Hydrochemical conditions of water bodies of the Zhaiyk-Caspian Basin

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Abstract

***Objective**: To evaluate toxicity levels of the water, bottom sediments and aquatic life in the Ural, Kigach Rivers and North-Eastern Caspian Sea. The stages and tasks are as follows:*

The ecological state of the Ural River is an important component of the hydrochemical regime of the Zhaiyk-Caspian basin water bodies. The Ural and Kigach transboundary are prone to pollution from various territories in the upper and middle currents. This in turn has an impact, although not a significant one, on the state of the Northeast Caspian. Research conducted by us during winter, flood, post-flood periods and in the fall, showed a constant source of pollution in the water body, which increases during the flood period. In order to detect the source of pollution in the Ural River, water was taken from the territory where the reservoir flows from the tributaries flowing into the Chagan River, Ilek River to the flood. Our studies have shown that the composition of water in the tributaries of the Ural River - the river Ilek within the Aktobe region is very different. So, at the mouth of the Ilek river, there were high rates of nitrites of 4.5 MPC, of permanganate oxidability of 6.08 mg / dm^3, and of an oil content of 1.9 MPC.

Keywords

Zhaiyk-Caspian basin, the Ural river, the Kigach river, the North-eastern Caspian sea, toxicants, petroleum products, sturgeons

I. INTRODUCTION

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 a total population of about 4.5 M people. The largest tributaries are the Or, Sakmara, Ilek, Chagan Rivers. Below the Uralsk, there is no lateral inflow. The reduced river flow were 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 [1].

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 bio-production processes occur in the peripheral (coastal and shelf) zones where the main biomass of marine flora and fauna are concentrated[2]. 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 of the biota of the North-Eastern Caspian Sea. Study of chemical composition of seawater and marine sediments is fundamental in 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. Along with hydrocarbons, heavy metals are significant environmental pollutantsof the North-Eastern Caspian Sea - products of both natural origin (dissolved and sedimentary forms) and components of industrial runoff.

Therefore, the problem of obtaining information both on pollution levels and the biological hazard of pollutants is becoming increasingly important for forecasting and addressing possible dangerous consequences of chemical pollution. For that reason, biological studies of the effects of pollutants on humans and animals have played an important rolein the overall set of studies related to the ever-increasing environmental pollutants [3], [4].

II. MATERIALS & METHODS

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, the North-Eastern Caspian Sea, the Kigach River and its estuary.

Collection of samples to assess

hydrochemistry and toxicology was conducted within expedition flights at 7 permanent observation stations: the Ural and Kigach Rivers and their seashores.

Toxicology studies were conducted in spring, summer and autumn 2017. Water/sediment samples for the analysis of heavy metal, petroleum product content were collected at 21 stations, so the 7 stations are located at the Ural River Delta, 3 stations - at the Kigach River (eastern arms of the Volga River Delta). The study of the north-eastern part of the Caspian Sea was conducted at 5 stations (Table 1).

The report presents the study materials for the spring, summer and autumn periods of the current year and summarizes separate materials for long-term observations. 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).

Table 1 - The amount of collected and processed hydrochemical and toxicity material (sample)

Study description	**Study areas**		
	Ural River	Ural River seashore	Kigach River
Chemical analysis of water	55	18	7
Toxicology analysis of water	35	18	8
Bottomsediments	24	18	8

Toxicology studies were conducted in the first half of May 2017. Water/sediment samples for the analysis of heavy metal, petroleum product and boron content were collected at 15 stations, so the 7 stations are located at the Ural River Delta, 3 stations - at the Kigach River (eastern arms of the Volga River Delta). The study of the north-eastern part of the Caspian Sea was conducted at 5 stations. Hydrochemical and hydrological studies were conducted in tandem with the expedition on the Bala Oraz ship.

Ordinary fish samples for toxicology analysis were collected at the North Caspian Sea, the Volga-Ural inter fluve, the Kigach River. Samples of muscle tissues and individual organs of sturgeons for analysis of toxic compounds were collected at the Ural, the Atyrau fish-breeding farm. A total of 36 water samples were collected and processed for analysis of toxic compounds.

