



ECOLOGICAL MONITORING OF THE ENVIRONMENT IN THE COASTAL AREAS OF THE ARAZ RIVER

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ABSTRACT

The data of the content of heavy metals and radionuclides were studied by mass spectroscopy and radio spectrometry in the water and in the bottom sediments of the Araz River in the villages of Bajiravan, Karavelli, Karalar and Otuzikiler of the Imishli region of the Azerbaijan Republic. The ecological state of arable soils, pastures and agricultural plants grown in these places has been studied. An increased content of molybdenum, copper, manganese and other metals in soil and water samples was revealed. The morphological and biochemical indices in some agricultural plants grown in these places were studied.

KEYWORDS: heavy metals, radionuclides, pollution, bottom sediments, arable soils, mass spectrometry, ISP - MS, radio spectrometry.

INTRODUCTION:

Pollution of water and bottom sediments of rivers mainly occurs as a result of sewage discharges of industrial enterprises and settlements. The Araz River is the main water source of the Imishli region of Azerbaijan. Source of the river originates from the mountains of Turkey. Flowing through the mountainous regions of Armenia, it joins in the territory of Azerbaijan with the river Kura. In the upper reaches of the river, the water of mining enterprises for many years continue to flow into the Araz River. According to the Monitoring Department of the Ministry of Ecology and Natural Resources of Azerbaijan, hundreds of thousands of tons of solid acidic waters, salts of heavy metals and other wastes of mining enterprises of Meghri, Kajaran, Kafan and Dastakert are thrown into the tributary of the Araz -Okchuchay River. Separate times, the amount of copper in water is 25-50 times higher than the norm, and phenols in 6-15 times. As a result of the activity of the "Metzomor" NPP, 12-16 thousand tons of wastewater are discharged into the river per day [1]. It should be noted that the population of the coastal villages of the Imishli region use the waters of the Araz River for both drinking purposes and for irrigation of arable land. Various contaminants in the water entering the soil pass through the ecological links from one chain to another, eventually enter the human body. Soil is the environment with which a person is connected throughout his life. She has the ability to influence his health. When contaminated with toxicants, soil can become a source of various diseases. To assess the health of soil and water, different methods of research are used depending on the goal. In addition to anthropogenic pollution, natural disasters can also affect the release of pollutants into the environment. So, in 2010 floods on the Kura and Araz rivers led to the flooding of many villages of Sabirabad, Saatli and Imishli districts. Several months under the water left many agricultural lands and pastures. After the retreat of the water, the flooded areas were under a muddy layer and, as a result, the quality of the Araz River water and its use become a matter of special concern. Heavy metals are the most common toxic substance in natural and waste inputs. They accumulate in the microorganisms of the introductory objects and soil plants, then fall into the stern of domestic animals, and along the natural food chain into the human body [2].

Excess concentrations of heavy metals in water bodies lead to problems related to human health. In recent years, the number of scientific publications devoted to the study of the composition of water bodies and methods for their purification has been growing.

This article is devoted to the study of the composition of water, arable soils irrigated by the water of the Araz River and pastures that have been under water due to frequent flooding. The main purpose of the research was not only to study the composition of water and soil along the river, but also to identify sources of contamination with heavy metals.

The possibility of using the mass spectrometry method with inductively coupled plasma in the elemental analysis of natural and drinking waters, soils and bottom sediments is studied.

MATERIALS AND METHODS:

Field studies of the chemical composition of the sediments of the Araz rivers were carried out in the period 2015-2017. Sampling of bottom sediments and soil was carried out from the upper 10-20 cm of sediments. Field studies of the chemical composition of the Araz river bottom sediments were carried out in the villages of Bajiravan, Karalar, Karavelli and Otuzikiler of Imishli region. In the course of the research samples of bottom sediments in the river were selected. Araz on the stretch between Bajiravan-Otuzikyler at a distance of 60 km. The

