1±5.7	14.6±1.3	2.7±0.4	51.6±7.7
strong	6.storage facilities of pre-treated municipal and industrial effluents	7.7±2.2	8.2±1.5	19.4±1.9	13.6±1.9	6.8±0.2	227.2±63.1
average for fresh water bodies		4.0±0.6	17.5±1.3	38.6±4.4	14.1±1.1	5.1±0.4	119.8±25.5
mineralized, TDS more than 2000 mg dm^{-3}							
background	7.underground and ground waters	no data	0.3±0.3	1.5±1.5	1.4±0.9	0.05±0.05	no data
	8.water bodies of plains and mountains	0.8±0.8	158.2±130.8	22.2±13.5	9.1±4.0	14.6±9.9	67.9±49.8
moderate	9.water bodies of plains	4.2±0.6	31.2±3.1	13.5±1.6	19.4±1.8	3.9±0.6	31.3±4.1
strong	10.storage facilities of pre-treated municipal and industrial effluents	1.3±0.2	10.4±2.1	15.1±5.2	6.3±0.2	no data	67.5±9.8
average for mineralized water bodies		4.5±0.8	30.1±9.2	17.5±0.2	20.3±2.1	8.1±3.3	49.4±6.4
AVERAGE for all water bodies		3.3±0.3	18.7±0.7	24.0±1.6	14.2±0.5	1.4±0.1	71.2±8.8
MPC in water bodies intent for fishery		0.5	1.0	10.0	10.0	5.0	10.0

3. background mountainous lakes and reservoirs – Zn>Cu>Pb>Cr>Ni>Cd
4. background water bodies of plains – Ni>Pb>Cu>Zn>Cd
5. water bodies of plains with moderate anthropogenic load – Ni>Zn>Cu>Pb>Cr≈Cd
6. storage facilities of pre-treated municipal and industrial effluents – Ni>Zn>Pb>Cu>Cd≈Cr

TDS more than 2000 mg dm^{-3}

7. background underground and ground waters – Zn≈Pb>Cu>Cr
8. background water bodies of plains and mountains – Cu>Ni>Zn>Cr>Pb>Cd
9. water bodies of plains with moderate anthropogenic load – Ni≈Cu>Pb>Zn>Cd≈Cr

