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Assessment of the Ecological State of the Katnakhbyur River

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ABSTRACT

The article presents the results of the assessment of the pollution of the Katnakhbyur river. The purpose of this work is to study the ecological state of the river and identify the main pollutants. The article presents an integral assessment of the ecological state of the river based on hydrobiological and hydrochemical indicators. The article uses the method of field research and observations, geographical and descriptive methods. The article compared the results of the analysis of water samples taken from the site of the villages of Armanis and Urasar. For comparison, a section of the Katnakhbyur River in the village of Urasar was adopted as a reference. The results of the analysis of the water sample taken from the site of the village of Armanis show that in comparison with the site of Urasara, there is an increase in a number of metals. The high concentration of heavy metal compounds in this area is due to the impact of the Armanis deposit. The article uses data from the Center for Hydrometeorology and Monitoring of the Ministry of the Environment.

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Introduction

The problems of clean water and protection of surface water bodies are becoming more and more significant as the anthropogenic impact on the environment increases. Small rivers are an important link in landscape systems, since they perform the functions of a regulator of their water regime, ensure the redistribution of moisture, determine the hydrological and hydrochemical specifics of medium-sized basins. In recent decades, when the scale of human economic activity has sharply increased and its impact on the environment has increased, the issues of conservation and rational use of small rivers have become particularly acute. Small rivers are the initial links of large water systems, and the consequences of the negative impact of human economic activity on them are manifested earlier and more sharply [1].

In Armenia,the mining sector has a significant impact on the ecological state of rivers. The main types of the mining activities are: extraction and processing of ferrous, non-ferrous, alloying metals, precious and semi-precious stones, chemical raw materials, non-metallic industrial raw materials, extraction of mineral energy raw materials [2].

In addition to the depletion of non-renewable resources, the mining industry has an adverse effect on the environmental situation in the regions where the mining objects are located, including [3].

- Deterioration of the growing conditions of plants and the habitat of animals and people
- Pollution of the air by fine dust emissions, as well as nitrogen and carbon oxides, etc.
- Pollution of the air by gaseous emissions
- Pollution of surface water and groundwater by mining waste water
- Drainage of reservoirs, felling of trees and violation of the soil surface for the possibility of mining.

Aquatic ecosystems play a huge role in the existence of all life on the planet. It is impossible to imagine most of the natural and anthropogenic processes without water. The issue of protecting aquatic ecosystems and the rational use of their resources is a matter of life on Earth. Decision-making in this area should be based on reliable information about the state of water bodies and trends in its changes [1]. Modern scientific and technological progress around the world is directly related to the global use of natural resources and the accumulation of man-made waste [4].

These impacts on nature and the environment directly affect animals, plants and humans. Thus, an increase in harmful emissions into the atmosphere leads to the emergence of various diseases, cutting down trees leads to a decrease in the oxygen produced and the formation of a greenhouse effect. Pollution of underground and surface waters makes them unsuitable or temporarily unsuitable for use as a source of water supply in cities, for drinking, as well as for agricultural needs. Therefore, it is necessary to apply various measures and means to reduce the harmful impact of the mining industry on the environment [5].

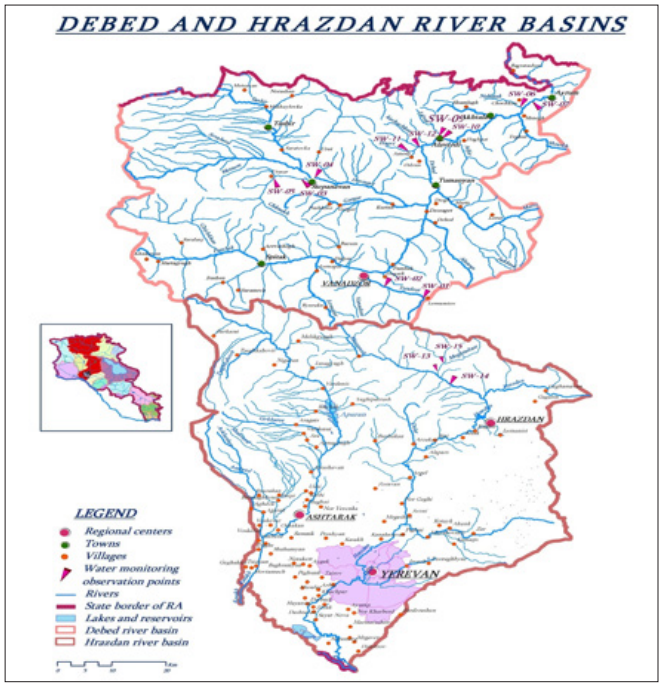
The purpose of this study is to quantitatively assess the impact of anthropogenic activities on the ecological state of the Katnakhbyur River. The main task was to identify the impact of the mining industry on the ecological state of the river by comparing the results of the analysis of water taken from two sections of the

river. As a reference, the results of the analysis of water taken from the site of the village of Urasar were used.

