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Research Article

Distribution and Identification of Sources of Heavy Metals in the Voghji River Basin Impacted by Mining Activities (Armenia)

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The objective of this research is to assess the distribution of heavy metals in the waters and sediments of the Voghji River and its tributaries impacted by mining activity and to reveal the real source of each of the heavy metals in the environment for assessing the pollution level of heavy metals. Voghji River with two main tributaries (Geghi and Norashenik) drain two mining regions. To identify distribution and pollution sources of heavy metals, the water and sediment samples were collected from eight sampling sites. The results of statistical analysis based on data sets of the period 2014–2016 showed that, after the influence of drainage water and wastewater of mining regions, heavy metal contents in the Voghji River basin dramatically increased. The waters of the Voghji River were highly polluted by Mn, Co, Cu, Zn, Mo, Cd, and Pb. The relation of metals content was highly changed due to anthropogenic impact disturbing the geochemical balance of the Voghji River. The water quality based on only heavy metal contents in the source of the Voghji River belongs to "good" chemical status, and in the sources of Geghi and Norashenik Rivers it is "moderate." The water quality of Voghji and Norashenik Rivers is sharply worsening after the influence of mining activity, becoming "bad" chemical status. The research revealed the pollution sources of each metal.

1. Introduction

Impact of mining on aquatic ecosystems became an issue of increasing concern. Mining by its nature consumes, diverts, and seriously pollutes water resources [1–3]. Mining and milling operations, together with grinding, concentrating ores, and disposal of tailings, provide obvious sources of contamination in the surface environment, along with discharge or overflow of wastewater, runoff from rainfall or snowmelt, drainage from the toe of waste piles, and discharge of impacted groundwater to streams and springs. Water pollution problems caused by mining include acid mine drainage, metal contamination, and increased sediment levels in streams [4, 5]. The generation of acidic drainage and the release of water containing high concentrations of dissolved metals from mine wastes constitute an environmental problem of international scale [6–8]. Chemical leaching of metals occurs when precipitation from rainfall or snowmelt infiltrates through ore or waste materials and dissolves or desorbs metals from the solid material. As a consequence, streams transport high contents of toxic trace elements such as As, Cd, Pb, Zn, Cu, Sb, and Se [9].

Heavy metals are an important class of pollutants which can produce considerable harm to the environment when they are above certain concentrations [10–12]. These elements can be leached into the surface water or groundwater, taken up by plants, and can bond semipermanently with soil components such as clay or organic matter, which later affect human health [13]. After heavy metals enter into a water body, they can harm aquatic organisms, and, through the processes of chemical adsorption and physical precipitation, heavy metals can accumulate in the sediments of the water environment [14]. Heavy metal contents of the surface sediments are generally significantly higher compared with those in the water body, so it is very important to explore the heavy metal contents in the surface sediments [15, 16].

Heavy metals are defined as metallic elements that have a relatively high density compared to water. With the assumption that heaviness and toxicity are interrelated, heavy metals also include metalloids, such as arsenic, that are able to induce

Table 1: Summary of sampling sites (water and sediment) of the Voghji River basin.

Site	River	Location description
1	Voghji	Upstream of the Kajaran city before confluence with ZCMC
2	Voghji	Downstream of the Kajaran city, after confluence with ZCMC
3	Voghji	Upstream of the Kapan city, after runoff Geghi River
4	Voghji	Downstream of the Kapan city, after runoff wastewaters of KPM, Kavart, and Geghanush
5	Norashenik	Before confluence wastewater of tailings dam of Artshvanik
6	Norashenik	Mouth
7	Geghi	Source
8	Geghi	Mouth

toxicity at a low level of exposure and nonmetal selenium [17].

The mining industry is developed in the Republic of Armenia (RA). Due to the lack of adequate management and planning, as well as poor operating experience and waste management, this branch of industry is one of the main sources of water pollution and of the environment, in general, with heavy metals (Pb, Cu, Ni, Cd, Mo, As, etc.). Previous studies in the Voghji River basin [18–21] have all found elevated concentrations of heavy metals and trace elements such as As, Cu, Mo, Sb, Cu, Co, Ni, and Zn in the surface waters and sediments. The pollution problems were reported in soils located near kindergarten and schools of the Kapan and Kajaran cities [22, 23].