number of samples was calculated on the basis of the area under study of the site at a rate of 1 sample per 1 ha. The studies were carried out using the mass spectrometer with inductively coupled plasma of the firm Agilent-Technologies 7700 ICP-MS (USA), which has a high low detection (ng / l) of elements and their isotopes with a wide range (up to 10 orders) of the linear ranges of the linearity of the calibration curve. In the literature there is a lot of information on various aspects of the use of ISP-MS, a large number of articles have been published [3-6]. The method of preparing the samples was as follows. Selected samples of Araz river bottom sediments were washed with 65% nitric acid (HNO₃) at a temperature of 700 °C for 24 hours with constant mixing. Then, after filtering out the liquid, samples of 0.1, 0.5, 1, 5 and 10% HNO₃ were prepared. A solution of the internal standard (BC) with a concentration of 3 mg / l was prepared by dilution with 1 vol. % HNO₃ of the corresponding single-element standard 1000 mg / l Rh. In all the test samples, the BC concentration equal to 25 mg / l was created by adding the required volume of the prepared solution. For each of the identified elements, the calibration was carried out in the range of contents given on the site of the INVITRO laboratory. The signals of the analytes given in Table 1 were investigated.

Table 1: The content of heavy metals in the waters of the Araz River and wells

Compound	Mass	Conc	Units	Quant by	Det	Ratio	ISTD
Cr	52	0,329	ppb	Area	Pulse	2,995E-02	Sc
Mn	55	2,240	ppb	Area	Pulse	6,728E-02	Sc
Co	59	0,088	ppb	Area	Pulse	1,233E-02	Sc
As	75	7,626	ppb	Area	Pulse	1,068E-01	Ge
Mo	95	215,906	ppb	Area	Pulse	8,862E-02	Rh
Th	232	25,923	ppb	Area	Pulse	7,761E-06	Lu
U	238	13,210	ppb	Area	Pulse	1,484E-02	Lu

The study was carried out in the "standard mode" of the ICP-MC device (Table 2).

Table 2: The value of the operation parameters of the instruments in the "standard mode".

Parameter	Range
RF power generator	1400-1500 W
The flow rate of argon through a nebulizer	1,15-1,25 л/мин
Depth of sampling	7,5-8,5 мм
Potential on the lens-extractor	2-4 V

The content of radionuclides was measured on a Canberra HPGe radio spectrometer. The study of photosynthetic activity of plants (wheat) was studied on a portable Mini-Pam device in the study areas.

RESULTS AND ITS DISCUSSION:

In analyzing the ecological situation, bottom sediments are one of the most informative objects of research. By accumulating pollutants coming in for a long period of time, bottom sediments are an indicator of the ecological condition of the territory, an integral indicator of the level of pollution. Proceeding from this, in the first of our studies, we paid the greatest attention to the investigation of the Araz bottom sediments. The standards for the content of heavy metals and

radionuclides in soil and water in the countries of the former USSR differ from those of the United States and European countries. The conducted studies in the bottom sediments of the Araz River in the villages of Bajiravan and Karalar showed that the content of some heavy metals is higher than normal. The content of Mn, Mo, Cu, Al in the waters of the Araz River also exceeds the maximum permissible concentration (MPC). The presence of Fe, Mn and Mo in groundwater and wells turned out to be above the norm. In some wells, the molybdenum content in water is 50-100 times the MPC. Increase of the molybdenum content is observed in the rivers close to the metal enrichment plants. At low concentrations, molybdenum helps the normal development of the organism (vegetable and animal). It belongs to the category of microelements. Excess of molybdenum in water leads to disruption of normal metabolism. Increased molybdenum content was observed in almost all samples of bottom sediments and in well waters. The participation of molybdenum in biological processes in certain quantities is necessary for the functioning of plants, animals and humans, but even at low intake levels it is prone to accumulation in biogeocenoses, and its concentration can reach dangerous values. Neutral and slightly alkaline waters are less favorable for migration of most metals, which precipitate in such waters in the form of insoluble hydroxides, carbonates and other salts; anionogenic elements, including molybdenum, migrate relatively easily [7]. Pollution of soils in the pastures of the villages of Bajiravan and Karaveli can be considered weak. The carried out analyzes of soils in the agricultural lands of the villages of Bajiravan, Karaveli, Karalar and Otuzikiler showed that the content of heavy metals and radionuclides basically corresponds to the normative indices. In the village of Bajiravan in the pasture, located 50-100 meters from the Araz River, on some soil samples the presence of Cu and Fe exceeded the norm by 2-3 times. In the course of the work, we investigated the aluminum content in the waters of the Araz River and in the waters of the wells of the inhabitants. Aluminum plays an active role in the life processes of living organisms, but its excess has a harmful effect on plants, starting with a concentration of 1 mg / l of water. Forming insoluble compounds with phosphates, aluminum violates their uptake by the roots [8,9]. Aluminum inhibits the absorption of calcium, magnesium, iron, B6 and C vitamins and some sulfur-containing amino acids [10,11]. A high concentration of aluminum in water disrupts the central nervous system and weakens the immune system in children. The study of the aluminum content in the water of the Araz River showed in some samples an excess of the MPC in 3-5 times.

