HYDROCHEMICAL CONDITIONS OF WATER BODIES OF THE URAL-CASPIAN BASIN

Tulemisova G., Amangosova A., Abdinov R., Kabdrakhimova G., A. Orynbasarova

Kh. Dosmukhamedov Atyrau state university, Atyrau, e-mail: tulemisova62@mail.ru

The global environmental issues of technogenic pollution occur pressure on natural forms of the pathology of all living organisms and inevitably have an adversely affect on them. In recent years, hydrobionts have become objects of study of the outdoor pollution level. Numerous publications, including reports of World Health Organization Expert Committees allow us to conclude that there is evidence to suggest about the rising aggressiveness of environment. One of the important aspects of such insufficiently controlled process is the contamination of the micro elementary nature. At the present stage, the ecological state of transboundary rivers is especially important. These rivers include the Ural River flowing through the territory of the Russian Federation and the RK, and flowing into the Caspian Sea. The article presents the results of a study of the hydrochemical regime of the rivers of the Ural-Caspian basin in different periods of 2017. In the work for comparison, the data on the state of chemical indicators of drinking water in the region are characterized. In order to determine the state of the hydrochemical regime in the lower and upper reaches of the Ural River, the indicators of the Ilek River, the flow in the Aktyubinsk Oblast and the Chagan River, the flow of the river in the West Kazakhstan region are given.

Keywords: The Ural-Caspian Basin, the Ural River, tributaries, the hydrochemical conditions, pollution, oil products

Environmental problems in the third largest river in Europe, the Ural River Basin have remained extremely tense. Meanwhile, there are 70 cities and settlements with total population of about 4.5 mln people. The total length of the river is 2428 km and its catchment area is 237 thous. km^2. The length of the river in the territory of Kazakhstan makes 1084 km, including length within the boundaries of West Kazakhstan Region – 761 km. The largest tributaries are the Or, Sakmara, Ilek, Chagan Rivers. Below the Uralsk, there is no lateral in flow. The reduced river flow cause due to national water supplies and evaporation of the extensive floodplain. The river flow is formed at the top of the basin, mainly within the boundaries of Russian Federation (Kurmangaliyev R.M., 2008) [3].

The Ural-Caspian Drainage Basin is located in the western part of the Republic of Kazakhstan and occupies the territory of four regions with a total area of 640,8 thous. sq.km, including Atyrau – 118,6 thous.km^2, Aktobe – 205,3 thous.km^2 (except for the territories of Ayteke Bi and Irgiz regions), West Kazakhstan – 165,8 thous.km^2, Mangystau – 151,3 thous.km^2. On the whole almost 2 mln people live in this region. The main direction of economic activity is the oil and gas field development, agriculture and fisheries. Intensification of agricultural and fish production largely depends on the regional water supply (Onayev M.K., 2013) [6].

Preserving fish diversity in the Caspian Sea basin are one of the most pertinent issues: the commercially valuable fish catches has been steadily decreasing, the low-value ichthyofauna has not been developed, the quality of fish populations has been decreasing, that suggest a violation of their genetic pattern. There are troubling trends in the current state of commercial stocks of sturgeons in the Caspian Sea. Over the past 10 years fish catches have decreased by 10-fold in the Ural-Caspian basin.

The areas for exploration and development of hydrocarbons in the North-Eastern Caspian Sea coincide with the areas for feeding and migration of sturgeons and other commercially valuable fish, the concentration of foraging planktonic and benthic organisms. The large-scale development of oil and gas fields in the North-Eastern Caspian Sea is associated with environmental risk, as the most intensive bioproduction processes occur in the peripheral (coastal and shelf) zones where the main biomass of marine flora and fauna are concentrated [1, 2,7].

The deterioration of the quality of the water condition due to external natural and anthropogenic factors and the continuing unstable state of marine biota, the technogenic load will inevitably lead to ecosystem degradation and irreparable damage the biota of the North-Eastern Caspian Sea. Study of chemical composition of seawater and marine sediments is fundamentalfor solving the problems involving transformation and integrated use of water bodies. Transitionalrunoff within the upper and middle reaches of the river also contribute to pollution [4, 8].

