NEUTRALIZATION AND PURIFICATION OF NATURAL WATERS FROM HEAVY METALS IN COASTAL ARAZ RIVER

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By mass spectroscopy with inductively coupled plasma, data on the content of heavy metals in the Araz River in the villages of Bajiravan, Karavelli, Karalar and Otuzikiler of the Imishli district of the Republic of Azerbaijan were studied. The ecological condition of arable soils, pastures and agricultural plants grown in these places has been studied. Increased content of molybdenum, copper, manganese and other metals in soil and water samples was revealed. And also investigated and developed the process of cleaning and neutralizing the soil from heavy metals, through the influence of strong electric fields and discharges. The possibility of cleaning the soil from a certain name of heavy metals by exposure to ozone water has been identified.

Keywords: heavy metals, contaminants, bottom deposits, arable soils, mass spectrometry, ICP-MS.

INTRODUCTION

Pollution of river waters and bottom sediments is mainly due to releases of sewage and wastewater from industrial plants and human settlements. The Araz River is the main water source of the Imishli region of Azerbaijan. It originates from the mountains of Turkey. Flowing through the mountainous regions of Armenia, it connects in Azerbaijan with the Kura River. In the upper reaches of the river in Armenia, for many years the dumping of mining enterprises of Kajaran, Meghri and Kafan into the Araz River has continued. According to the Monitoring Department of the Ministry of Ecology and Natural Resources of Azerbaijan, hundreds of thousands of tons of solid acid water, salts of heavy metals and other waste of mining enterprises Megri, Kajaran, Kafan and Dastakert are thrown into the tributary of the Araz Okchuchay River. Individual times, the amount of copper in water was 25-50 times higher than normal and phenols 6-15 times. As a result of the activities of the Metsomor *NPP*, 12-16 thousand tons of wastewater are emitted into the river per day [1]. It should be noted that the population of the coastal villages of the Imishli district uses the waters of the Araz River both for drinking purposes and for irrigation of arable land. Various pollutants, entering the soil in water, pass through environmental links from one chain to another; at the end they enter the human body. Heavy metals are the most common toxic substance in natural and wastewater inlets. They accumulate in microorganisms of introductory objects and soil in plants, and then enter the feed of domestic animals and along the natural food chain into the human body [2].

Although heavy metals may have a positive effect on the viability of algae in a certain balance in an introductory environment, exceeding their concentrations in reservoirs leads to problems directly related to human health. Therefore, the number of scientific publications on the study of the composition of reservoirs and their purification methods is growing so rapidly. This article is devoted to the study of the composition of water, arable soils irrigated by the water of the Araz River. The main goal of the research was not only to study the elemental composition of water and soil with an inductively coupled plasma mass spectrometer and to identify sources of contamination with heavy metals, as well as a detailed description of the process of cleaning soil and water from heavy metals by ozonation.

RESEARCH MATERIALS AND METHODOLOGY

Field studies of the chemical composition of the bottom sediments of the Araz Rivers were carried out in the period 2020-2021. Sampling of bottom sediments and soil was carried out from the upper 10-20cm sediments. Field studies of the chemical composition of the bottom sediments of the Araz River were carried out in the villages of Badzhirevan, Karalar, Karavelli and Otuzikiler of the Imishlinsky district. During the studies, samples of bottom sediments were taken in the river. Araz on the segment between Bajiravan-Otuzikiler at a distance of 60km. The number of samples was calculated based on the area of the area under study based on 1 sample per 1ha. Studies were carried out in the "standard mode" of operation of a mass spectrometer with inductively coupled plasma from Agilent-Technologies 7700 *ICP-MS* (USA), which has a high low range of detections (ng/l) of elements and their isotopes in wide (up to 10 orders) dynamic ranges of linearity of calibration dependence (tab.1.2). There is a lot of information in the literature on various aspects of the use of *ICP-MS*, a large number of articles are published [3-7]. The sample preparation procedure was as follows. The samples were treated with 65% nitric acid (HNO$_3$) at a temperature of 700C for 24 hours with constant stirring. Samples of 0.1, 0.5, 1, 5 and 10 vol% HNO$_3$ were then prepared by filtration. An internal standard (*BC*) solution with a concentration of 25mg/l was prepared by dilution with 1 vol.% HNO$_3$ of the corresponding one-element standard with 1000mg/l *Rh*. In all test samples, a *BA* concentration of 25mg/L was created by adding the required volume of prepared solution.

Table 1.

Metal content 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

Table 2.