The copper content in samples of well waters was within the norm. In the samples of arable soils and pastures of the village of Bajiravan, the copper content exceeded the MPC 4 times. Manganese falls into rivers mainly in the leaching of minerals and ores containing manganese. It is known that mining enterprises, metallurgical plants, mines can be sources of pollution of waters with a high content of copper and molybdenum. The increased content of molybdenum was also observed in the bottom sediments of the river in the area of the villages of Bajiravan and Karalar. Bottom sediments are capable of depositing metals in the form of various compounds. Heavy metals in bottom sediments are in the process of constant migration, at which their continuous exchange through the geochemical barrier system "water environment - bottom sediments" [12]. The content of manganese in some water samples of the Araz River and in the waters of the well exceeded the MPC by 3-5 times.

Table 3: The content of heavy metals in the soils of the bottom sediments of the Araz River and pasture in the village of Bajiravan (Imishli region)

Heavy metals	Araz, bottom sediments -1 mq/kq	Araz, bottom sediments -2 mq/kq	Arable soils mq/kq	Pasture soil mq/kq
Fe	38.2	28.7	11.5	9.6
Mn	37.9	27.4	14.22	13.88
Zn	1.24	0.68	1.35	0.97
Cu	12.98	5.14	6.19	6.39
Mo	23.4	39.2	3.1	12.6
Sn	0.21	0.12	0.02	0.03
Cr	0.15	0.12	0.06	0.05

A study of the heavy metals content of As, Pb, Cr, Zn, Co, Ni, Sn in the waters and bottom sediments of the Araz River in the areas of the villages of Bajiravan and Karalar showed that the content of these metals does not exceed the MPC. In one sample of water in the well (village Bajiravan), an elevated lead content was observed (exceeding the MPC by 4 times). We also conducted a radioecological study of water samples, pasture soils and agricultural lands. The concentration of radionuclides in these samples was within the limits of the MPC. In all samples of bottom sediments, the presence of U-238 and Th-232 was observed.

In the villages of Karaveli and Bajiravan, morphological indices and photosynthetic activity of wheat irrigated with water from the Araz River were studied in the field. It is known that the stress factor can act on the genome of plants, which is then passed on to the next generation [13]. The purpose of these studies was to study the effect of the Araz River water on the chlorophyll content and on the morphological parameters of plants grown under these conditions. The values obtained corresponded to regional indices.

Table 4: Indicators of PS II activity in wheat plants in the Karaveli area

N	F ₀	F _m	Y ₀
1	818	4065	798
2	886	4065	782
3	438	2192	800
4	423	2020	790
5	376	1990	811

Table 5: Indicators of PS II activity in wheat plants in the Bajiravan area

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Below are the concentrations of heavy metals and radionuclides in the waters of the Araz, in the well waters, in the soils of pastures and bottom sediments.

