

ECOLOGICAL ASSESSMENT OF THE IMPACT OF ARAZ RIVER POLLUTION ON THE ENVIRONMENT IN COASTAL REGIONS OF AZERBAIJAN

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Abstract. The ecological state of the water and soil in the coastal settlements of the Araz River, in the villages Bajiravan, Javadkhanly, Shakhverdili, Shammadli and Gebektala of the Imishli region of the Republic of Azerbaijan, was studied. The compositions of the water and soil samples were investigated via mass spectrometric and radio spectrometric methods. Applying the ICP-MS method to analyze water, soil and other environmental objects provides a unique opportunity to use stable isotopic tracers to control the dissolution stage of each analyzed sample. The amounts of heavy metals and radionuclides in well water in the courtyards of the local population were determined. The degree of contamination of soil and plants in cultivated areas has been studied. The content of molybdenum, copper and manganese in some water and soil samples exceeded standard values. Concentrations of molybdenum that were many times higher than the permissible limit were recorded in the waters of the Araz River and wells with drinking water. According to the research, further pollution of the Araz River in the studied areas can cause irreparable harm not only to the population's health but also to livestock.

Keywords: Mass spectrometry, heavy metals, radionuclides, molybdenum, well waters, bottom sediments, chlorophyll fluorescence.

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1. Introduction

The environmental tensions that have arisen in recent decades can be resolved through consistent, practical solutions to environmental problems. In this regard, rethinking all spheres of human activity and first, science, as a decisive factor in socioeconomic development, is of key importance. The pollution of surface waters and soil with various toxicants is one of the clearest indicators of the general deterioration of the natural environment. The rate of accumulation of pollutants in water and soil ecosystems because of technogenic activity significantly exceeds the rate of natural

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biodegradation and existing technologies do not allow for dealing with such pollution quickly and effectively (Chapman *et al.*, 2003; Wang *et al.*, 2004).

One of the categories of dangerous water and soil pollutants is heavy metals, which occupy one of the leading positions among all environmental pollutants. Many representatives of this group, such as lead, copper, zinc and cadmium, even in very small quantities, can cause immunological, oncological and other types of diseases. Scientists from different countries have shown that approximately 70% of heavy metals enter the human body through food (Wong *et al.*, 2005; Wyszowska *et al.*, 2003).

More than 70% of Azerbaijan's freshwater resources originate from the Kura and Araz Rivers, which flow from Turkey through Georgia and Armenia before reaching the Caspian Sea within Azerbaijan's borders. These rivers are heavily polluted with industrial and domestic waste across the territories of these countries. In recent years, the pollution of the Araz River with waste of mining enterprises has been discussed in international environmental organizations (Report of UNEP 2022, Human Rights Council 2023, 2024). This situation has been extensively documented in Iranian media and in reports from Azerbaijan's Ministry of Ecology and Natural Resources. The primary pollutants in these waters are heavy metals and radionuclides, pervasive in both natural environments and waste materials. They accumulate in soil and vegetation, entering the food chain through livestock and eventually impacting human health (Enholt, 1985). Exceeding the concentration of heavy metals in water bodies leads to problems associated with human health. Agricultural fields in all areas bordering Iran are irrigated with water from the Araz River. The water of the Araz River is a source of drinking water for the inhabitants of these regions. In 2015-2017, a study was carried out on the ecological state of soil, water and plants in the territories of the Imishli and Saatli regions within the framework of an international grant from the STCU (Science and Technology Center in Ukraine) under project number 6029. The project examined the ecological state of the environment in villages flooded during the 2010 flood. In some villages located along the Araz River (Hadzhikasimli, Kamalli, Garavalli, Bajiravan, Garalar, Otuzikilar, etc.), the degree of pollution of water and bottom sediments of the Araz River, as well as crop soils, was studied (Mammadli *et al.*, 2020).

There are two primary categories of analytical methods used to detect heavy metals: electrochemical and spectrometric methods. As microelectronics technology advances, electrochemical methods are experiencing new developments. Historically, these methods had been increasingly replaced by spectrometric methods over time. Among the spectrometric methods for the determination of heavy metals, the first method involves atomic absorption spectrometry with different atomizations of samples: atomic absorption spectrometry with flame atomization and atomic absorption spectrometry with electrothermal atomization in a graphite cell. The main method for determining several elements simultaneously is inductively coupled plasma-mass spectrometry (ICP-MS). In addition to ICP-MS, other spectrometric methods have detection limits that are too high for the determination of heavy metals in water (Evans, 1995; Taylor, 2001).

