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SOURCES OF POLLUTION BY XENOBIOTICS AND PATHOGENIC MICROORGANISMS OF CROSS-BORDER RIVERS OF AZERBAIJAN

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Abstract: The comprehensive sensory, analytic-chemical, physical-chemical and microbiological analyzes of numerous water samples taken from upper and lower layers of the largest rivers of Azerbaijan - Kur and Araz were carried out. Sources of the anthropogenic emissions polluting these cross-border rivers are defined. The dose rate of ionizing radiation in nearby territories along the watercourse of these rivers and on minerals of water samples was measured and the levels of all types of ionizing radiation were estimated.

Keywords: industrial wastes, inorganic emissions, concentration of the isotope, heavy metals, microorganisms.

1. Introduction

The main water-bearing and long-term rivers of Azerbaijan (the Kur and Araz) originate from mountain tops of Turkey, flowing on border or across the territory of other countries arrive on the territory of Azerbaijan, intercrossing on the Sabirabad district and flowing further in one stream passing the delta of Neftchala, flow into the Caspian Sea. These rivers can be polluted by the emission of toxic industrial wastes into small rivers flowing into these cross-border rivers and from both adjacent territories.

Pollution of the larger rivers flowing through the territory of the country by various anthropogenous emissions promote to increase of the content of xenobiotics in objects of the environmental nature. Therefore, there is a need for carrying out complex (radiological, chemical, biological) monitorings for providing accumulation of objective information on a condition of the environment and allowing to predict tendencies, speeds of emergence of ecological dangers and the happening changes on the territory of the Azerbaijan Republic, including on border territories.

As a result of determination of level of pollution by various organic and inorganic emissions (xenobiotics) the most larger rivers of Azerbaijan having contacts with territories of three other neighboring countries, using results of the conducted researches appear possibilities for planning of preventive and directive actions and carrying out processes chemical and radiological purification and disinfection of water [1-4].

2. Methodical part

Identification and determination of quantities of the reactants used in experiments, the analyzed anthropogenous organic and inorganic emissions, harmful chemicals, heavy metals, radionuclides are carried out besides traditional analytical-chemical methods, also using modern research physical-chemical methods.

For sampling of water were used in advance sterilized dishess, transportation and storage of samples of water were carried out according to requirements of standards 24481-80 and 18968-73. İn addition to radiometric measurements were carried out the express analyses with microbiological test napkins and sensory assays in all possible cases on places of sampling. To determine the conformity of water samples to the requirements of standards 2874-82, AZS 216-2006, AZS 282-2007 for "Drinking Water" the comprehensive sensory, analytical-chemical, physical-chemical and bacteriological analyzes were conducted in accordance with the requirements of standards 2761-84, 3351-74, 2874-82, 18164-72, 4151-72, 4011-72, 4245-72, 4386-81, 18963-73, 4595-49, 18826-73, 18190-72 [4-6].

Microbiological rapid tests were carried out with a test napkins manufactured by R-Biopharm (Germany) and equipped with certificates of the quality control system ISO 9001 and 13485. Determination of the microorganism's count and types in stationary laboratory conditions was carried out using selective culture media produced by Hi-Media (India) and Condalab (Spain), incubators with automated thermostats and colony counters.

Rate of the dose of ionizing radiation were measured using radiometers "Radiagem-2000" equipped with alpha, beta and gamma radiation detectors and "Inspector-1000" produced by "Canberra" corporation and by portable radiometer-identifier "IdentiFINDER" produced by corporation "ThermoScientific", which measures dose rate and identifies radioactive isotopes.

For conducting of physical-chemical analyzes of water and minerals of water samples were used the steam sterilizers "LDZX-30FBS" and "Tengor", the "GFL-2304" biodisstilator, the "TDL-5M" and "TD5A-WS" centrifuges, the "Canberra" gamma spectrometer with HPGe germanium detector, scanning electron microscope "SEM" with X-ray tube, "XRF" X-ray fluorescence spectrometer, laboratory electronic scales, pH-meters, derivatograph, automatic micropipettes equipped with appropriate tips, laboratory mixing-heating tiles, bulb heaters, heat-resistant glass and ceramic laboratory glassware, laboratory refrigerators and evaporators, metal paws and tripods, Petri-cups, colony counters, membrane filters and other laboratory analytical and chemical installations and equipment [4-6].