However, inadequate information is available on the concentrations and distribution of heavy metals and trace elements in the Voghji River basin. The aim of this study was therefore to investigate the distribution of heavy metals (Ti, Fe, Mn, V, Cr, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Pb) in the waters and sediments of the Voghji River and its tributaries impacted by mining activity; to reveal the source of each of heavy metals in the environment and correlation between parameters, to assess the pollution level of heavy metals; and to estimate the temporal variability influence in concentrations of heavy metals.

2. Materials and Methods

2.1. Study Area. Voghji River is a left tributary of Aras River located in the southeast of Armenia. The sources of Voghji River are mountain springs and small lakes of the Kaputjugh Mountain at an elevation of 3650 m above sea level located in the west-southern part of Armenia. The total length of the River is 82 km (in Armenia 52 km) and the catchment basin area is 2337 km^2 (in Armenia 1240.47 km^2). The largest tributaries are Geghi and Norashenik. On its way, the stream is fed by groundwater, rain, and melting snow and has perennial flow throughout the year. Mean annual water discharges of the Voghji, Norashenik, and Geghi Rivers are estimated to be 334.3, 69.7, and 135.3 million m^3 or 10.6, 2.21, and 4.29 m^3/s, respectively [24].

The Voghji River passes through the two mining districts. One of them is Zangezur copper-molybdenum combine (ZCMC) which is located in the upstream of the Voghji River in the territory of the Kajaran city, in the southeast of Armenia. ZCMC is the largest in the region open pit mine which extracts copper and molybdenum-rich ore, afterwards producing two separate concentrates of copper and molybdenum. ZCMC produces 21 Mt of ore (and the similar amount of waste) annually. Besides the basic elements, a number of valuable associated elements exist in the ore, such as Pb, Zn, Cd, As, Co, and Ni. The slurry tailings, 33% of which is water, are transported from the plant of ZCMC to the tailings dam of Artsvanik by pipeline. The tailings dam of Artsvanik is located in the gorge of the same river. After precipitation of slurry tailings, the surface water of tailings dam flows into the Norashenik River. Besides, drainage waters (surface and ground) from open pit mine also flow into the Voghji River in the territory of Kajaran city.

The second mining district (Kapan Polymetal) is located in the downstream of the Voghji River, 1.5 km east of the town of Kapan in the southeast of Armenia. Kapan Polymetal (KPM) is fully mechanized underground mine with a current capacity of approximately 400 ktpa, a conventional 750 ktpa flotation concentrator, and various infrastructure facilities. The mine produces gold-copper-silver and zinc concentrate. Tailings of KPM are discharged into the tailings dam of Geghanush located in the gorge of the same river. After precipitation of slurry tailings in the tailings dam, the tailing liquid flows into the Geghanush River and then Voghji River. Near the city of Kapan, the abandoned mine of Kavart (not belonging to KPM) is located which is considered a possible source of metal's pollution. The waters of Kavart rich in heavy metals mix with surface and groundwaters in different ways.

2.2. Sample Collection and Analysis. Water and sediment samples were collected at 8 sampling sites of the Voghji River basin in the period 2014–2016 (see Figure 1, Table 1). The sampling sites were selected with the aim of covering the whole stream from its source to its confluence with two mining areas. The sampling sites were categorized in two groups: sampling sites 1, 5, and 7 are located in the source of rivers, which have the minimal anthropogenic influence representing the background state of the river basin; sampling sites 2, 4, and 6 bear the influence of mining activity and untreated wastewater of the cities.

Water samples were collected on a monthly basis. The frequency of sampling in the sources of Voghji (WS-1), Geghi (WS-7), and Artsvanik (WS-5) Rivers was less compared to