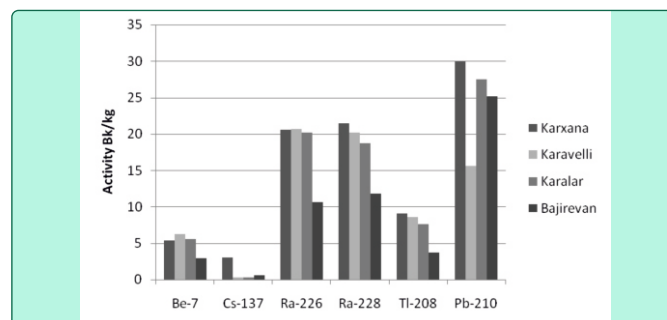


Fig 1: The content of radionuclides in the bottom sediments of the Araz River

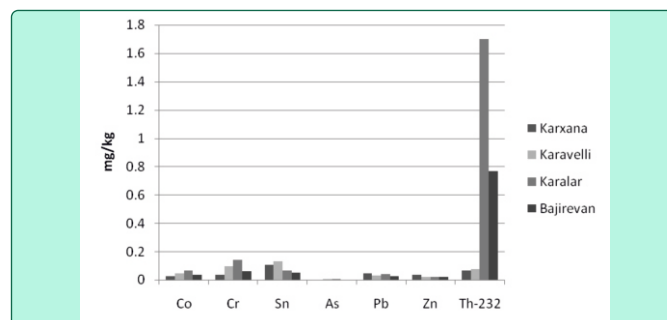


Fig 2: The presence of heavy metals in bottom sediments of Araz river

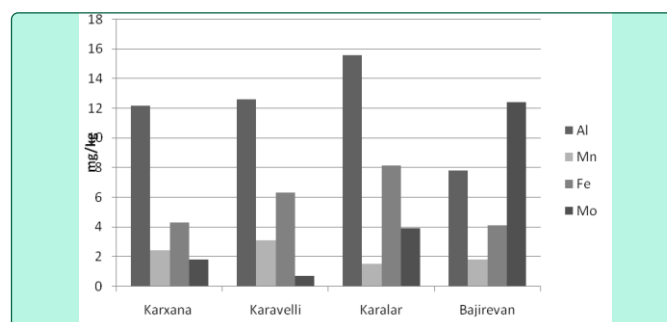


Fig 3: The presence of heavy metals in bottom sediments of Araz river

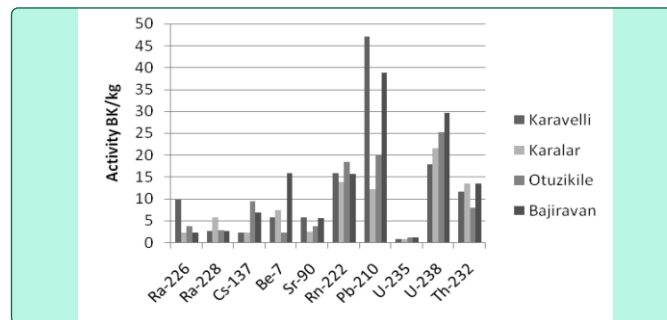


Fig 4: The presence of radionuclids in pasture soils

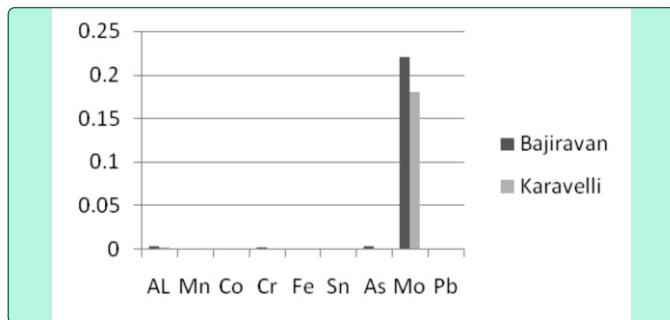


Fig 5: The presence of heavy metals in the waters of Araz River

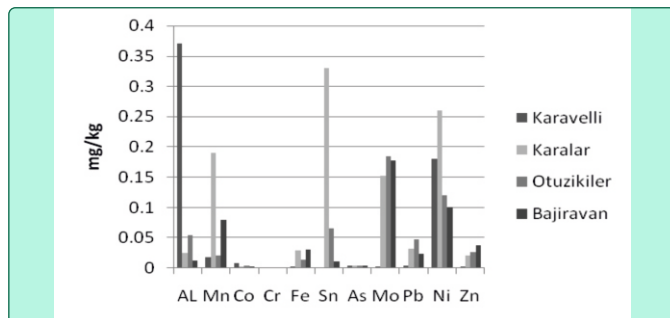


Fig 6: The presence of heavy metals in agricultural lands

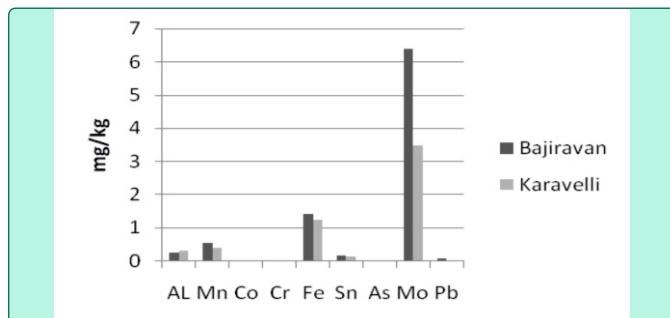


Fig 7: The presence of heavy metals in well waters in the villages of Karavelli and Bajiravan

CONCLUSIONS:

The ecological state of water, bottom sediments, soil and plants in the coastal settlements of the Araz River in the Imishli region of the Republic of Azerbaijan was studied. It was found that the content of Mo, Cu, Al, Mn in the studied water and soil samples of the study areas is higher than the normative indices. The level of concentration of molybdenum in the waters of the Araz River and in the wells of local residents many times exceeding the MPC was recorded. It has been established that, with the simultaneous presence of several heavy metals in sediments and wastewater, the soil affects differently the dependence on the ratio.

Therefore, in recommendations for treatment facilities (in particular biological), it is necessary to take into account the concentrations of heavy metals that can be either active or not affecting biological processes. A study was conducted to study the quantitative content of heavy metals and radionuclides in agricultural lands and pastures. Morphological and physiological indices of plants grown in these agricultural areas are investigated. According to the conducted studies it can be considered that the continued contamination of the Araz River water in the investigated areas may further seriously damage the health of the population.