The advantages of inductively coupled plasma mass spectrometry include their high sensitivity and consequently, the small quantities of samples required to determine the content of heavy metals. Moreover, to carry out several steps (atomic absorption analysis, spectrophotometry, spectropolarimetry), the sample must be transferred into solution, which makes such analyses of the content of heavy metals quite high.

In the presented article, as a continuation of these works, the amount of heavy metals and radionuclides hazardous to public health was determined in soil and water samples taken from the household plots of the local population in the coastal areas of the Araz River in the villages of Bajiravan, Javadkhanly, Shakhverdili, Shammadli and Gebektala. Research was carried out from 2018-2023 in the villages of Bajiravan, Javadkhanly, Shakhverdili, Shammadli and Gebektala, located along the Araz River. The article also examines the composition of water, arable soils irrigated with water from the Araz River and pastures that are under water due to frequent floods. The purpose of our research was to study the environmental situation in the villages of Bajiravan, Javadkhanly, Shakhverdili, Shammadli and Gebektala, located on the banks of the Araz River and to determine the degree of contamination of the soil and water used by the local population in their garden plots.

2. Materials and methods

During autoclave decomposition of the samples, nitric acid HNO_3 (nitric acid 65%) was used, deionized water with a resistivity of 18.2 MOhm cm was used, as were solutions of multielement and single-element standards (High-Purity Standards, USA). To store the solutions, we used glass volumetric flasks with a ground stopper (GOST 1770-74), disposable polyethylene bottles with a capacity of 20 ml and disposable polyethylene tubes with volumes of 15 and 50 ml (Labcon, USA). All the dishes were presoaked for at least 4-5 days in 5% HNO_3 and washed with deionized water before use.

To carry out mass spectral analysis of the elements, a quadrupole mass spectrometer Agilent Technologies ICP-MS 7700; USA) was used with the following operating parameters: generator output power 1300 W; a set of standard nickel cones; quartz conical spray chamber cooled to 3°C; flow rate of plasma-forming argon flow 13 l/min; argon auxiliary flow rate 0.9 l/min; flow rate of argon in the nebulizer, 0.95 l/min and flow rate of the analyzed sample, 0.8 ml/min. There is sufficient information in the literature on various aspects of the use of ICP-MS (Nurubeili, 2018; Nurubeyli & Ahmadova, 2021; Nurubeyli *et al.*, 2020). The radionuclide content was determined using a Canberra (USA) HPGe radio spectrometer. The maximum quantum yield of fluorescence in seedlings was measured on a MINI-PAM fluorimeter (Germany). The background radiation was measured with an MKS-AT1125 dosimeter. The selected samples were treated with 65% nitric acid (HNO_3) at 70°C for 24 hours with constant stirring. Next, after filtering the precipitate, samples of 0.1, 0.5, 1, 5 and 10 vol % HNO_3 were prepared. An internal standard (IS) solution with a concentration of 25 mg/L was prepared by diluting the corresponding single-element standard (1000 mg/l Rh) with 1 vol. HNO_3 . For all the studied samples, a IS concentration of 25 mg/l was created by adding the required volume of the prepared solution. Water samples were taken from sections of the Araz River passing through the territory of these villages, as well as from wells and groundwater in household plots of the population. Analysis of water samples was carried out over the course of 24 hours. Soil and bottom sediment samples for analysis were taken from the upper (0-20 cm) layers, 1 kg each.

3. Results and discussion

At the beginning of our research, we analyzed samples of water and bottom sediments from the Araz River in the areas of the villages of Bajiravan, Javadkhanly, Shakhverdili, Shammadli and Gebektala. Water and bottom sediments from wells and irrigation canals were also examined. In these villages, irrigation canals were built from the Araz River for the irrigation of agricultural fields and household use. Toxicants discharged into rivers are highly likely to migrate from soil to plants in agricultural fields. For this reason, ecological monitoring of soil and plants was also carried out in cultivated areas. Based on the results of the studies, it was established that the molybdenum content in well water samples is many times higher than the maximum permissible concentrations. The amount of iron, manganese and copper in the well-water samples was also several times greater than normal. It should be noted that the molybdenum content in water samples, bottom sediments and soil exceeded the maximum permissible concentration (Figures 1, 2, 3).

Groundwater on the Kura-Araz Plain is often located at a depth of 1-5 meters from the Earth's surface. In some cases, groundwater may mix with well water. The local population widely uses well water to irrigate agricultural fields and for household purposes. The regular use of well water for various purposes creates a risk of life-threatening heavy metals and other toxicants entering the human body.