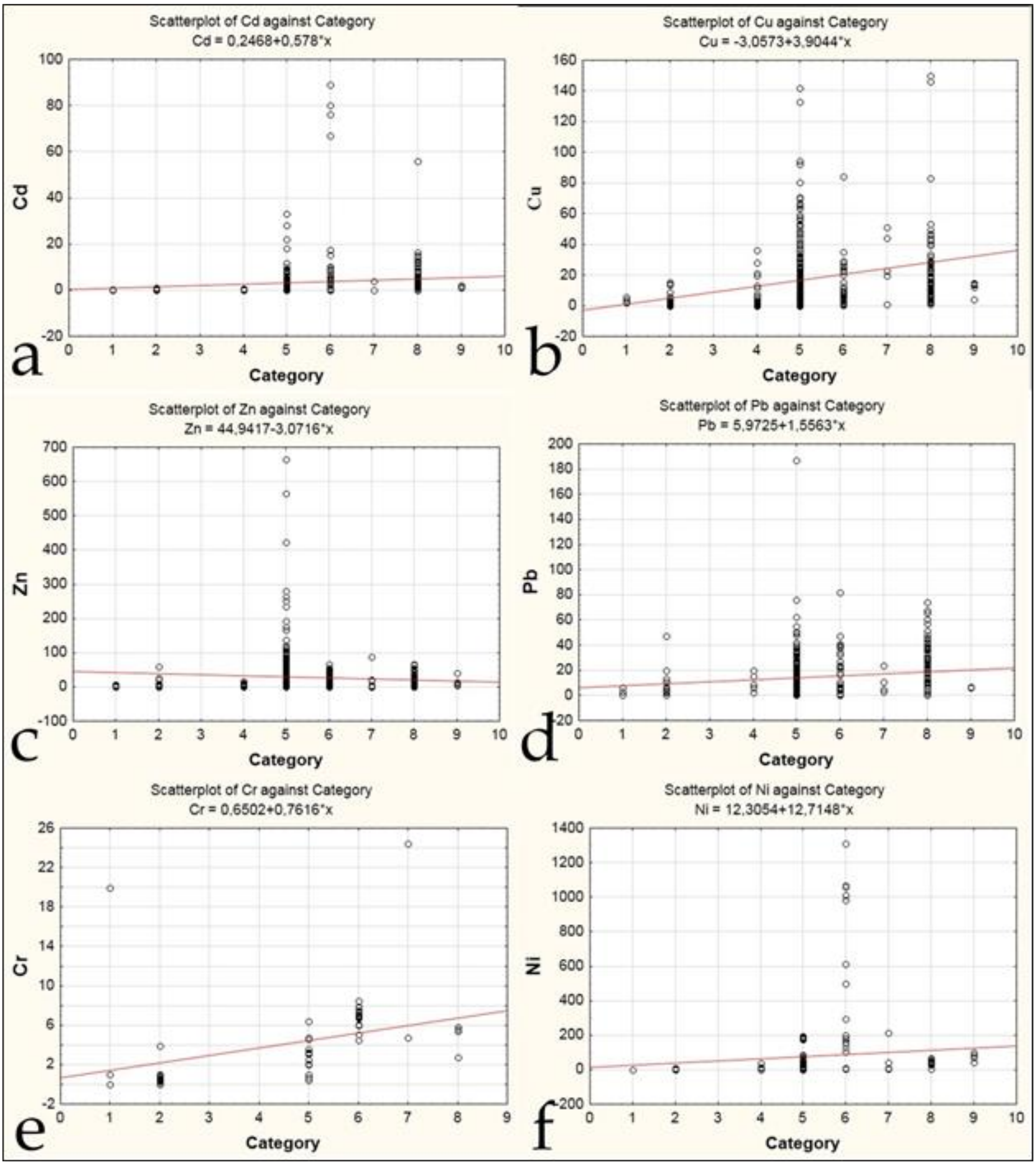

Figure 2. The heavy metals content (µg dm^{-3}) dynamic in the studied water bodies of Kazakhstan

Fresh water bodies: 1. background underground and ground waters, 2. background mountain rivers, 3. background mountain lakes and reservoirs, 4. background water bodies of plains, 5. plain water bodies with a moderate level of anthropogenic impact, 6. water bodies with a strong level of anthropogenic impact

Mineralized water bodies: 7. background underground and ground waters, 8. background water bodies of plains, 9. plain water bodies with a moderate level of anthropogenic impact, 10. water bodies with a strong level of anthropogenic impact

10. storage facilities of pre-treated municipal and industrial effluents – Ni>Zn>Cu>Pb>Cd

So, according to the average values, most of the studied water bodies contained Ni and Zn in the highest concentrations. Further sequence of metals was inconsistent, but most water bodies contained Cd and, less often, Cr in minimal amounts. The only exceptions were fresh storage facilities of pre-treated municipal and industrial effluents; they contained Cd in approximately same concentrations as Cr.

Figure 2 (a, b, d) shows that the largest range of fluctuations and the maximum absolute concentrations of Cd, Cu and Pb were recorded in the plain water bodies with a moderate level of anthropogenic impact (fresh and mineralized) and fresh storage facilities of pre-treated municipal and industrial effluents. The largest range of fluctuations and maximum values of absolute concentrations of Cr, as well as Zn and Ni, were recorded in the fresh water bodies with a moderate level of anthropogenic impact and fresh storage facilities of pre-treated municipal and industrial effluents (Figure 2e, c, f). In background water bodies, a high Zn concentration at 176 µg dm^{-3} was recorded only once in the groundwater of the Eastern Kazakhstan. The increased content of Pb, at the level of 13.0-47.0 µg dm^{-3}, was found in only three samples of water from the background mountain rivers of Southern and South-Eastern Kazakhstan. At the same time, increased concentrations of Cu – up to 1.6-6.5 µg dm^{-3}, were recorded in 67% of water samples from background water bodies.

Comparative analysis of average values showed that fresh background underground and ground waters (number 1 in Table 2) was characterized by higher Zn concentrations and lower absolute concentrations of Cu, Cd, Pb, and Ni than that of mountainous background rivers and lakes (number 2 and 3 in Table 2). In the direction from underground and ground waters to background water bodies of plains (Table 2), the average content of Zn decreased, and of Cu, Cr and Ni – increased. The highest concentrations of Pb were detected in background mountainous water bodies and water bodies of plains.