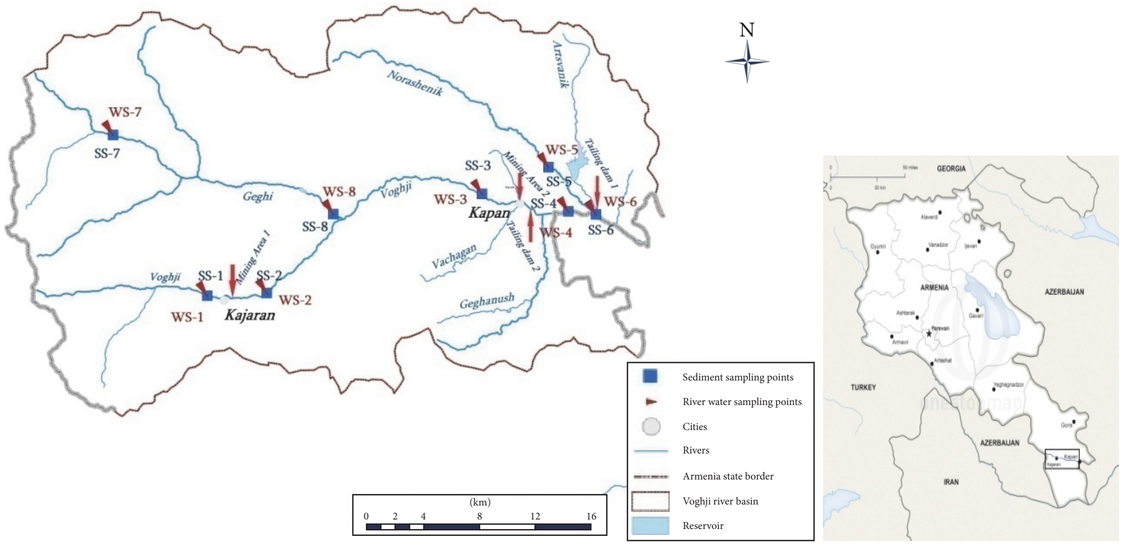

Figure 1: Map of the study area and location of sampling points: (mining area 1) ZCMC; (mining area 2) KPM; (WS) water sampling sites; (SS) sediment sampling sites; red arrows indicate pollution sources.

the other sites. Sediment samples were collected during the summer period in June and August.

Collection and handling of water and sediment samples were conducted in accordance with standard methodology (ISO 5667-3, -6, and -12). Water samples were collected in polypropylene plastic bottles. The water samples were acidified at the time of collection with nitric acid. Double-distilled nitric acid was used for water sample conservation. The samples were stored at 4°C and transported to the laboratory.

Sediment samples were collected using the appropriate sampler. Samples were transported to the laboratory, air-dried in the laboratory at room temperature until stable weights were recorded, and subsequently sieved through 2 mm mesh. Then dried sediments samples were placed into the digestion vessel with 12 mL of HNO_3/HF (3 : 1 v/v) solution and digested in a microwave digestion system (Speedwave MWS-3, Berghof, GmbH).

An inductively coupled plasma-mass spectrometer (ICP-MS, PerkinElmer ELAN 9000, USA) was used to determine the concentrations of Ti, Fe, Mn, V, Cr, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, and Pb in the sediment and water samples.

The standard curves were obtained using separate solutions containing known concentrations of each heavy metal (PerkinElmer, Pure Grade Atomic Spectroscopy Calibration Standard, USA) diluted with deionized water. For the calibration procedure, single element and multielement calibration standard solutions were used. For the preparation of standard solutions, deionized water (18.2 MOhm/cm) purified by Thermo Scientific Barnstead Easypure II and argon gas with the purity of 99.998% were used.

The background interferences from the plasma gases, air entrainment, and solvent were corrected by subtraction of reagent blank signals. The isobaric spectral interferences originating from the polyatomic ion species involving the sample matrix elements eliminated by selecting a suitable isotope were corrected or reduced by applying interference correction equations. To adjust the matrix effect and improve accuracy the internal standard ^{115}In was used.

2.3. Data Analysis. The data was analyzed using descriptive statistics: maximum, minimum, mean, standard deviation, variation coefficient, kurtosis, and skewness are reported. Box-and-whisker plot was used for visualisation kurtosis and skewness. Box-and-whisker provides a powerful tool for the analysis of pattern, which helps to evaluate the sources of changes as well as to assign the parameters that are associated with these sources. The Pearson correlation analysis was used to determine whether there was a linear association between the trace elements. Based on the value of correlation coefficient "r," the correlation between two parameters can be termed as positive or negative. Analyses were conducted using SPSS 19.0 (IBM, NYC, USA).

Assessment of pollution level of heavy metals in the Voghji River was done based on national water quality standards [25]. According to these standards, water quality is classified into 5 classes: "excellent" (I class), "good" (II class), "moderate" (III class), "poor" (IV class), and "bad" (V class). The classification system of water quality is based on background concentrations of heavy metals for each water basin management area, and the first class of system corresponds to the background concentration. The classification scheme is given in Table 2.