3. The discussion of the results

Complex sensory, analytical-chemical, physico-chemical and microbiological analyzes of samples of water, soil and vegetation were conducted in stationary laboratory conditions. The presence of anthropogenic xenobiotics and their amounts in soil and water samples were studied, as well as cases of contamination of these samples with toxic substances, radionuclides and microorganisms.

The dose rate from the natural radioactive background were detected in the surrounding Araz landscape in the territory of the Nakhchivan AR varies in the range 0.03-0.08 μSv/h and the alpha radiation intensity is within 0-0.11 Bq_{eq}/sm^2. The dose rate from the natural radioactive background in the territory of the Beylagan and İmishli regions varies in the range 0.03-0.04 μSv/h and the alpha radiation intensity is 0 Bq_{eq}/sm^2. The concentration of the ^{22}Na and ^{40}K isotopes in the stream of the Araz river along the territory of the Nakhchivan AR varies in intervals 0.26-0.58 Bq/l. The concentration of the ^{22}Na and ^{40}K isotopes in the stream of the Araz river along the territory of the Beylagan-İmishli regions varies in intervals 0.18-0.38 Bq/l. The concentration of the ^{22}Na and ^{40}K isotopes in the stream of the Kur river along the territory of the Mingachevir-Sabirabad regions varies in the intervals 0.1-0.2 Bq/l.

For comparison, the concentration of the isotope ^{22}Na (radiation intensity) in the samples of drinking water supplied to enterprises and for population in the cities of Nakhchevan and Baku respectively is 0.32 Bq/l and 0.28 Bq/l, and the concentration of the isotope ^{40}K respectively is

0.18 Bq/l and 0,16 Bq/l (these values are low results typical for natural spring waters), the dose rate of gamma radiation from natural radioactive background in these cities varies respectively in the intervals 0.04-0.07 μSv/h and 0.01-0.04 μSv/h, the intensity of alpha radiation varies respectively in the intervals 0-0.01 Bq_{eq}/sm^2 and 0-0.04 Bk_{eq}/sm^2.

To identify areas along the path of the Araz River, where there are sources of pollution, at the crossing of the Sadarak region with the borders of Turkey and Armenia, after the Customs Transition Gate and at the intersection of the territory of the Ordubad region with the borders of the Iranian Islamic Republic (IIR) and Armenia, and further on, at the territory of the Beylagan district were removed the samples in accordance with the requirements of the relevant standards, conducted radiometric measurements, sensory and express analyzes. The microbiological analysis of water samples was carried out on the same day already under stationary laboratory conditions, i.e. incubation of microorganisms of water was carried out at the corresponding temperatures in the appropriate selective culture media and further analytic-chemical and physical-chemical researches were conducted.

For the comparative demonstration of the ecological state, chemical, radiological and bacteriological indicators, the results of a comprehensive analysis of drinking water supplied to enterprises and population of the city of Nakhchivan are shown in Table 1. The results of microbiological analyzes, presented in Table 1, show that the pathogenic microorganism's count in each liter samples of water, taken from Araz River, at the crossing of Nakhchivan Autonomous Republic with the borders of Turkey and Armenia is above the maximum permissible norm. The microorganism's count in the water of the Araz River after Customs Transition Gate in the Sadarak region is increasing, this count is significantly reduced in the Araz river at the intersection of the Ordubad region with the borders of the IIR and Armenia, but again flowing through parts of the territory of Armenia in Araz River at the intersection of the Beylagan region with the boundary of the IRR the pathogenic microorganism's count is increasing, i.e. the following pollution of the Araz River occurs at the intermediate area situated between Ordubad and Beylagan.

Table 1

The results of organoleptic, analytical-chemical, physico-chemical and microbiological analyzes of water samples taken from the Araz River in the Beylagan and Sabirabad districts, in the territories of the Sadarak and Ordubad districts of the Nakhchivan AR and drinking water samples, supplied to enterprises and population of the city of Nakhchivan.