Concentrations of petroleum products in water and bottom sediments were 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 [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.

III. RESULT & DISCUSSION

Study for the hydrochemical regimes of rivers of the Ural-Caspian basin are important in describing the ecological and toxicological state of the water body. This would be especially relevant to 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. Since there are no industrial facilities discharging to the water body within the Atyrau region and the city of Atyrau, we believe that all these contaminants flowthrough the upper reaches. Early studies of Russian scientists [6] and Kazakhstani researchers [1], [7] studying the upper reaches of the Ural River have described such event.

Table 2 shows the data of the hydro-chemical regime and the ecological state of the Ural River water and drinking water in various seasons

Table 2 - Hydrochemical regime data of the Ural River in different periods

Indicators	pH level	Alkali nity, mg *eq/ dm^3	Hard-ness, mg *eq/ dm^3	Nitri-tes, mg/ dm^3	ORP, Eh, mV	Salini-ty, NaCI, mg/ dm^3	EC, µS/cm	Perman-ganate oxidiza-bility, mg/dm^3	Bo-ron, 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 3 - Hydrochemical data of the rivers of the Ural-Caspian basin, May

Indicators	pH level	Alkali nity, mg *eq/ dm^3	Hard-ness, mg *eq / dm^3	Nitri-tes, mg/ dm^3	ORP, Eh, mV	Salini-ty, NaCI, mg/ dm^3	EC, µS/cm	Perman-ganate oxidiza-bility, mg/dm^3	Bo-ron, mg/ dm^3	Petro-leum produ-cts, mg/ dm^3
Ilek River, 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

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

correspond to the values of the hydrochemical regime of the river [8]. 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 2).

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 2).

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 com-mon 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 3). Research has shown that the composition of the Ural River, the Ilek River and its tributaries in the Aktobe region vary considerably. So that, there were high nitrite levels at the Ilek River mouth – 4,5 MPC (Table 3), permanganate oxidability – 6,08 mg/dm^3 and petroleum products – 1,9 MPC. Reduction for these indicators were determined in the Chagan River. This suggests that no pollution were found in the territory of the West Kazakhstan Region. Although, the 2016 research [9] showed increased concentration of petroleum products. Excess salt concentrations were found in the Ural River, Atyrau region, along the University zone typically the

standards. Hydrocarbonates and carbonates were within established standards, although these indicators have been decreased during winter–spring seasons (Table 2). The salinity and the electrical conductivity (the EC) of the water bodies

Caspian Lowland. This area showed increase in concentration of nitrites – 2,4 MPC (Table 3). Other indicators in the Ural River were within established standards. During this period drinking water complied with the sanitation quality (Table 3).

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 4). The Lower Damba section one of the most contaminated area - 6.40 mg/dm^3 (Table 4).

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 Kigach River. The research of state of the river and its hydrochemical regime were con-ducted at the flood stage, by collecting water sam-ples from the 3 stations. The indicators generally correspond to the spring period (Table 5). pH levels of water were within the level of the Ural River. According to the nitrite concentrations, Kamy-shinka station is the most polluted area – 2,5 MPC, while the value in the Ural River amounted to 3.1 MPC. The salt concentrations have been relatively lower than in the Ural River. Compared to 2015/2016, there were no significant changes [10].

Concentration of petroleum products in the Kigach River waters in 2017 were found comparatively lower than those reported for the 2015/2016 [8]. Also no cases of exceedance of the MPC values have been detected. In spring this year, the amount of potassium permanganate oxidation compounds were found to be similar to 2015/2016.

Boron concentration were found to be similar to previous years [10], with an amount lower than in the Ural River (Table 5). Alongside with other rivers, the Kigach River cannot be identified as the most polluted water, as it was found that there was slight exceedance of sanitary standards in all stations.

The study of the North-Eastern Caspian Sea was conducted during the fall after flooding. The studies of the squares of the Ural River mouth and the Kashagan field (75, 78) showed increased concentrations of petroleum products and relatively high values of salinity.