Materials and methods of research

During the current year, study was carried out based on the R & D Schedule on six relatively isolated water bodies of the Ural-Caspian

Basin: Ural River, its estuary, tributaries of Ilek and Chagan River.

Collection of samples to assess hydrochemistry and toxicology was conducted within expedition flights at 7 permanent observation stations: the Ural Rivers and their seashores.

The hydrochemical conditions of the Ural River in winter were estimated based on observations. Hydrochemical analysis included the following complex of parameters: pH, ORP, oxygen concentration, nitrite nitrogen content in water, permanganate oxidizability, alkalinity, BOD_5, water hardness, salinity, electrical conductivity, chlorides and sulfates. Analyses were conducted according to the most recognized hydrochemical methods (ST ISO 9863-1-2008. Water quality. Determination of alkalinity).

Concentration of petroleum products in water and bottom sediments was measured by the Fluorate 02-2M by fluorescent method in accordance with the PND F14.1:2:4.35-95 and PND F 16.1:2:21-98 (PND F, 98) [5].

Boron concentration was also measured by the Fluorate 02-2M by fluorescent method, without sample preservation. Permanganate oxidizability was determined according to the method of oxidation of organic compounds with potassium permanganate in an acid medium. The concentration of oxygen and BOD_5 were measured based on the dissolved oxygen content by an Anion-7051 oxygen meter within 5 days after sampling. The specific electrical conductance (SEC) and the content of NaCl ions, i.e. salinity, were also measured by the Anion-7051 portable fluid analyzer. The water pH and its oxidation-reduction potential (ORP) were measured by an Anion-7051 portable fluid analyzer.

Results of research and their discussion

Study for the hydrochemical regimes of rivers of the Ural-Caspian basin are important for describing the ecological and toxicological state of the water body. This would be especially relevant for the characteristics of the water bodies in different periods of the year. So it can be a useful way to identify the nature of pollutants entering into the river basin. Table 1 shows the data of the hydrochemical regime and the ecological state of the Ural River water and drinking water in various seasons of 2017. It also contains the indicators of flood period, winter and summer seasons. The pH levels of the samples are normally similar to magnitude. No special seasonal fluctuations were observed. Although, the pH level of drinking water in February was within the limits of sanitary standards.

Hydrocarbonates and carbonates were within established standards, although these indicators have been decreased during winter–spring seasons (Table 1).

The salinity and the electrical conductivity (the EC) of the water bodies correspond to the values of the hydrochemical regime of the river (Tulemisova and others, 2017) [9]. The high indicators in the winter and their reduction to the beginning of the flood period are naturally occurring situation. Study of qualitative composition of pollutants was conducted to determine the content of nitrites, boron, petroleum products and easily oxidized organic compounds.

The amount of nitrites of the toxic oxides of nitrogen 1-3 times higher than the MPC values. There are extremely high concentrations of nitrites in spring before the flood period. Their concentrations have increased during flood period, sometimes have maintained same limits. The content of nitrites varies within the MPC limits during winter (Table 1).

In this respect, the quality of the drinking water is much cleaner. The content of potassium permanganate oxidation compounds are much less during the winter than the spring period, which is typical for this water body (Table 1).

This year boron content in the Ural River is much less than previous periods. However, its contents increase during the flood period. Petroleum products are always found in the Ural River. In winter and early spring, concentration of petroleum products is lower than the MPC values, but their concentration have increased 1,1 times before the beginning of flood period. Drinking water complies with the sanitation quality. Among all the quality indicators nitrites appear to be constant all the periods. This suggests that nitrites have not been washed out during flood period, representing constant source of pollution.

It is common knowledge that the primary pollutants enter the water bodies in the spring period. However, studies we have conducted over the last three years suggest that pollution appears to be constant, which increased only slightly for the flood period.

In order to obtain the pollution sources of the Ural River, water samples were collected from the territory in the reservoir flows and its tributaries (Table 2).