№	Parameters	Requirements of standarts (2874-82)	Actual results						
1	2	3	4	5	6	7	8	9	10
1.	Transparency, sm	>30*	>30*						
		>10**	-	>30	>30	>30	>30	>30	>30
2.	Turbidity, °	≤1,5	0	0	0	0	0	0	0
3.	Sludge	0 or traces	0	0	0	0	0	0	0
4.	Color, °	≤20*	0	0	0	0	0	0	0
5.	Odors, at 20 ° C, points	≤2*	0	1-2	1	1	0	0 (1)	0
		≤3**							
6.	Tastes, at 20 ° C points	≤2*	0	2	1	1	0	0 (1)	0
		≤ 2**							

7.	Activity (pH)	6,0-9,0	6.8	7.1	7.2	7.7	7.6	7.6 (7.7)	7.6
8.	Dry residue, mg/l	100÷1000*	166	**1645**	595	950	330	470 (880)	570
9.	Total hardness, mg-eq/l	7.0*	1.6	**15**	5.4	**8.7**	3.2	4.4 (8.1)	5.3
10.	Hydrocarbonate hardness, mg-eq/l	<7*	0.7	-	-	-	-	-	-
		are not standardized **	-	7.1	1.4	2.5	1.2	2.3	1.4
11.	Zinc, mg/l	5	0	0.01	0.01	0	0	0	0
12.	Phenol, mg/l	0.001	0	0	0	0	0	0	0
13.	Sulphides, mg/l	0.05	0	0	0	0	0	0	0
14.	Iodine, /Bromine/, mg/l	0.001-0.02 standardized **	0.02 /Br/	**0.15 /Br/**	0.05 /Br/	0.02 /Br/	0.02 /Br/	0.02 /Br/	0.02 /Br/
15.	Residual chlorine, mg/l	0-0.5*	0-0,01	0	0	0	0	0	0
16.	Chlorides, mg/l	350*	36	55	90	90	33	78 (90)	80
17.	Nitrates, mg/l	45*	4.4	12.8	3.4	7.0	4.5	6 (7)	5
18	Cadmium, mg/l	0*	0	0	0	0	0	0	0
19	Silver, mq/l	are not standardized **	0	0-0.01	0	0	0	0	0
20	Strontium, mg/l	7.0*	0.7	9	2.3	4	1.2	2 (3.5)	2
1	2	3	4	5	6	7	8	9	10
21	Arsenic, mg/l	0.05*	0	0.005	0.005	0.003	0	0	0
22	İron, mg/l	0.3* 1**	0.2	0.2	**1,0**	0.01	0.01	0.01	0.01
23	Lead, mg/l	0.03*	0	0	0	0	0	0	0
24	Mercury, mg/l	0* 0.001**	0	0	0	0	0	0	0
25	Nitrites, mg/l	0-0.1* 0.1**	0.05	0.1	0.1	**0.3**	0.05	0,05 (0,10)	0,06
26	Sulphates, mg/l	500	18	318	68	155	40	81 (132)	85
27	Na, K, W, mg/l	** are not standardized	23; 9; 0.03	56; 12; 0.1	58; 22; 0.05	38; 9; 0	17; 1,3; 0	32;2; 0 (36;3; 0)	33; 2; 0
28	E.coli, count of bacteria in 1 l	≤3* ≤9**	3 3	**20-26**	**20**	**30-40**	**14-19**	**22 (35)**	**15**

29	Coli-titr, amount of water in which 1 bacterium was detected, ml	>300* >100**	333 333	50-40	50	28	67	50 (30)	67
30	Saprophytic microorganisms in 1 ml	100*	0	8	6	10	6-8	7 (10)	8
	Aspergillus/1ml		0	0	0	1	1	1 (1)	1
	Candida al./1ml		0	6-8	6	6-9	5	6 (8)	6
31	St.aureus, St.epidermidis in 1 1iter	0	0 /St_{aur}/, 0 /St_{epid}/	0 /St_{aur}/, 16/St_{ep}/	**1**/St_{aur}/, 8 /St_{ep}/	**8** /St_{aur}/, 20 /St_{ep}/	**1** /St_{aur}/, **3** /St_{ep}/	**2;** 12 /($St_{a,}$ St_{ep}/ (**6**;15) /$St_{a,}$ St_{ep}/	**1** /St_{aur}/, **5** /St_{ep}/
32	Pathogenic microorganisms (Salmonella), count/ 1 l.	0	0	**0-1**	**3-6**	**6-10**	0	**1 (1-3)**	**0-1**