The value of the operating parameters of the devices in the "standard mode"

Parameter	Range
RF generator power	1400-1500 W
Flow rate of argon through the sprayer	1.15-1.25 l/min
Sampling depth	7.5-8.5 mm
Potential on the extractor lens	2-4 V

RESULTS AND DISCUSSION

Studies of the composition of the Araz River in the villages of Bajiravan and Karalar in the Imishli region showed that the content of heavy metals is increased. The content of Mn, Mo, Cu, Al in the waters of the Araz River also exceeds the maximum permissible concentrations (MPC). The presence of Fe, Mn and Mo in groundwater and wells was above normal. In some wells, the content of molybdenum in water is 50-100 times higher than MPC.

Although iron is not a toxic substance, its presence in water leads to a deterioration of its organoleptic and taste properties and the appearance of brown precipitate on the surfaces that come into contact with water. Manganese is a pollutant that is classified as a hazardous substance.

Both pollutants shall be removed from the water up to the level specified in the standards. In particular, for drinking water, the norm for manganese and iron content is specified in SanPiN 2.1.4.1074-01 "Drinking water. Hygienic requirements for water quality of centralized drinking water supply systems "and SanPiN 2.1.4.1116-02" Drinking water. Hygienic requirements for the quality of water packed in containers. "

Often, iron and manganese are contained in water as organic compounds, which greatly complicate the filtration process. Standard methods of deiron and demanganation of water (aeration, liming, cation) in this case are ineffective. In Azerbaijan, this problem is especially relevant in oil-bearing areas, where water almost always contains a large amount of impurities of organic substances (petroleum products) and dissolved gases, has increased chromaticity and turbidity.

Currently, the problem of increasing concentrations of molybdenum in water bodies that significantly exceed the permissible values is being updated. The participation of this element in biological processes in certain quantities is necessary for the functioning of plants, animals and humans, but even at low levels of admission it is prone to accumulation in biogeocenoses, and its concentration can reach dangerous values. In addition, molybdenum has recently become one of the controlled indicators; with the high cost of environmental charges for its discharge, the interest of enterprises in treating waste water from molybdenum increased. Neutral and slightly alkaline waters are less favorable for migration of most metals, which in such waters precipitate in the form of insoluble hydroxides, carbonates and other salts, anionic elements, to which molybdenum belongs, migrate relatively easily [8].

Soil analyses carried out in the agricultural lands of the villages of Bajiravan, Caravelli, Karalar and Otuzikiler showed that the content of heavy metals and radionuclides is mainly in accordance with regulatory indicators. In the village of Bajiravan, in a pasture located 50-100 meters from the Araz River, the iron content on some soil samples, the presence of Cu and Fe exceeded the norm by 2-3 times. Analyses of some water samples of the Araz River also showed an excess of MPC by 5-10 times (table 3). During the work, we investigated the aluminum content in the waters of the Araz River and in the waters of the wells of residents.

It is known that mining and processing plants, metallurgical plants, mines can be sources of water contamination with a high content of copper and molybdenum. We observed an increased content of molybdenum in the bottom sediments of the river in the Bajiravan and Karalar villages. Bottom deposits 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 occurs through the geochemical barrier system "water medium - bottom sediments" [9]. Increased molybdenum content can be observed in rivers that are located near metal enrichment plants. At low concentrations, molybdenum helps the normal development of the body (both plant and animal). It falls into the category of micronutrients. Excess molybdenum in water leads to disruption of normal metabolism. Increased molybdenum content was observed in almost all bottom sediment samples and well waters. In some samples, the concentration of Mo exceeded MPC tens and hundreds of times.

Table 3.

The content of heavy metals in the bottom sediments of the Araz River and Pasture   soil in the Bajiravan area (Imishli region)

Heavy metalls	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

In samples of arable soils and pastures of the village of Badzhiravan, the copper content exceeded the MPC by 4 times. Manganese enters rivers mainly during leaching of minerals and ores that contain manganese [10]. The manganese content in some samples of the water of the Araz River and in the waters of the well exceeded the MPC by 3-5 times.

In the above cases, the pre-oxidation of organic compounds by ozone is necessary. By oxidizing complex compounds, ozone causes precipitation of iron and manganese. After that, it remains only to filter water from precipitated metals using coal and sand filters or by prolonged settling.

Ozone is very useful for the oxidation of iron or manganese in complex connection with anionic groups and substances giving higher chromaticity to water. By oxidizing these complex compounds, ozone eliminates the chromaticity of water and causes iron and manganese deposition. The oxidation process converts soluble salts to insoluble salts, so subsequent filtration or settling of water is necessary to free it from precipitation. Oxidation of metals by ozone is effective at any values   of pH found in natural waters.