Table 1

Hydrochemical regime data of the Ural River in different periods

Indicators	pH level	Alkalinity, mg *eq/ dm^3	Hardness, mg *eq/ dm^3	Nitrites, mg/ dm^3	ORP, Eh, mV	Salinity, NaCI, mg/ dm^3	EC, µS/cm	Permanganate oxidizability, mg/dm^3	Boron, mg/ dm^3	Petroleum products, mg/dm^3
Ural River, January	8,1	4,3	7,10	0,20	-0,07	671,0	1357	3,28	0,24	0,0447
Tap water	8,0	4,0	7,03	0,05	-0,06	630,2	1320	3,20	0,15	0,0318
Ural River, February	7,9	3,6	6,84	0,08	-0,08	712,3	1457	1,84	0,43	0,0405
Tap water	7,5	3,5	6,74	0,05	-0,07	700,1	1405	1,60	0,20	0,0350
Ural River, March	8,0	3,5	6,5	0,20	-0,06	472,0	1047	4,80	0,19	0,0667
Tap water	7,9	3,25	6,3	0,15	-0,06	469,0	964	3,05	0,10	0,0495
Ural River, April	8,2	3,25	6,70	0,25	-0,04	328,0	675	4,32	0,25	0,0695
Tap water	7,6	2,6	6,1	0,05	-0,03	140,0	278	2,88	0,06	0,0152
Ural River, June	7,8	2,85	4,80	0,15	-0,05	453,0	924	6,20	0,18	0,0487
Tap water	7,5	2,65	4,50	0,15	-0,04	440,0	912	3,5	0,07	0,0371
MPC	6,5-8,5	3,5-5,0	3,5-7,0	0,08	-	-	-	10-15	0,50	0,05

Table 2

Hydrochemical data of the rivers of the Ural-Caspian basin, May

Indicators	pH level	Alkalinity, mg•eq/ dm^3	Hardness, mg•eq / dm^3	Nitrites, mg/ dm^3	ORP, Eh, mV	Salinity, NaCI, mg/ dm^3	EC, µS/cm	Permanganate oxidizability, mg/dm^3	Boron, mg/ dm^3	Petroleum products, mg/ dm^3
IlekRiver, Aktyubinsk, 03.05.17	8,09	5,5	5,9	0,16	-0,046	204,8	426	4,80	0,11	0,057* 0,288**
Ilek River, end of the village Georgiyevka 03.05.17	7,90	5,9	5,2	0,35	-0,037	316,0	652	6,08	0,07	0,090 0,460
Ural River, top of the city Uralsk, 04.05.17	7,97	4,0	3,1	0,12	-0,040	159,4	333	6,24	0,04	0,026 0,131
Ural River, end of the city Uralsk, 04.05.17	7,67	3,1	3,2	0,15	-0,041	160,6	335	6,00	0,06	0,021 0,107
Chagan River, 04.05.17	7,76	3,7	3,0	0,10	-0,029	167,2	350	4,40	0,02	0,030 0,150
Ural River, Atyrau, University 05.05.17	7,81	4,3	3,2	0,20	-0,042	173,5	362	4,54	0,08	0,018
Tap water	7,05	3,1	3,6	0,05	-0,022	148,7	311	2,72	0,03	0,019
Ural River, Atyrau, University 11.05.17	8,05	3,25	3,3	0,25	-0,055	328,0	675	5,20	0,06	0,027
MPC	6,5-8,5	3,5-5,0	3,5-7,0	0,08	-	-	-	10-15	0,50	0,05

Table 3

Data on the hydrological-hydrochemical regime of the Ural River by the end of flood period

Sampling site	pH level	ORP, mV	Alkalinity, mg•eq/ dm^3	Hardness, mg•eq/ dm^3	Nitries, mg/ dm^3	O_2 mg/dm^3	Salinity, NaCI, mg/dm^3	EC, µS/cm	Permang.oxid., mg/dm^3	Boron, mg/ dm^3	Petroleum products, mg/ dm^3
Bugorky	7,3	-0,011	4,8	4,0	0,15	6,30	160,0	303	5,84	0,06	0,05* / 0,25**
Institute	6,9	+0,003	4,9	4,0	0,12	7,87	174,6	367	6,08	0,00	0,009 / 0,045
University	7,8	-0,046	5,3	3,3	0,13	7,86	172,2	358	5,76	0,07	0,01 / 0,05
Balykshy	8,0	-0,049	4,4	3,2	0,13	7,15	175,2	368	5,92	0,760	0,06 / 0,30
7 station	7,2	-0,008	5,0	3,5	0,14	6,98	181,2	379	5,20	0,05	0,005 / 0,023
Lower Dambs	7,3	-0,015	4,8	3,80	0,12	8,52	178,6	374	6,40	0,09	0,018 / 0,093
Top of the canal	7,9	-0,048	4,6	3,5	0,13	9,91	180,9	377	5,12	0,08	0,019 / 0,097
Tap water	7,4	-0,019			0,05		188,0	391	4,24	0,07	0,012
MPC	6,5-8,5		3,5-5,0	3,5-7,0	0,08	6,0	-	-	10-15	0,50	0,05