In soil samples taken from pastures, agricultural fields and coastal areas, molybdenum content exceeded the norm by 2-4 times (Figures 4, 5, 6). The content of other heavy metals in the arable and pasture soils of the residents was within normal limits.

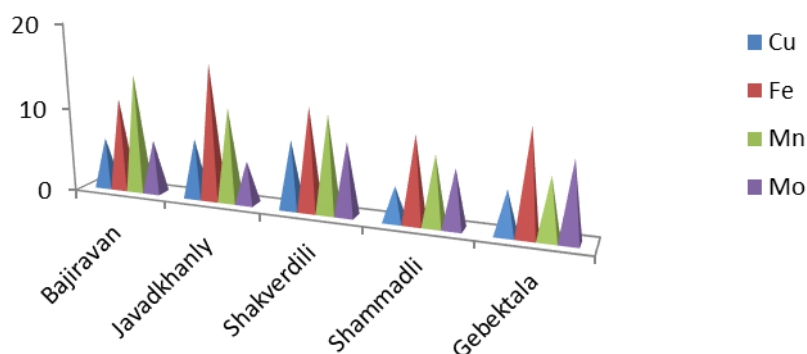


Figure 1. The amount of heavy metals in the samples taken from the bottom sediments of the Araz River (mg/kg)

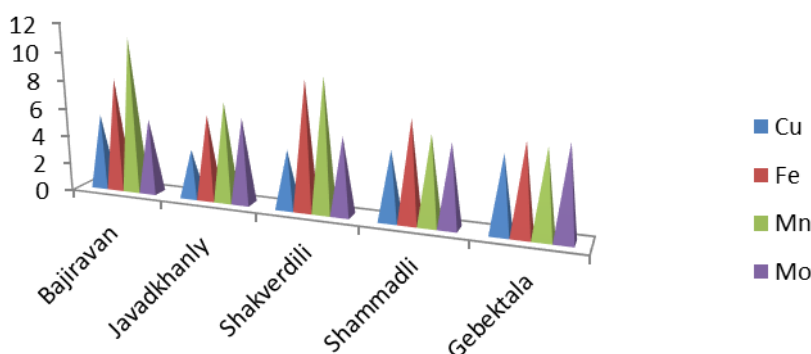


Figure 2. The amount of heavy metals in samples taken from bottom sediments irrigation canals (mg/kg)

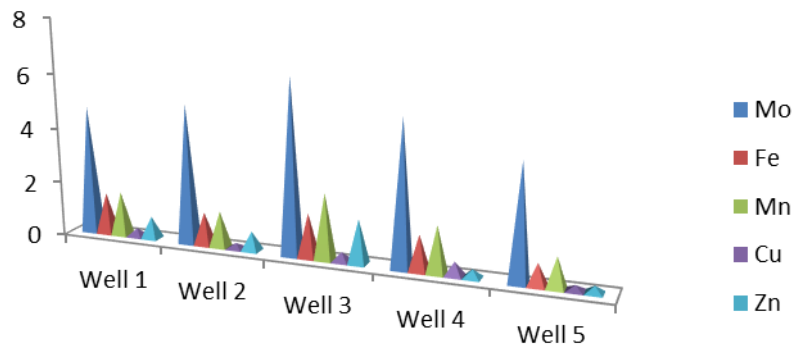


Figure 3. Amount of heavy metals in well water samples (mg/l) (Bajiravan - Javadkhanly)

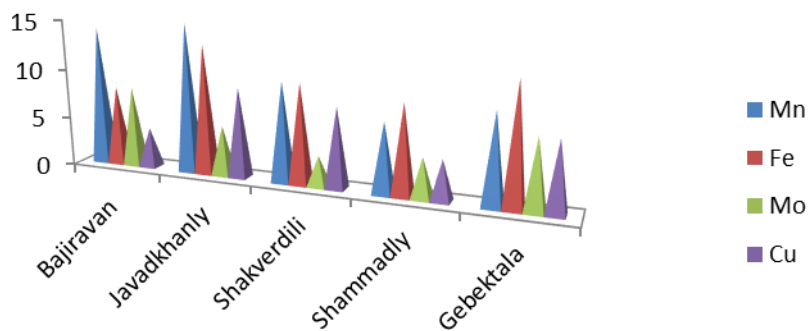


Figure 4. Amount of heavy metals in soil samples taken from agricultural fields (mg/kg)