The amount of ozone required for dehydration and demanganation is selected experimentally. Typically, the ratio is as follows: 1 mg ozone per mg iron and 4 mg ozone per 1 mg manganese. More precise values can be obtained by conducting experiments with water samples and starting a pilot plant. The study of the process of cleaning and neutralizing the soil from heavy metals by the influence of the electric field of the barrier discharge was carried out on the installation shown in figure 1.

Consider the chemistry of the interaction of ozone with iron and manganese.
Ozone production:

1. Atmospheric air is cleaned of strong pollutants and particles using a pre-treatment filter.

2. Purified air enters the oxygen concentrator, where it is converted into a gas mixture with 85-95% oxygen content.

3. Oxygen is supplied to the ozone generator. Ozone is produced in its cells under the influence of corona discharge from oxygen.

Explanation of the figure:

• Water with a high content of iron and manganese enters the contact vessel.

• Water bubbling occurs in the contact vessel (gas bubbles are passed through the liquid bed). As a result, iron and manganese are oxidized to insoluble compounds.

• Some of the connections are seated directly in the contact container. Periodically, the contact vessel is flushed to remove sludge.

• Another part of the compounds exists as water-suspended particles. After the contact vessel, the ozonated water undergoes mechanical purification in coal and sand filters, where metal residues are removed from it.
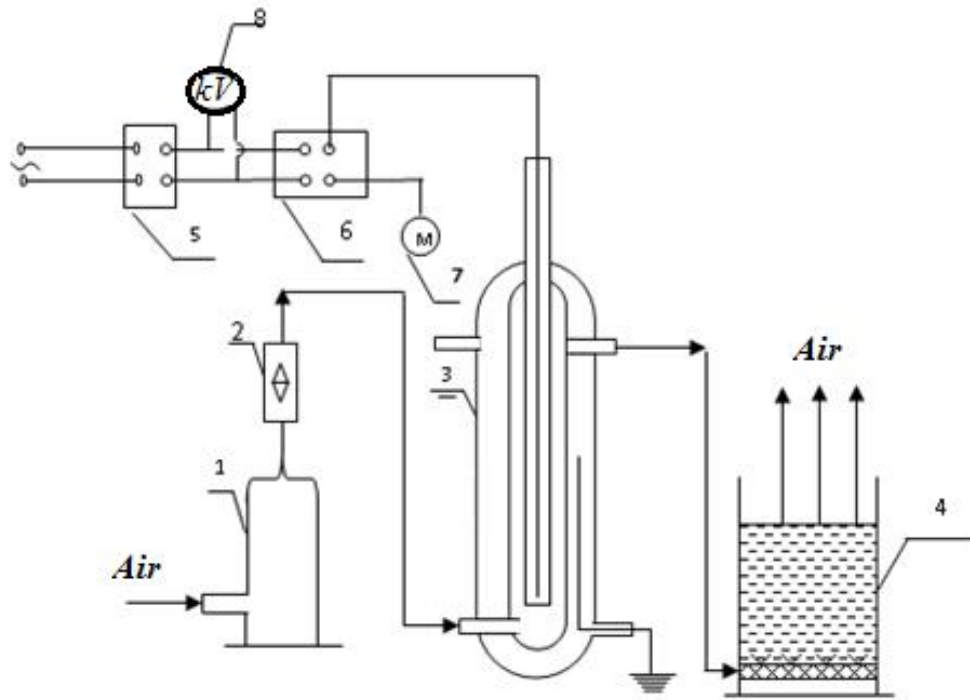
Fig. 1. Laboratory plant for cleaning and neutralization of soil from heavy metals, by means of electric field of barrier discharge: 1 - compressor for air supply; 2 - rheometer-flowmeter; 3 shows a reactor for creating a barrier discharge; 4 - bubbling absorber with water; 5 - AI-80 high-voltage transformer; 6 - LATR-9A avtotransfomator; 7 is a milliampermeter; 8 - kilovoltmeter.

Tables 4 show the results of quantitative analysis of soil samples, and bottom sediments of the Araks River purified before and after ordinary water. As the analysis of these tables shows, the content of heavy metals in the source soils exceeds the maximum permissible concentration (*MPC*).

Studies of the composition of water taken from the Araks River and wells showed that the content of heavy metals is increased (Table 5). The content of Mn, Mo, Cu, Al in the waters and bottom sediments of the Arax River also exceeds the *MPC*. The presence of Fe, Mn and Mo in groundwater and wells was above normal. In some wells, the content of molybdenum in water is 50-100 times higher than *MPC*.