Since there are no established national sediment quality guidelines in Armenia, the results of heavy metals in sediments have been compared with the Canadian Interim Sediment Quality Guidelines (ISQG) proposed by the Canadian

Table 2: Water quality assessment objectives of heavy metals for Voghji River basin.

Heavy metal	Quality class				
	I	II	III	IV	V
Zn, μg/L	3	100	200	500	>500
Cu, μg/L	4	24	50	100	>100
Cr, μg/L	0.5	10.5	100	250	>250
As, μg/L	0.3	20.3	50	100	>100
Cd, μg/L	0.1	1.1	2.1	4.1	>4.1
Pb, μg/L	0.1	10.1	25	50	>50
Ni, μg/L	0.6	10.6	50	100	>100
Mo, μg/L	15	30	60	120	>120
Mn, μg/L	4	8	16	32	>32
V, μg/L	0.4	10	20	100	>100
Co, μg/L	0.09	0.18	0.36	0.72	>0.72
Fe, mg/L	0.03	0.06	0.5	1.0	>1.0
Sb, μg/L	0.5	1	2	4	>4
Ti, μg/L	1.5	10	20	100	>100
Se, μg/L	1.1	20	40	80	>80

Sediment Quality Guidelines for the Protection of Aquatic Life [26].

3. Results and Discussion

3.1. Heavy Metals in Waters of Voghji River and Its Tributaries. The data in Table 3 show a summary of the descriptive statistics of the heavy metals in waters of the Voghji River and its tributaries. The high CV implies that measured concentrations for all metals varied between stations ($p < 0.05$; ANOVA).

The spatial distribution of some heavy metals in the waters of Voghji, Norashenik, and Geghi Rivers was analyzed as box-and-whisker plots (See Figure 2).

They display batches of data with five values being used to describe the data set. The length of the box represents the interquartile range, which contains 50% of the values, and the heavy horizontal line inside the box indicates the median. The "whiskers" are lines that extend from the box to the highest and lowest values.

Spatial distribution pattern proved to be a powerful tool in identifying the contamination hotspots and possible sources of heavy metals. The comparison of heavy metal contents observed in the sources of rivers and other sites allows distinguishing geological and anthropogenic origins of pollutants.

The highest Cu concentration in the waters of Voghji River and its tributaries (median value 71.3 μg/l) (see Figure 2) was observed at WS-4, approximately 30–60 times higher compared to the background sites WS-1, WS-5, and WS-7 (see map, Figure 1). The Cu concentration is an order of magnitude higher compared to WS-3, too. This phenomenon states that the waters of Voghji River are polluted by Cu in the territory of Kapan city and the pollution source of Cu is the wastewater of KPM. There is also a potential of diffuse pollution with Cu from the abandoned mine of Kavart. Another source of Cu pollution of Voghji River, although not as large as the wastewater of KPM, is ZCMC with its Artsvanik tailings dam which is evident from the increase in the concentration of Cu after Kajaran city and in the mouth of Norashenik compared to the source of Voghji (WS-1) and Norashenik (WS-5) rivers. The Cu concentration variation around the median value also is higher due to the uncontrolled point and nonpoint contamination.

The spatial distribution patterns for Co and Fe are similar to Cu with observed highest concentration values in the WS-4 (see Figure 2 and Table 3).

The median values of Zn and Mn were significantly higher ($p < 0.001$) in WS-6 and WS-4 (see Figure 2). They were about two orders of magnitude higher than the highest concentrations of Zn and Mn measured in the other sites which are connected to the inflow of wastewater both from the Artsvanik tailings dam and KPM. The concentrations of Zn and Mn in WS-6 (mouth of Norashenik) after the influence of wastewater of Artsvanik tailings dam increase 99 and 55 times, respectively. The range of variation in the median value also is higher.