Table 4 - 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	Nitrites, 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

* - concentration of petroleum products for the 100 ml fixed sample
** - concentration of petroleum products for the 500 ml fixed sample

Table 5 - Data on the hydrochemical regime of the Ural and Kigach Rivers by the flood period

Sampling site	pH level	Alkalinity, mg *eq/ dm^3	Hardness, mg *eq/ dm^3	Nitrites, mg/ dm^3	Chlorides, mg/ dm^3	Salinity, NaCI, mg/ dm^3	EC, µS/cm	Permanganate oxidizability, mg/dm^3	Boron, mg/ dm^3	Petroleum products, mg/ dm^3
Kigach River, Sand	8,20	4,6	4,2	0,10	34,0	206,7	430,0	5,20	0,06	0,052
Kigach River, Kamyshinka	8,00	4,5	4,6	0,20	32,9	211,1	439,0	4,40	0,10	0,025
Kigach River, Bogatinsky	8,40	4,5	4,3	0,12	38,3	165,7	346,0	4,72	0,10	0,037
Ural River, 19.04.17	8,2	6,5	6,1	0,25	154,2	338,0	695,0	4,32	0,48	0,035
Tap water 28.04.17	7,00	4,0	4,5	0,05	93,0	208,0	433,0	3,04	0,19	0,017
MPC	6,5-8,5	3,5-5,0	3,5-7,0	0,08	300	-	-	10-15	0,50	0,05

Table 6 - Hydrochemical data in the North-Eastern Caspian Sea, September 2017

Sampling site	pH level	Alkalinity, mg *eq/dm^3	Nitrites, mg/ dm^3	Hardness, mg *eq/dm^3	Salinity, NaCI, mg/dm^3	EC, µS/cm	Permanganate oxidizability, mg/dm^3	Boron, mg/ dm^3	Petroleum products, mg/dm^3
sq 12	8,0	4,7	0,05	26,0	8,290	15,10	5,10	0,048	0,0303
sq 25	6,5	5,3	0,10	25,0	6,070	11,20	5,30	0,043	0,0225
sq 75	8,5	5,0	0,07	23,4	5,169	9,590	4,90	0,055	0,1280
sq 78	7,9	5,0	0,06	24,8	5,400	10,00	5,80	0,052	0,0211
sq 105	8,0	4,8	0,05	23,0	4,570	8,580	5,12	0,064	0,1010

The pH level of water in these squares amounted to 6,5-8,5, having the most favourable rate available to the sq. 12. Alkalinity values are approximately the same magnitude (Table 6). Boron concentrations were within established standards except for sq. 75. The concentration of nitrites exceeded MPC values within the sq. 25.

One of the most polluted areas found is square 75 among all the study areas. The study of fall samples in the rivers of the Ural-Caspian basin showed a decreased rate of pollution, compared with spring samples (Table 7). 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 sig-nificantly (Table 7). It should be noted that such event is a typical process nor the salinity has shar-ply increased both the Ural River and the squares of the North-Eastern Caspian Sea (Table 6). 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.

CONCLUSIONS

The Ural-Caspian basin is the most im-portant 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 basinwhich affect hydro-bionts' natural habitat. The anthropogenic impacts on coastal and marine ecosystems increased im-measurably. 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 multidi-rectional factors on the formation of biological resources. In that context, the continuous moni-toring of ecological status of the North-Eastern Caspian Sea and the Ural and Kigach Rivers is of the utmost importance.

Table 7 - 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	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	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	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	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	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

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

The MPC values for petroleum products exceeded 2-3 times in the Kigach River, the Ural River, Uralsk, sq. 75 of the North-Eastern Caspian Sea. The MPC values for the tributaries of the Ilek River and the Chagan River were greater than 1,8 MPC. Autumn studies have shown that the source of the pollutants loads into the Ural River is its tributary in the Aktyubinsk region, the Ilek River and the Chagan River at the Uralsk.

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