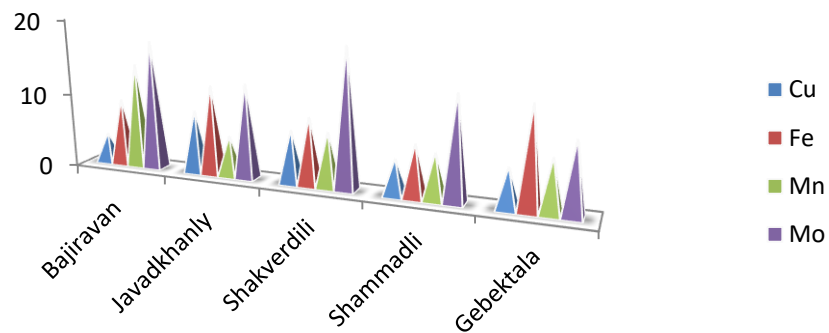


Figure 5. Amount of heavy metals in soil samples taken from coastal soils (mg/kg)

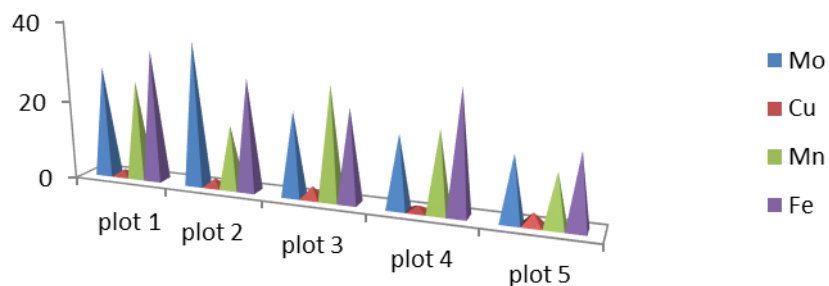


Figure 6. Amount of heavy metals in soil samples taken from pasture (mg/kg) (Bajiravan – Javadkhanly)

During the radioecological studies, we first measured the level of background radiation in fields irrigated with water from the Araz River and in coastal pastures. The radiation background in the studied areas was within the normal range (5 - 9 $\mu\text{R}/\text{hour}$). The composition and activity of radionuclides were studied in soil samples taken from agricultural fields and pastures. The results of these measurements are shown below.

Table 1. Composition and activity of radionuclides in soil samples from pastures and arable fields in the studied villages

Radionuclides (Bq/kg)	Ra 226	Ra 228	Rn 222	U 238	U 235	Th 232	Be 7	Sr 90	Cs 137	Pb 210
Pasture soils	3-12	4-8	11-20	17-28	1-4	8-14	3-16	2-7	5-13	10-38
Arable soils	4-9	2-7	12-18	20-35	2-5	11-16	5-19	3-6	3-10	13-42

The content of radionuclides in these samples was within the maximum permissible concentration limits (Table 1).

It is known that heavy metals suppress the process of photosynthesis in plants (Küpper *et al.*, 1996). Chlorophyll fluorescence is a useful tool for determining photosynthetic activity. Measuring chlorophyll fluorescence makes it possible to assess the influence of stress factors on the process of photosynthesis in plants (Kalaji *et al.*, 2018; Joshi *et al.*, 2004; Guo *et al.*, 2015; Muslumova *et al.*, 2022a; Mammadli *et al.*, 2021). The maximum quantum yield of Photosystem 2 (PS2) is used to assess the maximum efficiency of PS2 and is denoted by F_v / F_m , where $F_v = F_m - F_0$ is the variable fluorescence, F_0 is the initial fluorescence level, F_m is the maximum fluorescence level: $F_v / F_m = (F_m - F_0) / F_m$.

For most plants, the F_v/F_m value is 0.83. Decrease in this value may indicate the stressful state of the plant (Schreiber, 2004; Maxwell *et al.*, 2000). Many studies on plant stress have also shown that the F_v/F_m ratio can be used as an indicator of heavy metal toxicity (Rau *et al.*, 2007; Chen *et al.*, 2015, 2018). Based on this, we studied the effect of water and soil pollution on chlorophyll fluorescence in wheat grown in the fields and garden plots of residents. Measurements of the maximum quantum yield of fluorescence in wheat fields were carried out at 30-40 points in each plot.