In the case of Sb, Mo, Se, As, and Cd the median values were significantly higher in WS-6, 4.78, 340.1, 4.0, 4.0, and 1.93 μg/l ($n = 29$), respectively (see Figure 2 and Table 3). The concentration increase between WS-6 and WS-5 is about 2-3 orders of magnitude. It is connected to the inflow of wastewater from Artsvanik tailings dam. In spite of observed higher concentrations of Sb and Mo in the mouth of Norashenik (WS-6), the impact on Voghji River is not so big because of differences of water quantity of Norashenik and Voghji Rivers (See Section 2.1). This pattern indicates that wastewater of KPM is not polluted by Sb and Mo. The increase in concentrations of Sb, Cd, and Mo is observed also at the WS-2 due to the point and nonpoint contamination of ZCMC. The concentration of Cd increases at WS-4 due to the impact of wastewater of KPM.

The spatial distribution pattern of Pb has similarity with Cd (See Table 3). The variation of mean concentration Pb within sampling sites is more than 80% indicating that the difference between the concentration of background and influenced sites is large. As observed from the data (Table 3) Pb content in the Voghji River increased due to the impact of wastewater of ZCMC and KPM.

The variability of mean concentrations of Cr, Ni, and Ti between sampling sites is 37%, 49%, and 41%, respectively. A little increase in the content of Cr and Ti was observed only at the WS-2 (0.97 and 5.05 μg/l) (Figure 2). Ni concentration slightly increases at WS-2 and WS-6.

The spatial distribution pattern of V differs from other metals. Under the influence of ZCMC, a small increase in the concentration of V was observed in WS-2 which is much lower than the concentration observed in WS-5. The content of several heavy metals, such as Ti, Cr, Co, Ni, Sb, and Pb, is higher at WS-5 comparing to the other two background sites (WS-1 and WS-7).

Overall, in the Norashenik River, the concentrations of Mn, Mo, Zn, Cd, and Sb were dramatically increased under the influence of wastewater of the Artsvanik tailings dam. In

Table 3: Arithmetic mean (AM) concentrations, standard deviation (SD), and variation coefficient (VC %) of heavy metals in waters of Voghji River and its tributaries during the period 2014–2016 (units are μg/L, except Fe and Mn for which units are mg/L; N represents the number of data).

WS	BS	Fe	Mn	Ti	V	Cr	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb	Se
1 (N = 24)	AM	0.038	0.004	1.82	0.243	0.395	0.082	0.927	3.07	3.21	0.938	5.83	0.045	0.044	0.039	0.765
	SD	0.03	0.002	0.66	0.12	0.24	0.057	0.36	1.51	1.88	0.56	2.85	0.02	0.03	0.03	0.798
	VC	69	54	36	51	60	70	38	49	59	60	49	48	71	87	104
2 (N = 29)	AM	0.183	0.023	5.54	1.06	1.030	0.316	1.67	10.9	4.75	1.79	111.6	0.372	0.39	0.397	7.69
	SD	0.14	0.02	3.12	0.76	0.57	0.24	0.67	5.66	4.77	0.95	94.2	0.34	0.36	0.47	7.94
	VC	74	102	56	72	55	76	40	52	101	53	84	92	92	119	103
3 (N = 29)	AM	0.074	0.004	2.79	1.17	0.559	0.157	1.07	5.62	1.59	1.94	46.3	0.153	0.33	0.463	1.38
	SD	0.05	0.00	2.05	0.42	0.29	0.12	0.46	2.14	1.25	0.77	17.5	0.07	0.19	0.56	1.09
	VC	68	62	74	36	51	73	43	38	78	40	38	46	59	121	79.0
4 (N = 29)	AM	0.376	0.181	3.95	1.36	0.677	2.57	2.92	82.5	105.5	1.51	64.2	1.18	0.778	0.329	1.81
	SD	0.189	0.137	2.38	0.875	0.436	1.95	2.00	51.3	84.6	0.818	65.1	0.779	0.851	0.238	1.36
	VC	50	76	60	64	64	76	68	62	80	54	101	66	109	72	75.3
5 (N = 15)	AM	0.110	0.003	4.14	4.61	0.716	0.227	1.28	1.28	0.94	0.688	1.19	0.009	0.116	0.099	0.728
	SD	0.078	0.00	1.98	1.62	0.50	0.10	0.56	0.44	0.67	0.19	0.48	0.01	0.07	0.10	1.14
	VC	71	56	48	35	69	44	44	34	72	27	40	59	61	100	157
6 (N = 29)	AM	0.236	0.178	6.18	6.90	0.790	0.720	2.150	11.5	82.1	4.59	400.5	1.891	5.87	0.522	4.25
	SD	0.21	0.14	4.68	5.80	0.70	0.51	1.22	7.79	50.4	2.29	217.5	0.78	3.43	0.47	2.57
	VC	88	77	76	84	57	70	57	68	61	50	54	41	58	90	60.6
7 (n = 15)	AM	0.075	0.005	2.12	0.647	0.297	0.126	0.805	1.51	1.39	0.616	7.15	0.036	0.084	0.048	1.57
	SD	0.06	0.01	1.21	0.32	0.25	0.06	0.37	0.47	1.05	0.46	2.95	0.02	0.05	0.04	2.08
	VC	85	99	57	49	86	44	46	31	75	75	41	42	58	93	132
8 (N = 29)	AM	0.077	0.011	2.76	0.840	0.503	0.150	1.025	3.23	2.35	1.14	15.3	0.057	0.166	0.114	1.71
	SD	0.07	0.01	2.40	0.35	0.46	0.07	0.53	1.75	1.79	0.61	12.2	0.04	0.12	0.15	2.09
	VC	86	59	87	42	92	47	52	54	76	53	79	63	69	129	122