Material and Methods

Sampling and field methods

The Katnakhpyur river is located in the Lori region of the Republic of Armenia, is a right tributary of the Dzoraget. It starts from the northern slopes of Gugarats and joins the mother river 2 km northeast of the village of Katnakhbyur. The length is 12 km .



Katnaghbjur River- v. Armanis. This site is impacted by the Armanis Polymetallic Mine and Mining-Processing Plant.The Armanis polymetallic mine is located in the Lori region, around the town of Stepanavan, in the basin of the Katnaghbyur (Chknagh) river.It was exploited in 1967-1985. The mineral consists mainly of sphalerite, chalcopyrite, pyrite, galena and hematite minerals. There is natural gold (in quartz veins), silver, quartz, gypsum, carbonates and bismuth compounds. The mine has been operating since 1998 in an open way and was suspended in 2015. The final products were copper concentrate, lead concentrate and zinc concentrate. The mine has not been operated since 2016, but the remnants continue polluting the environment.

Sampling was carried out on two sections of the river. The dates and time of the transport of the field survey were coordinated with the experts responsible for the sampling. The total field survey took about four days. The field protocols were completed by the sampling team for each sampling site. The protocols include detailed information about the river basin, name and type, site number and geographical coordinates, sampling date and time, weather and the results of water quality field parameters, name of the surveyor with signature and additional comments.

During field work on site, the following indicators of water in rivers are measured: water temperature (0C), oxygen concentration: DO (MG/L), oxygen saturation O2-Sat (%), pH, power lines (EC in the glossary, EC is European Commission ;-))s/cm).

In the field, the water samples were not filtered. For ammonium ions, the water samples were stabi-lized with sulphuric acid (H_2SO_4), for nitrite ions with chloroform ($CHCl_3$) and for heavy metals with nitric acid (HNO_3).

The surface water samples were transported to the HMC laboratory for the further processing and analysis in boxes with dry ice to keep samples cool. Samples were delivered on the same day/ within 3 hours. Field survey dates, geographical coordinates, meteorological and hydrological conditions are presented in Table 1.

Table 1: Sampling dates and information on meteorological and hydrological conditions

River	Date	Site location	Pressure type	Target of investigation	Weather conditions	Hydrology	Latitude	Longitude
Katnaghbyur	15.10.2020	v. Armanis	Mining -Armanis Polymetallic Mine and Mining-Processing Plant	To investigate Polymetallic Mine and Mining-Processing Plant pressure on to the river Katnaghbjur	*Sunny*	*enough water*	41°00’36.6	44°21’28.2
Katnaghbyur	15.10.2020	v. Urasar, Up to mining site	reference	_	*Sunny*	*enough water*	41°00’49.6	44°17’41.6

Laboratory analyses

The HMC laboratory analysed 40 physio-chemical parameters (Table 2) from each of the 2 sampling sites. The field team handed over the data to the chemical laboratory staff and were included in the test report. Samples taken from rivers taken to the laboratory are analyzed, as a result of which the following parameters are determined: Water temperature (WT, °C), Oxygen concentration (DO, mg/L), Oxygen saturation (O2-Sat,%), pH, Electric conductivity (EC, CS/cm), Total suspended solids (TSS, mg/L), Biological oxygen demand (BOD5, mg/L), Chemical oxygen demand (BOD5, MG/L), Chemical oxygen demand (k2cr2o7) (COD, MG/L), ammonia-n (NH4-N, MG/L), orthophosphate, as P (PO4-P, Mg/L), Nitrate-n (No3-N, MG/L), Total phosphorus (TP, MG/L), Chloride (CL, MG/L), sulfate, Total ION (SO4, MG/L), Calcium (Ca, Mg/L), Magnesium (Mg, MG/L), Sodium (Na, mg/L), Potassium (K, mg/L), Lithium (Li, mg/L), Beryllium (Be, mg/L), Boron (B, mg/L), Aluminum (Al, mg/L), Titanium (Ti, mg/L), Vanadium (V, mg/L), Chromium (Cr, mg/L), Iron (Fe, mg/L), Manganese (Mn, mg/L), Cobalt (Co, mg/L), Nickel (Ni, mg/L), Copper (Cu, mg/L), Zink (Zn, mg/L), Arsenic (As, mg/L), Selenium (Se, mg/L), Strontium (Sr, mg/L), Molybdenum (Mo, mg/L), Cadmium (Cd, mg/L), Tin (Sn, mg/L), Stibium (Sb, mg/L), Barium (Ba, mg/L), Lead (Pb, mg/L). The physio-chemical parameters were measured according to the appropriate ISO standard methods (table 2).