On average for fresh background water bodies (numbers 1-4 in Table 2), the content of all heavy metals was at a lower level than for water bodies, exposed to moderate (number 5 in Table 2) and strong anthropogenic impact (number 6 in Table 2). In turn, comparison between water bodies with a moderate and strong level of anthropogenic impact led to the following conclusions. According to the Student's *t*-test, average concentrations of Cu and Zn were statistically significantly higher and average concentrations of Cd, Cr, and Ni were statistically significantly lower in fresh water bodies of plains with moderate anthropogenic impact than in water bodies with a moderate and strong level of anthropogenic impact (Table 2). The differences between the average concentrations of Pb in water bodies with moderate and strong anthropogenic impact were not statistically significant.

In mineral background hot springs (number 7 in Table 2), the content of heavy metals was minimal compared to other mineralized water bodies. The highest average concentrations of Cu, Zn, Ni and Cr were recorded in mineralized background water bodies (number 8 in Table 2), of Pb – in mineralized water bodies of plains with moderate anthropogenic impact (number 9 in Table 2). Mineralized water bodies with strong anthropogenic impact (number 10 in Table 2) were characterized by a relatively low content of heavy metals, with the exception of Ni. The average Ni content in mineralized water bodies with strong anthropogenic impact was approximately two times higher than in mineralized water bodies with moderate anthropogenic impact, but it was comparable with background values.

Comparison of fresh (TDS<2000 mg dm^{-3}) and mineralized water bodies (TDS>2000 mg dm^{-3}) allowed to make the following conclusions. The mineralized water bodies were characterized by a higher content of Pb, Cr, Cd and Cu and lower concentrations of Ni and Zn compared to fresh water bodies (Table 2).

Table 3. Coefficients of Spearman Rank Correlation between the content of heavy metals in the water bodies of Kazakhstan and environmental factors

Factors	Heavy metals					
	Zn	Cu	Cd	Pb	Ni	Cr
Altitude, a.s.l.	-0.207	-0.299	0.128	0.104	*-0.334*	*-0.798*
Area, km^2	0.288	0.124	*0.446*	0.181	0.322	0.322
Depth max, m	*0.369*	-0.027	*0.478*	0.278	0.387	-0.265
Water temperature max, °C	*0.509*	0.199	0.213	0.156	*0.678*	*0.436*
Water temperature during the sampling period, °C	*0.303*	0.204	0.227	0.197	*0.308*	0.300
Depth of station, m	*0.391*	0.199	0.229	0.124	0.169	0.011
Transparency, m	0.231	0.185	0.304	0.200	*0.309*	*-0.391*
pH	0.338	0.315	*0.445*	0.046	*0.401*	-0.145
TDS, mg dm^{-3}	-0.097	0.240	*0.401*	0.270	*0.595*	*0.752*

Statistically significant values of the Spearman correlation coefficients are in *italics*, for P<0.05.