the Geghi Rivera little increase in concentration values of Mn, As, Sb, and Pb was observed.

The variation coefficient (VC) was used to investigate the variability of concentrations during the sampling period (2014–2016). The most seasonally variable metals are Pb, Fe, and Se (see Table 2). VC values for Pb were higher than 80% (86–136%) at all sampling sites with the exception of WS-4. At the background sites with the exception of WS-7, VC values are less than 80% (except Se and Pb), indicating less variability of heavy metals at background sites. At WS-7 the variable metals (CV > 80%) are Fe, Mn, Cr, and Pb. The highest values during the year were observed from March to May and partly from October to November. Heavy metal content increases in the spring due to the snowmelt and precipitation in the catchment. Runoff waters from mining area and mine drainage are considered nonpoint pollution source of heavy metals.

To distinguish the pollution sources, heavy metals were also analyzed through Pearson's correlation. The correlation analysis was done for the observed 15 heavy metals based on the data for the period 2014–2016 (See Table 4). Only the strong and positive ($r > 0.7$) correlation among metals were taken into account. Among the metals, the only not-correlated metal is Ni.

At site 2, the number of correlated parameters and values of correlation coefficient increase. A strong correlation was found among 9 metals (Ti, V, Co, Cu, As, Mo, Cd, Pb, and Fe). After the mining and processing molybdenum and copper, the composition of river water has changed. The correlated metals are associated with the composition of local minerals: molybdenum, chalcopyrite, magnetite, and pyrite.

At site 3, the strong correlation was observed for 5 pairs. At site 4, the correlation coefficients were decreased from 0.95 to 0.70 among 13 pairs. The high correlation indicates that these elements shared the same artificial sources.

In the source of Norashenik River (WS-5) the strong correlation was observed only among 3 metals (Fe, Mn, and Ti). These metals are the main components of several common minerals and rocks. At site 6, the number of correlated parameters and values of correlation coefficient increase. The correlation was found among 8 pairs, and the correlation coefficients were changed from 0.76 to 0.7.

At site 7, the correlation coefficients were decreased from 0.87 to 0.70 among 12 pairs. Although WS-7 is considered as background site from the correlated pairs, it is evident that anthropogenic impact exists. The most correlated pairs were observed at the WS-8. At site 8, the correlation coefficients were decreased from 0.93 to 0.70. It indicates that these metal pairs likely originated from the same sources.