Treatment of samples with ozonated water at different voltages of 8*kV* and 14*kV* is shown in Figures 2 and 3. As can be seen from the figures after treatment with ozonated water, at voltages of 8*kV* and 14*kV*, in soils at different depths of 0-10*cm* and 10-20*cm*, a decrease in the concentration of elements Ni, Pb, Mo and Al by 80-98% is observed.

Table 4.

The content of heavy metals in bottom sediments and pasture soils taken in villages near the Araks River.

Heavy metals	Bottom deposits Arax - 1 mg/kg		Bottom deposits Arax - 2 mg/kg		Arable soils mg/kg		Pasture soil mg/kg	
	Analysis of the outcome sample	Cleaning with normal water,	Analysis of the outcome sample	Cleaning with normal water,	Analysis of the outcome sample	Cleaning with normal water,	Analysis of the outcome sample	Cleaning with normal water,
Fe	38.2	37,3	28.7	26,22	11.5	10	9.6	8,13
Mn	37.9	36,7	27.4	25,45	14.22	13,8	13.88	12,5
Zn	1.24	1,18	0,68	0,5	1.35	1,2	0.97	0,89
Cu	12.98	11,33	5.14	5,12	6.19	5,9	6.39	5,78
Mo	23.4	22,4	39.2	38,98	3.1	2,41	12.6	11,3
Al	12,15	11,55	12,95	11,86	14,98	13,73	8,15	7,1

Table 5.

Heavy metal content in the waters of the Araks River and drinking water wells.

Compound	Mass	Conc.	Units	Quant by	Det	Ratio	ISTD
Al	27	2,329	ppb	Area	Pulse	2,995E-02	Sc
Mn	55	212,240	ppb	Area	Pulse	6,728E-02	Sc
Fe	56	100,088	ppb	Area	Pulse	1,233E-02	Sc
Cu	64	79,626	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

Concentrations of heavy metals Mn, Mo, Cu, Al in arable and pasture soils and bottom sediments of the Araks River treated with ozonated water decreased by 50-60% at stresses of 8 kV (a and b), 14 kV (c and d) (fig. 2).

What explains this change in metal concentrations after soil treatment with ozonated water at 8-14 kV.
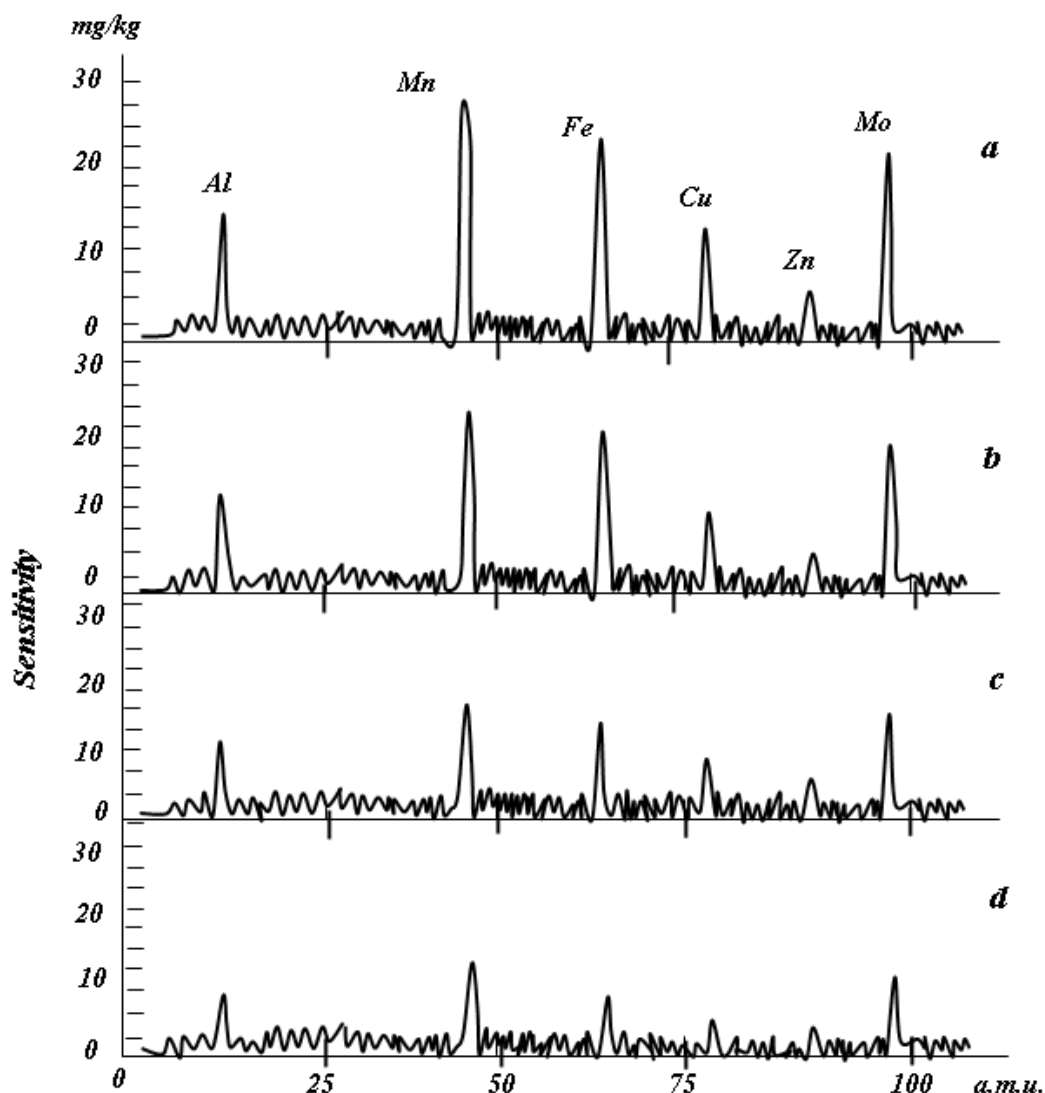