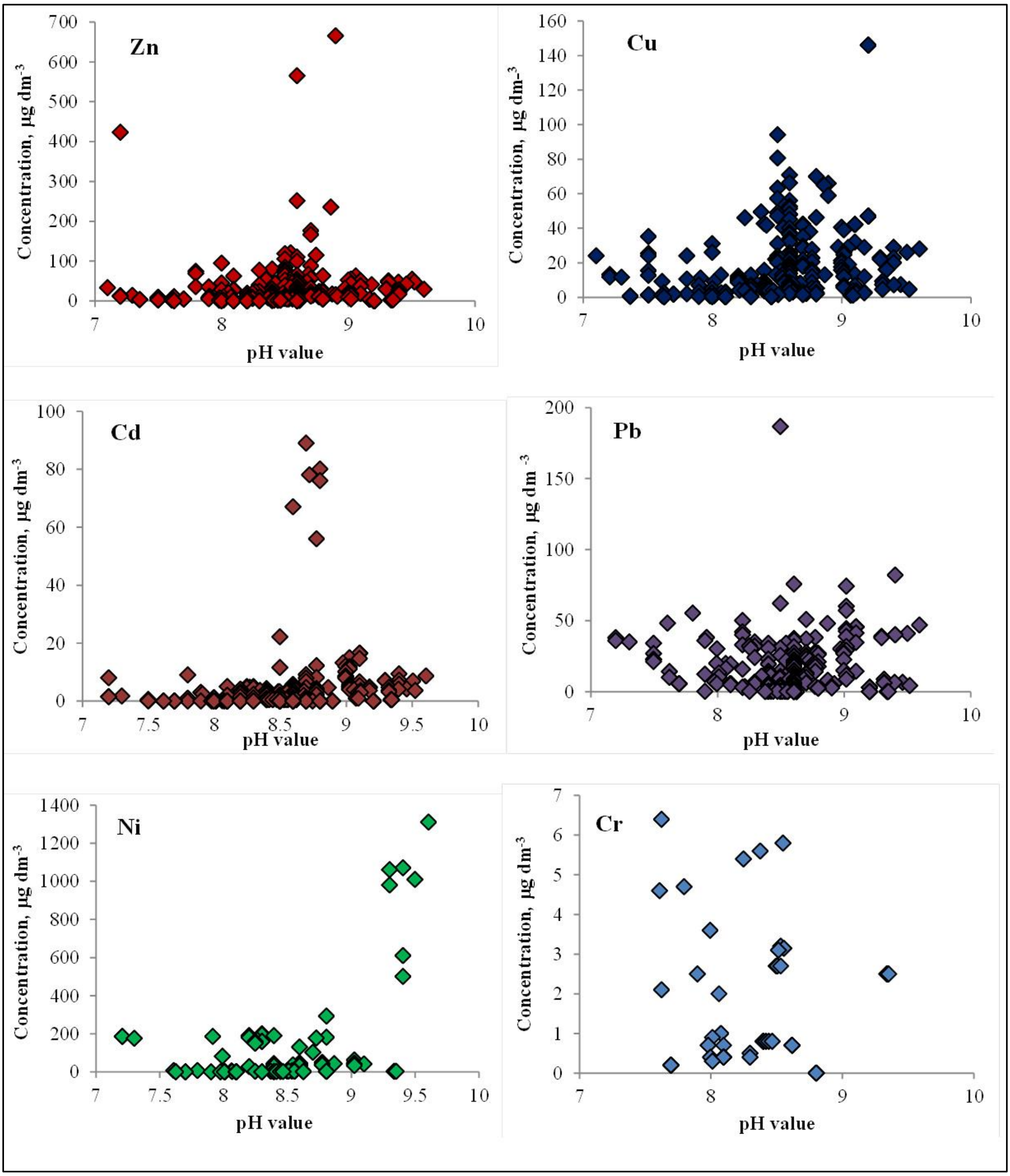

Figure 3. The relationships between heavy metals content and water pH in Kazakhstan's water bodies.

Analysis of the Relationship between the Content of Heavy Metals in Water and Other Environmental Factors

As was shown above, the average contents of heavy metals in fresh and mineralized water bodies were different (Table 2). However, the values of the rank correlation coefficient between TDS and absolute concentrations of Zn, Cu, Cd, and Pb were statistically significant, but low (Table 3). Moderately pronounced positive relationship was recorded between the TDS and the absolute content of Ni and Cr. The shift of pH value towards alkaline supported the accumulation of Cd and Ni in water bodies. Maximum depths and transparency of water did not affect the content of heavy metals in water. The content of Cr and, to a small extent, Ni increased against the altitude gradient, i.e. in the direction from mountainous water bodies to the water bodies of plains. The concentrations of Zn, Ni and Cr were higher in well-heated water bodies.

Table 4. Results of stepwise regression analysis of the influence of external factors on the content of heavy metals in Kazakhstan's water bodies

Metal	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
Zn	Depth b*=0.418	Depth b*=0.491 Transparency b*=-0.19	Depth b*=0.522 Transparency b*=-0.17	Depth b*=0.517 pH b*=-0.20	Depth b*=0.491 Transparency b*=-0.18 pH b*=-0.21	Depth b*=0.472 pH b*=-0.19
Cu	Depth b*=0.284	Depth b*=0.238 pH b*=0.220	Depth b*=0.290 pH b*=0.316 Depth max b*=-0.23	Depth b*=0.321 pH b*=0.300 Depth max b*=-0.23 Altitude b*=-0.16	Depth b*=0.317 pH b*=0.386 Depth max b*=-0.30 Altitude b*=-0.23 Temperature b*=-0.21	Depth b*=0.312 pH b*=0.409 Depth max b*=-0.32 Altitude b*=-0.25 Temperature b*=-0.20
Cd	-	-	-	-	-	pH b*=0.228
Pb		Depth max b*=0.295	Depth max b*=0.338 Temperature b*=0.337	Depth max b*=0.273 Temperature b*=0.348	Depth max b*=0.335 Temperature b*=0.347 Transparency b*=0.185	Depth max b*=0.336 Temperature b*=0.380 Transparency b*=0.212
Ni	pH b*=0.640	pH b*=0.683 Area b*=-0.39	pH b*=0.751 Area b*=-0.37 Transparency b*=-0.27	pH b*=0.797 Area b*=-0.31 Transparency b*=-0.22 TDS b*=-0.20	pH b*=0.745 Area b*=-0.33 Transparency b*=-0.19 TDS b*=-0.21	pH b*=0.715 Area b*=-0.32 Transparency b*=-0.23 TDS b*=-0.26
Cr	-	-	-	Altitude b*=-0.85	Altitude b*=-0.71 Area b*=0.369	Altitude b*=-0.71 Area b*=0.393