The transport storage, preservation and the chemical analyses were undertaken according to the accredited laboratory procedures together with the application of internal analytical quality controls.

Table 2: List of Parameters analyzed in the field and in the laboratory

Parameter	Unit	LOD	LOQ	Standards
Field measurements				
Water temperature (WT)	°C			
Oxygen concentration (DO)	mg/L			ISO 5814:2012
Oxygen saturation (O_2-Sat)	%			ISO 10523:
pH	-			ISO 10523:2008
Electric conductivity (EC in the glossary, EC is European Commission ;-))	µS/cm			ISO 7888:1985
Laboratory analyses				
Water temperature (WT, lab control)	°C			
Oxygen concentration (DO, lab control)	mg/L			ISO 5814:2012
Oxygen saturation (O_2-Sat, lab control)	%			ISO 5814:2012
pH (lab control)	-			ISO 10523:2008
Electric conductivity (EC, lab control)	µS/cm			ISO 7888:1985
Total suspended solids (TSS)	mg/L			ISO 11923:1997
Biological oxygen demand (BOD_5)	mg/L			ISO 5815:2003
Chemical oxygen demand ($K_2Cr_2O_7$) (COD)	mg/L			ISO 6060:1989
Ammonia-N (NH_4-N)	mg/L	0,003	0,004	ISO 7150-1:1984
Nitrate-N (NO_3-N)	mg/L	0,001	0,003	ISO 10304-1:2007
Orthophosphate, as P (PO_4-P)	mg/L	0,003	0,005	ISO 6878:2004
Total phosphorus (TP)	mg/L	0,005	0,01	ISO 17294:2016
Chloride (Cl)	mg/L	0,005	0,01	ISO 10304-1:2007
Sulphate, total ion (SO_4)	mg/L	0,025	0,05	ISO 10304-1:2007
Calcium (Ca)	mg/L	0,005	0,01	ISO 17294:2016
Magnesium (Mg)	mg/L	0,005	0,01	ISO 17294:2016
Sodium (Na)	mg/L	0,005	0,01	ISO 17294:2016
Potassium (K)	mg/L	0,005	0,01	ISO 17294:2016
Lithium (Li)	mg/L	0,00005	0,0001	ISO 17294:2016
Beryllium (Be)	mg/L	0,00005	0,0001	ISO 17294:2016
Boron (B)	mg/L	0,0005	0,001	ISO 17294:2016
Aluminum (Al)	mg/L	0,005	0,01	ISO 17294:2016
Titanium (Ti)	mg/L	0,0005	0,0010	ISO 17294:2016
Vanadium (V)	mg/L	0,00005	0,0001	ISO 17294:2016
Chromium (Cr)	mg/L	0,00005	0,0001	ISO 17294:2016
Iron (Fe)	mg/L	0,005	0,01	ISO 17294:2016
Manganese (Mn)	mg/L	0,00005	0,0001	ISO 17294:2016
Cobalt (Co)	mg/L	0,00005	0,0001	ISO 17294:2016
Nickel (Ni)	mg/L	0,00005	0,0001	ISO 17294:2016
Copper (Cu)	mg/L	0,00005	0,0001	ISO 17294:2016
Zink (Zn)	mg/L	0,00005	0,0001	ISO 17294:2016
Arsenic (As)	mg/L	0,00005	0,0001	ISO 17294:2016
Selenium (Se)	mg/L	0,00005	0,0001	ISO 17294:2016
Strontium (Sr)	mg/L	0,00005	0,0001	ISO 17294:2016
Molybdenum (Mo)	mg/L	0,00005	0,0001	ISO 17294:2016
Cadmium (Cd)	mg/L	0,00005	0,0001	ISO 17294:2016
Tin (Sn)	mg/L	0,00005	0,0001	ISO 17294:2016

Stibium (Sb)	mg/L	0,00005	0,0001	ISO 17294:2016
Barium (Ba)	mg/L	0,005	0,01	ISO 17294:2016
Lead (Pb)	mg/L	0,00005	0,0001	ISO 17294:2016

Discussion of results

According to the study conducted by the Blacksmith Institute (The Toxic Site Identification Program of Pure Earth) in Armanis schoolyard, soil samples contain up to 54 ppm of lead, 21.2 ppm of arsenic and 91.3 ppm of chromium. In a river water, 1.4 ppm of lead, 0.5 ppm of arsenic, 0.3 ppm of chromium and up to 0.6 ppm of cadmium were detected. According to another study, in the soil samples taken from Armanis community, up to 6,780 ppm of lead, up to 682 ppm of arsenic and up to 380 ppm of total chromium were detected.