N o t e : * – c oncentration of petroleum products for the 100 ml fixed sample; ** – concentration of petroleum products for the 500 ml fixed sample.

Table 4

Hydrochemical data of rivers of the Ural-Caspian basin, fall

Indicators	pH level	Alkalinity, mg *eq/ dm^3	Hardness, mg *eq /dm^3	Nitrites, mg/ dm^3	ORP, Eh, mV	Salinity, NaCI, mg/ dm^3	EC, µS/cm	Permanganate oxidizability, mg/dm^3	Boron, mg/ dm^3	Petroleum products, mg/ dm^3
Ilek River, Aktyubinsk, 09.10.17	8,00	4,8	5,7	0,20	-0,046	349,0	718	4,80	0,31	$\frac{0,008}{0,039}$
Ilek River, end of the village Georgiyevka 09.10.17	8,20	4,8	5,5	0,15	-0,037	388,0	808	4,77	0,27	$\frac{0,049}{0,223}$
Ural River, top of the city Uralsk 10.10.17	8,20	6,0	6,7	0,14	-0,040	537,4	1093	4,10	0,24	$\frac{0,028}{0,131}$
Ural River, end of the city Uralsk 10.10.17	8,00	6,0	5,8	0,16	-0,041	532,6	1083	4,00	0,26	$\frac{0,040}{0,181}$
Chagan River,beginning of a river 10.10.17	8,5	9,2	10,8	0,08	-0,029	808,2	1626	5,84	0,20	$\frac{0,035}{0,161}$
Chagan River, end of a river 10.10.17	8,00	5,7	6,0	0,14	-0,029	444,0	908	8,00	0,15	0,096
Ural River, Atyrau, University 11.10.17	6,50	5,5	5,4	0,10	-0,042	554,5	1126	4,50	0,12	0,035
Tap water	7,50	4,7	5,0	0,08	-0,022	544,0	1126	3,78	0,05	0,030
MPC	6,5-8,5	3,5-5,0	3,5-7,0	0,08	-	-	-	10-15	0,50	0,05

Research has shown that the composition of the Ural River, the Ilek River and its tributaries in the Aktobe region varies considerably. So that, there were high nitrite levels at the Ilek River mouth – 4,5 MPC (Table 2), permanganate oxidability – 6,08 mg/dm^3 and petroleum products – 1,9 MPC. Reduction for these indicators has determined in the Chagan River. This suggests that no pollution were found in the territory of the West Kazakhstan Region. Although, the 2016 research [10] showed increased concentration of petroleum products. An excess salt concentrations were found in the Ural River, Atyrau region, along the University zone typically the Caspian Lowland. This area showed increase in concentration of nitrites – 2,4 MPC (Table 2). Other indicators in the Ural River were within established standards. During this period drinking water complies with the sanitation quality (Table 2).

By the end of flood period, the ecological state of the Ural River was determined by the collection of water samples along the different sections of lower reaches of the water bodies. Water quality indicators such as pH, oxygen and petroleum product levels describe the presence of pollution in the upper reaches of the Ural River compared with the samples of the lower reaches (Table 3). The Lower Damba section one of the most contaminated area – 6.40 mg/dm^3 (Table 3).

This area includes all the settlements, so there are household wastes (illegal dumping), as well as extreme congestion of coastal vessels along the river bank. By the end of the flood period, the pollution inflow has slightly reduced.

The study of fall samples in the rivers of the Ural-Caspian basin showed a decreased rate of pollution, compared with spring samples (Table 4).