Low values of the coefficients of the rank linear correlation are associated with the nature of distribution of heavy metals within the gradient of external factors. As an example, we give the distribution of heavy metals in relation to water pH. Of the 6 metals, only Ni concentrations increased linearly with pH shifting from mildly alkaline waters to alkaline waters (Figure 3). Concentrations of Pb and Cr formed a cloud of dots, indicating the absence of a connection between the content of these metals in water and the pH value. The content of the remaining metals (Zn, Cu, Cd) increased within the pH gradient from 7.0 to 8.7, and then decreased, i.e. varied nonlinearly.

Changes in the concentrations of heavy metals within the gradient of other environmental factors occurred in a similar manner. The content of Zn, Cu, and Cd grew with increasing water temperature from 7 to 23°C, of Pb – from 7 to 25°C, and decreased at higher temperatures. For Ni and Cr, no regularities were observed.

Water bodies with TDS at about 1250-1350 mg dm^{-3} featured maximum concentrations of Ni, Cu, and Cd. The highest content of Zn was recorded in water bodies with TDS of water at about 950-1000 mg dm^{-3}. In conditions of higher TDS of water, the content of all heavy metals decreased.

Weak negative correlation between the altitude of location of a water body and the content of heavy metals was also due to the specifics of distribution of the analyzed parameters. Low concentrations of heavy metals were detected in water bodies located at altitudes of 20-180 m above sea level. These are mainly small background steppe lakes of Western Kazakhstan, as well as some floodplain lakes of Southern Kazakhstan. The highest concentrations of heavy metals were recorded in water bodies of plains located at altitudes of 190-500 m above sea level. Foothill and mountainous water bodies at an altitude of more than 600-700 m above sea level were generally characterized by a low level of toxic pollution.

Studying the influence of environmental factors on the accumulation of heavy metals by the method of stepwise regression analysis made it possible to draw the following conclusions. Deep-water parts of water bodies with low pH values were characterized by elevated concentrations of Zn (Table 4). The accumulation of Cu was also influenced by morphometry, but the concentration of this metal was higher in shallow alkaline water bodies of plains with low water temperature. The accumulation of Cd was regulated only by the pH of water. The highest concentrations of Pb were recorded in deep water bodies with high temperature and water transparency. Small water bodies with fresh alkaline water and low transparency were characterized by elevated Ni concentrations. Maximum concentrations of Cr were observed in large water bodies of plains. Thus, the leading factors contributing to the accumulation of 4 out of 6 metals were the morphometric characteristics of water bodies in combination with pH and temperature. A negative relationship with the TDS of water was found only for Ni.

Discussion

This study is the first experience of analyzing data on changes in heavy metal concentrations in Kazakhstan's water bodies, depending on natural and anthropogenic factors. Most of the water bodies surveyed by us have commercial fishing importance, and therefore the assessment of their toxic pollution level is of high relevance. We compared our data with the maximum permissible concentration in water bodies intent for fishery (MPC) (Guseva, 2002). According to the data in Table 2, background fresh water bodies were characterized by a low level of toxic pollution. Elevated concentrations of Cr, Zn and Pb were recorded only in few our water samples from the mountain water bodies. The content of Cu everywhere exceeded MPC by 1.6-6.5 times. The average content of Cu, Pb and Cr in our background water samples was higher than the concentrations of these metals in unpolluted waters of the mountain systems of Tien Shan, Alps and Western Sayans (Anishchenko *et al*., 2015; Zhaoyong *et al*., 2015; Tornimbeni, Rogora, 2012). Comparative analysis showed that in the background water bodies of Kazakhstan the average content of Zn and Cr was significantly lower, and the concentrations of Cu, Pb and Ni were close to the Clarke concentrations of these heavy metals in groundwater (Shvartsev, 2008).