Note: * - standard for drinking water;
** - standard requirement for spring water and water for technical use;
4 - samples of water taken from the water pipeline, supplying the city of Nakhchivan and its population with drinking water;
5 - samples of water taken from Araz river at the crossing of the Sadarak region of the Nakhchivan Autonomous Republic with the borders of Turkey and Armenia;
6 - samples of water taken from Araz river at the intersection of the territory of the Ordubad region with the borders of the IİR and Armenia;
7 - samples of water taken from Araz river at the crossing of the Beylagan district's territory with the boundary of the IIR;
8 - samples of water taken from Kur river at the crossing of the Mingaçevir region;
9 - samples of water taken from of rivers stream on the Suqovushan village after intercrossing (300 m) of Kur and Araz rivers:
-sample taken from surface part of stream;
- (sample taken from bottom part of stream);
10 - samples of water taken from of rivers stream after intercrossing (1 km) of Kur and Araz rivers on the Sabirabad district;

The results of microbiological analyzes presented in Table 1 show that the pathogenic microorganism's count in each liter samples of water taken from Araz River at the crossing of the Sadarak region of the Nakhchivan Autonomous Republic with the borders of Turkey and Armenia is above the maximum permissible norm, following the direction of the river flow after the Customs Transition Gate in the Sadarak region the microorganism's count in the water of the Araz River is increasing, this count is significantly reduced in the Araz river at the intersection of the Ordubad region with the borders of the IİR and Armenia, but again flowing through parts of the territory of Armenia in Araz River at the point of crossing the territory of the Beylagan region with the boundary of the IRR the pathogenic microorganism's count is increasing, i.e. the following pollution of the Araz River occurs at the intermediate area situated between regions Ordubad and Beylagan.

The results of the alanalytic-chemical and physical-chemical analyzes presented in Table 1 show that total quantity of inorganic substances in water samples taken from Araz River at the

crossing Sadarak region with the borders of Turkey and Armenia is above than the maximum permissible norm for drinking water by 3 times, the total quantity of inorganic compounds along the path of the river to the Ordubad region naturally decreases by a factor of 3 due to partial adsorption on silt soils, but in Beylagan-Imishli territory it is again increased by 50%, in river water, when the river enters the territory of Sadarak region, the concentration of strontium (^{88}Sr) is 30% higher than the maximum permissible norm, this concentration along the path of the flow of the river to the Ordubad region is naturally reduced by a partial adsorbtion on the silt-soils by 3-4 times, but in Beylagan-Imishli territory again increases by 2-3 times, the relative amount of sulphates and nitrates from Sadarak to Ordubad declining by 4-5 times, in Beylagan-Imishli territory again increased by 2 times.

The results of analytic-chemical, physical-chemical and microbiological analyzes show contamination by organic and inorganic emissions of the Araz river when it reaches the territory of the Sadarak region and its further contamination through parts of the territory of neighboring countries, located between the Ordubad region of Nakhchivan AR and Beylagan district.

In addition to the inrease of microorganism's count the concentration of chlorides and other halides, nitrites, sulphides, alkaline-underground metals in the water of the Araz River in the Sadarak region is also relatively increased up to the permissible limits, which is explained by the saturation of the Sadarak area with these compounds and by the following pollution of the river water by organic emissions after the Customs Transition Gate.

Despite the fact that the water of the Araz river is mostly cleared from inorganic pollutants naturally by adsorbtion on the silt-soil floort downstream from the territory of the Sadarak region to the Ordubad area, but to the Beylagan region, when passing through the territories of neighboring states, water of Araz river is polluted again by inorganic and organic emissions (an increase in the relative amount of inorganic substances, including strontium, sulphates, nitrates and nitrites, in addition to an increase of microorganism's count). This fact agrees well with the results of sensory, analytic-chemical, microbiological and physical-chemical analyzes of soil and water samples taken from these areas.

It should be noted that, there are no production enterprises near the site of the arrival of the Araz River to the territory of the Sadarak region from mount of Turkey, on the sites in the territory of IIR bordering with the territory from Nakhchivan AR to the Beylagan region of Azerbaijan and the small rivers flowing alongside the central production regions of Armenia merge into the Araz river. Therefore, it can be concluded that in both cases (before Sadarak and after Ordubad districts) the Araz River is polluted from the Armenian territories.