The Chagan River mouth is the only exception, in that the high rate of permanganate oxidation equal to 8,00 ml/dm^3, also the concentration of petroleum products – 0,096 mg/dm^3 (1,9 MPC), compared to other stations.

High levels of nitrite were found in the Ilek River and are 2 – 4 greater than the MPC. There are also consistently high levels of nitrite in the Ural River, Uralsk, although its concentration has significantly decreased compared to the flood period. In fall, the rates of mineralization, salinity and the EC of the water body have increased significantly (Table 4). It should be noted that such event is a typical process nor the salinity has sharply increased both the Ural River and the squares of the North-Eastern Caspian Sea. Summarizing the obtained results, it should be noted that sources of pollution such as nitrites, petroleum products were found in the upper reaches of the Ural River and the river flows towards the territory of Kazakhstan.

Conclusion

The Ural-Caspian basin is the most important area for the breeding of sturgeons and semi-anadromous fish species and has the leading position in the commercial fishing industry in Kazakhstan.

In recent years, there were significant changes over the entire basin affecting hydrobionts' natural habitat. The anthropogenic impacts on coastal and marine ecosystems have increased immeasurably. Due to the intensification of fishery and violation of breeding and feeding patterns, their numbers have dramatically decreased. Of particular concern is the increasing amount of offshore oil and natural gas development.

In order to assess the current state of the ecosystem functioning in the Ural-Caspian basin fisheries and predict its probable future behavior, it is necessary to analyze the influence of multidirectional factors on the formation of biological resources. In that context, the continuous monitoring of ecological status of the North-Eastern Caspian Sea and the Ural and Kigach Rivers is of the utmost importance.

Study of the hydrochemical regime components of the Ural River has shown that this year there were positive dynamics of parameter changes of the state of the Ural-Caspian basin waters.

References

1. Amirgaliyev N.A. Ecological and Toxicological State of the Ural-Caspian Basin and Some of Its Research Priority // Proceedings of the International Scientific Conference "The Current State and Ways to Improve Research in the Caspian Basin", Astrakhan, 2006, P.21-25.

2. Burlibayev M.Zh., Kurochkina L.Ya., Kashcheeva V.A, Erokhova S.N., Ivaschenko A.A. The Ural River delta and adjacent territories along the coast of the Caspian Sea. Astana, 2007, P.264.

3. Kurmangaliyev R.M. Ecological challenges of transboundary watercourse of Ural River and ways for its resolvement / R.M. Kurmangaliyev // Gilim zhane bilim. 2008. No. 3, P.91-97.

4. Leshan I.Yu., Khubitdinova A.F., Hydrochemical features of Ural River basin // Actual problems of the humanities and natural sciences, 2016., No.2-4 . P.11-13.

5. PND F 14.1:2:4. 128-98. Quantitative chemical analysis of waters. Procedure for mea-surement of mass concentration of petroleum products in samples of natural, drinking or waste water by fluorescence method with the Fluid Analyzer FLUORAT-02. In supersession of PND F 14.1:2:4.35-95; have been introduced in 2007-2018. M.: Lumeks, 2007. P. 24.

6. Onayev M.K . Use of water resources of the West Kazakhstan used in to land reclamation. // Science news of Kazakhstan. 2013., Edition 3 (117). P.186-190.

7. Ogar N.P. etc., Environmental monitoring of the North-Eastern Caspian Sea while development of oil fields. Almaty., 2014. P.70-73.

8. Shimshikov B.Ye., Izbassarova A.K. Hydrochemical and toxicological characteristics of the state // KazNU Bulletin. Ecological series. 2014, No.2 (41). P.163-167.

9. Tulemisova G.B., Abdinov R.Sh., Batyrbayeva G.U., Kabdrakhimova G.Zh., Mustafina A. Zh. Current state of hydrochemical regime of the rivers of the Ural-Caspian basin. // Proceedings of NAS RK. Chemistry and Technology Series. 2017, No. 1 (421), P.96-100.

10. Tulemisova G.B., Abdinov R.Sh., Kabdrakhimova G.Zh., Zhanetov T.B. Ecological conditions of the Ural River // KazNU Bulletin. Chemistry series. 2017., No. 2 (85), P. 18-24.