Given the absence of anthropogenic impact on the studied background water bodies, local increase in the concentrations of Cr, Zn and Pb and more frequently recorded elevated Cu concentrations are associated with natural factors. These include, in particular, the location of background water bodies in ore belts and geochemical anomalies that lie in the mountainous regions of Kazakhstan (Mazurov, 2005). The elevated Cu concentrations (up to 6.5 μg dm^{-3}) recorded in more than half of background water samples indicate that the MPC value of Cu per 1 μg dm^{-3} (Guseva, 2002) for Kazakhstan water bodies is understated.

In decreasing order of Clarke values in groundwater (Shvartsev, 2008) and in the granite crust (Dobrovolsky, 2003), the metals form the following line: Zn>Cu>Ni>Cr>Pb>Cd. Obviously, such sequence of metals (or similar one) should also be typical of background natural waters. In the background fresh and mineralized water bodies of Kazakhstan, Zn also occupied the first place in absolute average concentrations. In the fresh and mineralized water bodies with a moderate and strong anthropogenic impact, Ni was found in the highest concentrations. This suggests that the anthropogenic load leads not only to an increase in toxic pollution (Table 2, Figure 2), but also to a change in the ratio of heavy metals in aquatic ecosystems. Such transformation of chemical composition of water was observed in background water bodies of plains too, despite the absence of significant anthropogenic influence on them. In addition to anthropogenic pollution, the transformation of chemical composition of water can also occur in the presence of geochemical anomalies in the catchment basin.

Remarkably, in the fresh water bodies with moderate level of anthropogenic impact, the average content of Zn and Cu was higher than in the fresh water bodies with strong level of anthropogenic impact (sewage water storage facilities) (Table 2). One of the reasons that cause a high level of toxic pollution of water bodies of plains with moderate level of anthropogenic impact is the intake of runoff contaminated by heavy metals from agricultural areas (sewage that was not treated at treatment plants). It is well known that heavy metals are a part of complex fertilizers (Gorbunova & Shtulin, 2016) used in agriculture. As analysis of literature data has shown (Ahmedenov & Koshim, 2014; Ahmedenov, 2015; Buymova & Bubnov, 2012), pollution of catchment basins significantly contributes to the overall level of toxic pollution of not only surface, but also underground water sources. Relatively low concentrations of heavy metals registered by us in fresh and mineralized sewage water reservoirs (number 6 and 10 in Table 2), as well as in the sewage pond of Northern Kazakhstan (Zakarkina *et al*., 2011) indicate a fairly effective purification of industrial effluents at treatment plants.

Another crucial factor determining the ecological state of aquatic ecosystems is the intensity of biological processes. Due to the dumping of both industrial and domestic sewage, the concentration of biogenic and organic substances in the water bodies with strong level of anthropogenic impact (sewage water storage facilities) are at a higher level than in the water bodies with moderate level of anthropogenic impact. In this regard, quantitative variables of biological communities in sewage water storage facilities are higher than in water bodies polluted only by surface runoff (Krupa, 2012; Barinova, Krupa & Romanova*,* 2018). Effective purification of sewage water storage facilities occurs due to the biological activity of unicellular algae which accumulation of heavy metals by cell surface (Fargašova, Bumbálová & Havránek, 1997; Macfie & Welbourn, 2000; Novák, Jánószky, B-Béres, Nagy & Bácsi 2014; Bácsi *et al*., 2015) more intensively compared to that of macrophytes and ichthyofauna (Chizhikova, Sirotsky, Kharitonova & Utkina, 2011; Niemiec, Szeląg-Sikora, Sikora, Cupiał & Komorowska*,* 2018).