The chemical composition, sensory, physical-chemical and microbiological characteristics of water samples taken from surface and bottom parts of the Araz River on the Sadarak region bordering with Turkey and Armenia, after the Customs Transition Gate in the Sadarak region, in the area of the Ordubad district of the Nakhchivan AR bordering with IIR and Armenia and in the Beylagan-Imishli district do not meet the requirements of the AZS 282 standard for drinking water.

The chemical composition, organoleptic, physical-chemical and microbiological characteristics of water samples taken for comparative analysis from the water supply pipeline provides industrial enterprises and the population of Nakhchivan with drinking water meet the requirements of the standard AZS 282 for drinking water and is suitable for use as drinking water.

Contamination by organic emissions of the Kur river when it reaches the territory of the Azerbaijan, i.e. contamination of Kur river from Georgian territories and its further contamination from territory of regions of Azerbaycan were detected. Contamination by organic and inorganic emissions of the Araz river when it reaches the territory of the Sadarak region of

Nakhchivan AR and its further contamination through parts of the territory of neighboring countries, located between the Ordubad region and Beylagan district were detected.

There are no production enterprises on the sites in the territory of IIR bordering with the territory from Nakhchivan AR. The small rivers flowing alongside the central production regions of Armenia merge into the Araz river. Therefore, it can be concluded that in both cases (before Sadarak and after Ordubad districts) the Araz River is polluted from the Armenian territories.

The water samples taken from Araz and Kur Rivers do not meet the requirements of the AZS 282 standard for drinking water.

The analysis of the mineral composition of the water flow before and after the confluence of the two rivers showed that the comparatively light (low-mineralized) water flow of the Kura River, taking into account the inertia of a headway of a stream at first directs on upper of the total flow of the two merging rivers, more polluted and highly mineralized flow of the Araz River for the same reason fills the lower parts of the total flow. At a distance of 300 m after the merging of the two rivers, the amount of the mineral residue of lower layers of the total flow is only 20% lower than the mineral water residue of the Araz River, and the amount of the mineral residue of the upper part of the total flow is only 40% higher than the mineral water residue of the Kur River. İn proportion to an interfusing vector only after 1 km there is a complete mixing of the water of the two rivers and equalization of the concentration of minerals over the entire volume (upper and lower layers) of the total flow of the two merging rivers.

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ИСТОЧНИКИ ЗАГРЯЗНЕНИЯ КСЕНОБИОТИКАМИ И МИКРООРГАНИЗМАМИ ТРАНСГРАНИЧНЫХ РЕК АЗЕРБАЙДЖАНА

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Резюме: Проведены комплексные органолептические, аналитически-химические, физико-химические и микробиологические анализы многочисленных проб воды, отобранные с верхних и

нижних частей потока самых больших рек Азербайджана – из Кура и Араз. Определены источники загрязнения антропогенными выбросами этих трансграничных рек. Измерены значения мощности дозы ионизирующего излучения на прилегающих территориях по пути протекания этих рек и на минеральных остатках водных образцов, а также оценены интенсивности всех видов ионизирующего излучения.

Ключевые слова: производственные отходы, неорганические выбросы, концентрация изотопа, тяжелые металлы, микроорганизмы.

AZƏRBAYCANIN TRANSSƏRHƏD ÇAYLARININ KSENOBİOTİKLƏRLƏ VƏ PATOGEN MİKROORQANİZMLƏRLƏ ÇİRKLƏNMƏ MƏNBƏLƏRİ

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Xülasə: Azərbaycanın böyük çayları olan Kür və Araz çayaxarlarının üst və alt laylarından götürülmüş çoxsaylı su nümunələrinin kompleks orqanoleptik, analitik-kimyəvi, fiziki-kimyəvi və mikrobioloji analizləri aparılmışdır. Bu transsərhəd çayların antropogen tullantılarla çirklənmə mənbələri təyin edilmişdir. Çayaxarları boyu ətraf landşafdan və su nümunələrinin minerallarından ionlaşdırırcı şüalanma doza gücü ölçülmüş və bütün ionlaşdırıcı şüalanma növlərinin intensivlikləri qiymətləndirilmişdir.

Açar sözlər: sənaye tullantıları, qeyri-üzvi tullantılar, izotopun qatılığı, ağır metallar, mikroorqanizmlər.