REFERENCES:

1. Environment and security. Report of UNDP, UNEP, OSCE, 2004. ISBN: 82-7701-026-5
2. Enholm E. Environment and human health / L. Chemia 1985
3. Evans E.H. Inductively Coupled and Microwave Induced Plasma Sources for Mass Spectrometry. Cambridge: Royal Society of Chemistry, 1995. 107 p.
4. Nurubeyli TK, Nurubeyli ZK, Nuriyev KZ, Gurbanov K.B. Analyzing an Analysis of Solids by a Mass Spectrometer with Inductively Coupled Plasma, ZhTF 2017, Vol. 87, no. 2, C 117-121
5. Nurubeyli T.K. Effect of doubly charged ions in the formation of mass spectra of solids in an inductively coupled plasma mass spectrometer (ICP-MS) // Electronic Materials Processing 2017, Volume 53, N3, C 63-68
6. Taylor H.E. Inductively Coupled Plasma-Mass Spectrometry Practices and Techniques. San Diego: Academic Press, 2001. - 294 p
7. L.P. Sulimenko, L.B. Koshkina, T.A. Mingaleva, D.V. Makarov, V.A. Masloboev Study of the migration of molybdenum in the aquatic environments of the landscapes

of the Khibiny massif with the purpose of developing nature conservation measures Vestnik MSTU, vol. 18, No. 2, 2015, g. 345-355

8. Fleming, A.L., Foy, C.D., Agron. J., 1968, vol. 60, p. 172
9. Public Health Services Agency for Toxic Substances and Disease Registry, Atlanta, 1998, 143
10. Cannata, A., Nephrol. Dial. Transplantation, 1996, vol. 11, Suppl. 3, p. 6973.
11. IV Shugalei, AV Garabadzhiu, MA Ilyushin, AM Sudarikov Some aspects of the influence of aluminum and its compounds on living organisms. Ecological chemistry 2012, 21 (3); 172-186
12. Fokin DP, Frumin G.T. The content and distribution of metals in the bottom sediments of the eastern part of the Gulf of Finland // Society. Wednesday. Development (Terra Humana) - 2011. - No. 1. - C. 210-214
13. Mamedli S.A. Study of Pollination Type Genetic Instability in Nicotyanatabacuml. Cells IJSR - INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH / Volume: 3 | Issue: 10 | October 2014 • ISSN No 2277 - 8179