One of the natural factors that affect the content of heavy metals in aquatic ecosystems is the TDS of water. According to the average values, Pb, Cr, Cd and Cu are accumulated most intensively in the mineralized water bodies of Kazakhstan (TDS>2000 mg dm^{-3}), while Ni and Zn were recorded in higher concentrations in fresh waters. A similar tendency of growth in Cu and Pb content in background groundwater of various climatic zones of the Earth was observed within the TDS gradient (Shvartsev, 2008). The highest Clarke concentrations of Zn and Ni were also characteristic of mineralized waters in arid areas, but the second peak was observed in the fresh waters in tropics and subtropics. This indicates that, with a significant impact of the TDS on migration ability of heavy metals, this process is regulated by a complex of factors, including oxygen conditions (Tretyakova, Papina & Eirikh, 2008), chemical type of water, and age of water-bearing rocks (Panina, 2006).

With differences in average values in fresh and mineralized water bodies of Kazakhstan, the relationship between the absolute concentrations of heavy metals (excluding Ni) and the TDS value was statistically insignificant. Statistically significant, but weak relationships (Table 3) between the content of heavy metals and other environmental factors were due to the nonlinear distribution of heavy metals within the gradient of external factors. The content of Zn, Cu, and Cd increased within the pH gradient from 7.0 to 8.5 and further than that – decreased (Figure 3). According to the results of the regression analysis (Table 4), accumulation of heavy metals was regulated by pH and water temperature in combination with the morphometric parameters of water bodies. The relationship between the content of heavy metals and the altitude of location of a water body was indirect because with a decrease in altitude, there were corresponding changes of pH, temperature, TDS and others environmental variables.

Experimental data on the effect of temperature and pH values on the flow of heavy metals from bottom sediments into the water are similarly contradictory. Under experimental conditions, the release of heavy metals into water did not depend on temperature (Huang *et al*., 2017) or, on the contrary, was stimulated by temperature (Li, Shi, Li & Zhang, 2013). The influence of pH within the gradient from 7 to 9 on the flow of heavy metals from soils into water has not been established (Huang *et al*., 2017). It has been shown that the anionic forms of transition metals such as Cu, Zn, Cr, Cd, and Ni, migrate into water as the pH of the medium increases, and in the acidic medium they are actively absorbed by bottom sediments, usually in cationic form (Facce, Pellegrino, Ceoldo, Tibaldo & Sfiriso, 2011). There are also conflicting data (Li *et al*., 2013) on the higher rate of release of Zn, Cu, Cr, Cd, and Pb from soils into water at low pH values (4-7) than at high pH (8-10).

Thus, geological and physicochemical factors (location of water bodies in ore or geochemical anomalies, chemical type of underlying soils, oxygen conditions, pH values, TDS, temperature) together with the intensity of anthropogenic load determine a complex picture of the distribution of heavy metals in the surveyed water bodies of Kazakhstan. We described the general patterns of distribution of heavy metals in the water bodies of Kazakhstan depending on natural and anthropogenic factors in the first time. The obtained data on the background concentrations of heavy metals contribute to the clarification of the values of regional MPC of heavy metals in water bodies intent for fishery and, accordingly, to more correct assessment of the ecological state of Kazakhstan's water bodies. This study results can be a basis for the development of a new regional system for monitoring water quality and assessing anthropogenic impact on water bodies in Kazakhstan.

Conclusion

This paper based on our data obtained during 1997-2017 describes the main trends in the distribution of heavy metals in the water bodies of Kazakhstan depending on natural and anthropogenic factors. Background water bodies, located far from sources of anthropogenic pollution, were characterized by a low content of heavy metals, with the exception of Cu. The increased background concentrations of Cu established by us are due to the location of water bodies in polymetallic provinces and should be taken into account when developing regional MPC norms and assessing the overall level of toxic pollution of Kazakhstan's fresh water bodies. According to average values, the enrichment of water bodies with heavy metals occurred in two directions – with an increase in the anthropogenic load and an increase in the TDS of water. These are two interrelated processes, since the anthropogenic load increases in the direction from the background mountain ultra-fresh and fresh water bodies to more mineralized water bodies of plains. On the other hand, mineralized water bodies naturally accumulate all salts including heavy metal compounds in the absence of anthropogenic pollution.

A complex of multidirectional external factors, with the main factors difficult to reveal, regulates accumulation of heavy metals in aquatic ecosystems. According to our data, the leading regional factors contributing to the accumulation of heavy metals were the morphometric characteristics of water bodies in combination with pH and water temperature. In addition to analysis of our data, the contradictory results of experiments on the influence of physicochemical factors on the entry of heavy metals into water, cited in the literature, demonstrate of the complexity of the issue and the need for further research.

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