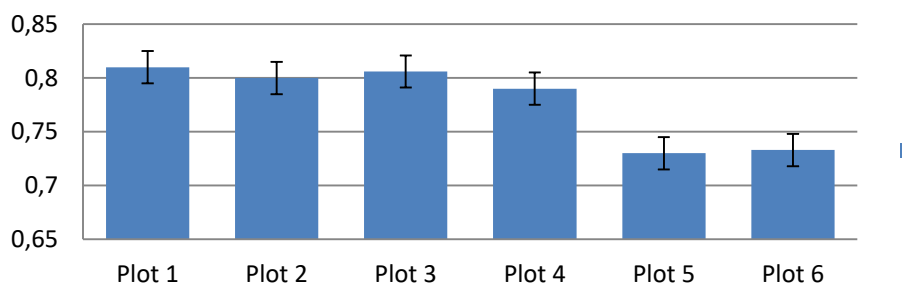


Figure 6. The maximum quantum yield of fluorescence - F_v / F_m

In the village of Bajiravan, in some areas of a wheat field located 250 meters from the Araz River, the level of maximum quantum yield of fluorescence in plants was

below the standard indicator (Figure 7, plots 5, 6). It should be noted that we did not observe any significant changes in morphological parameters of the studied plants.

The composition and number of heavy metals in the bottom sediments of rivers and lakes are important indicators of the state of the aquatic environment. Heavy metals are deposited in sediments through the process of adsorption, precipitation and diffusion (Ramirez *et al.*, 2005). Heavy metal pollution is a major threat to aquatic ecosystems due to the ability of heavy metals to easily reach the food chain. Once in the water system, heavy metals can settle in bottom sediments and become a long-term source of pollution. Some heavy metals that accumulate in sediments are dangerous even in small quantities. For this reason, analyzing the bottom sediments of water sources is extremely important. The degree of pollution risk can be determined based on these indicators (Wang *et al.*, 2024; Jaskuła *et al.*, 2021). During our research, we examined the ecological state of the bottom sediments of the Araz River and the irrigation canals flowing from the river. In many samples of bottom sediments from irrigation canals, molybdenum concentrations exceeded the permissible limits.

A low concentration of molybdenum contributes to normal development and does not pose a danger. However, when the amount of molybdenum exceeds the standard, it can cause many diseases. It is known that mining enterprises and metallurgical plants are the main sources of water pollution associated with copper and molybdenum. In water and bottom sediment samples from the Araz River and irrigation canals, the molybdenum content was also higher than normal. Molybdenum tends to accumulate in the body even at low concentrations. The constant consumption of such water can lead to its accumulation in the human body at dangerous levels. Molybdenum can also easily migrate from water into soil and plants. Molybdenum enters plants from the soil mainly in the form of molybdate (MoO_4). The molybdenum concentration increases in soil at pH values > 5 . It has been established that when the concentration of molybdenum in feed is in the range of 3 - 10 mg/kg, it becomes dangerous for farm animals (Neunhäuserer *et al.*, 2001; Eriksson *et al.*, 2017; Axelson *et al.*, 2018; Majak *et al.*, 2004; Gardner *et al.*, 2003).

Recently, serious attention has been given worldwide to the study of factors leading to genetic diseases. Genetic disorders that occur in childhood can cause negative health consequences in the future. The mutagenic activity of heavy metals and radionuclides has been proven at the cellular level using various test systems. Studies assessing the mutagenic activity of molybdenum compounds have revealed their high genotoxic effect. Exposure to high doses of molybdenum has also been found to cause DNA damage in plants (Neri *et al.*, 2006; Fu *et al.*, 1999; Holland *et al.*, 2011; Xiaoqing *et al.*, 2021; Lin *et al.*, 2022; Singh *et al.*, 2024; Özkan *et al.*, 2024). It can be concluded that regular use of contaminated water for drinking and irrigation can lead to serious environmental and genetic consequences. Periodic monitoring of the level of heavy metals, radionuclides and other hazardous toxicants in water and soil will help ensure environmental safety and public health in the coastal villages of the Araz River.

4. Conclusion

The ecological state of water and soil was studied in the villages of Bajiravan, Javadkhanly, Shahverdili, Shammadly and Gebektala. The composition and amount of heavy metals and radionuclides in soil and water samples taken from irrigation canals, wells, bottom sediments, agricultural lands and pastures were determined. The

composition and quantity of heavy metals and radionuclides in soil and water samples taken from irrigation canals, wells, bottom sediments, agricultural lands and pastures were determined. Our study showed increased content of Mo, Mn and Cu in some water and soil samples. The results of these studies indicate that the ongoing pollution of the Araz River water can cause serious damage to the environment and the health of the population living in coastal settlements.

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