As can be seen from the data in Table 3, f we compare the results of chemical analysis of water samples taken from the site of the village of Armanis and the village of Urasar, we will see that in the indicators of water analysis at the site of the village of Armanis, there is a rather large value of a number of indicators, compared with the results of the analysis of water taken from the site of the village of Urasar. In particular, we can note that Mg exceeds 2.7, Cl-1.9, SO4-7.7, Al-51, Fe-9.0, Mn-227.8, Co-139.2, Ni-14.5, Cu-28.3, Zn-981.7, As-1.5, Se-2.0, Pb-3.7, TSS-8.1 times.

Table 3: Results of chemical analysis of sampling in autumn 2020

River	Sampling site	WT field	DO field	O2-Sat field	pH field	EC field	SS	COD	BOD5	NH4-N	NO3-N	PO4-P	TP	DP	Cl	SO4
		°C	mg/L	%		µS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Katnaghbyur	Armanis village	10,8	9,54	86,1	8,1	342,4	15,4	5	3,27	0,3211	0,417	0,005	0,059	0,013	3,24	76,79
Katnaghbyur	Urasar village	14,1	9,86	95,9	8,5	270,6	1,9	15	2,79	0,0353	0,284	0,005	0,054	0,019	1,70	9,99

River	Sampling site	Ca	Mg	Na	K	Li	Be	B	Al	Ti	V	Cr	Fe	Mn
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Katnaghbyur	Armanis village	44,18	11,69	6,12	0,869	0,00120	0,00020	0,02991	2,61	0,0028	0,0091	0,0050	1,9587	3,4481
Katnaghbyur	Urasar village	49,79	4,28	5,75	0,659	0,00054	<0.0001	0,02799	0,05	0,0023	0,0056	0,0055	0,2166	0,0151

River	Sampling site	Co	Ni	Cu	Zn	As	Se	Sr	Mo	Cd	Sn	Sb	Ba	Pb
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Katnaghbyur	Armanis village	0,0219	0,0087	0,0279	1,4210	0,0041	0,0029	0,145	0,0006	0,0132	0,00028	<0.0001	0,0185	0,0005
Katnaghbyur	Urasar village	0,0002	0,0006	0,0010	0,0014	0,0026	0,0014	0,166	0,0005	<0.0001	0,00019	<0.0001	0,0226	0,0001

Hydrobiological studies were also carried out at these sites. According to the hydrobiological data, the water quality at the SS-02 has been assessed as high (Table 4). In the mouths of Katnaghbyur (SS-01) river no aquatic species were found.

Table 4: Ecological Status at the sampling sites

River	Site No.	Type of sampling site	Nr. of taxa	Nr. of individuals	nEQR	Ecological status	Water quality based on chemical parameters
Katnaghbyur	SW-01	I	0	0	0	Bad	Bad
Katnaghbyur	SW-02	R	29	1983	1	High	Moderate

(R=reference, I=influenced)

The investigation of the Katnaghbyur River in the village of Armanis (SS-03) showed that the influence of Polymetallic Mine and Mining-Processing Plant on the river Katnaghbjur is significant, clearly noticeable compared to the reference SS-05. In fact, the concentrations of the following parameters were increased significantly (Table 5):

Table 5: Increase of concentrations at site SS-01 (Armanis) compared to the reference site SS-02 expressed as ratio c(ss-01)/c(SS-02)

	Zn	Mn	Co	Cd	Al	Cu	Ni	Fe	TSS	SO4	Pb	Se
Ratio of c	981.7	227.8	139.2	132.3	51	28.3	13.4	9.0	8.1	7.7	3.7	2.0

According to the results of the water quality assessment based on chemical parameters, the quality of standard SS-02 water was assessed as poor, as the concentrations of Fe and Cd increased (Table 6). At the same time, these additives are 9 and 132 times, respectively.

Table 6: Assessment of water quality at the sampling sites of the Katnakhbyur river based on national water quality standards

RBD	River	Sampling site(Site No.)	Water quality indicator	Parameter quality class	Water quality general class
Debed	Katnaghbyur	Armanis village **(SW-01)**	Cu, V, Sn, Sulphate ion	Moderate	Bad
			Al	Poor	
			Zn, Cd, Mn, Co, Fe	Bad	
	Katnaghbyur	Urasar village **(SW-02)**	Fe	Moderate	Moderate

Conclusions

In general, the impact of Armanis on the ecological state of the river is very great. This indicates the indicators of the content of chemical elements obtained from the analysis results. As noted, after Armanis, the content of a number of chemical elements increases several times. The results of the analysis of water taken from the village of Armanis indicate that there is an increase in the number of chemical elements, of which the chemical elements MN, Co, Cd, Al, Cu, Ni, Fe can be especially noted. 227.8, 139.2, 132.3, 51, 28.3, 13.4, 9.0 even. These are quite high values, and we can say with confidence that the Armanis deposit negatively affects the ecological state of the river. Hydrobiological studies show that the ecological state of the Katnakhbyur River is quite bad. According to the conducted research, there is no wildlife here.

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