Fig. 2. The dependence of the sensitivity of the mass spectrometer on the mass of heavy metal ions in the bottom sediments of the Araks River, arable and pasture soils. Soil treatment with ozonated water: U = 8 kV at 15 min. (a), at 30 min. (b); U = 14 kV at 15 min. (c), at 30 min. (d).

Process of chemical oxidation of pollution in soils, soil, an underground and surface water is based on return of electrons from an external not steady layer of an electron shell of atoms of substances and elements that leads to transition of pollutant to less toxic and reactive form. Atoms of elements that have a small number of electrons in the outer electron layer are prone to electron recovery. The process is an integral part of the redox interaction of the contaminant and the chemical or reactive surface.

Ozone is formed from ordinary oxygen under the influence of smoldering electric discharge or ultraviolet radiation. Ozone, being one of the strongest oxidizers, has strong disinfectant properties. Ozone has a very high electron affinity (1.9 eV), which determines its properties as a strong oxidant, superior in this regard only to fluorine. Despite the high oxidative potential of ozone, it interacts extremely selectively. The reason for this selectivity is the polar structure of the ozone molecule, or more precisely, a positively polarized oxygen atom, which gives the entire molecule an electrophilic character. Therefore, molecules with high electron density are the most preferred reactive elements. In ozonation, unlike chlorination, oxidation reactions take place, such as with phenol and derivatives thereof, which lead to the opening of the aromatic ring and the production of non-toxic end products. These products are easily removed by filtration.

With metals, ozone forms non-reactive oxides (iron, manganese, aluminum oxide, etc.). The oxides precipitate and are easily eliminated by filtration. Organic substances containing iron and manganese are first destroyed by ozone, and then metals form oxides [11]. Ozone readily oxidizes iron and manganese salts to form insoluble substances, which can then be removed mechanically. If iron and manganese are contained in the form of organic compounds or colloidal particles (with a size of 0.1-0.01 microns), then the de-gelation and demanganation of water by conventional methods is ineffective. In this case, it is necessary to pre-oxidize complex organic compounds with ozone, leading to their cleavage, after which it becomes possible to remove iron and manganese by one of the usual methods. By oxidizing complex compounds, ozone converts soluble salts to insoluble salts, which are subsequently easily removed.

CONCLUSIONS

The ecological state of water, and soils in coastal settlements of the Araks River of the Republic of Azerbaijan were investigated. It was revealed that the content of Mo, Cu, Al, Mn in the studied samples of waters and soils in the studied areas is higher than the normative indicators. The level of molybdenum concentration in the waters of the Araks River and in wells with drinking water has been recorded many times higher than the *MPC*.

It has also been found that the presence of heavy metals in wastewater reduces the efficiency of treatment and does not fully take advantage of intensive technologies.

The process of soil treatment and neutralization from heavy metals by exposure to ozone water has been investigated and developed.

It was found that in soil treated with water, ozonized 15 and 30 minutes at both $8kV$ voltage and $14kV$ voltage, a significant decrease in the concentration of Ni, Pb, Mo, Cu and Al was observed.

The use of the *ICP-MS* method in the analysis of waters, soils and other environmental objects provides a unique opportunity to use stable isotopic labels to control the dissolution stage of each analyzed sample.

According to studies, it can be considered that further pollution of the Araks River in the studied territories can cause irreparable harm not only to the health of the population, but also to livestock.

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