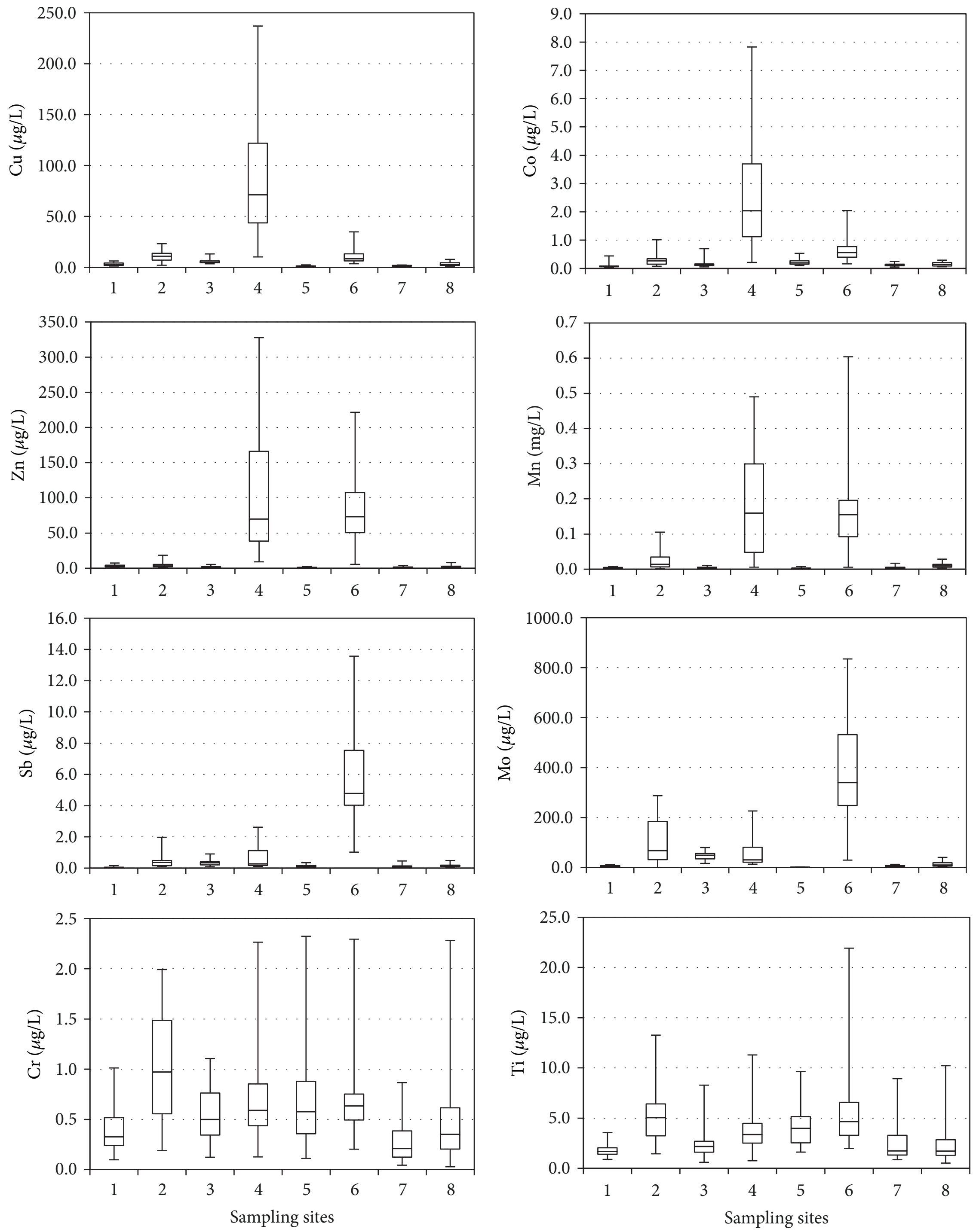

Figure 2: Spatial distribution of concentrations values of some heavy metals in the waters of Voghji River and its tributaries. Median, 25th and 75th percentiles are shown in the box; whiskers indicate the maximums and minimums.

3.2. Spatial Distribution of Heavy Metals in Sediments. The results of the analysis of heavy metals in Voghji, Geghi, and Norashenik Rivers sediments (see Table 5) showed an increase in heavy metal concentrations in the sediments at the downstream of Kajaran (SS-2), with the exception of Ti, Mn, and Fe, compared to SS-1 (source of Voghji River) associated with the drainage of mining territory of ZCMC. The highest concentrations of Cu, Zn, Mo, and Pb were observed at SS-2 and SS-3. At the SS-1, the average content of metals follows the order Fe > Ti > Mn > Cu > Zn > V > Mo > Pb > Ni > Cr > As > Co > Cd > Sb. At the SS-2, the average content of metals follows the order Fe > Ti > Cu > Mn > Mo > Zn > V >

Table 4: Correlation between metals in water of the Voghji River and its tributaries ($r > 0.7$).

WS	Pearson's coefficients of correlations between metals
1	Cu-V (0.70)
2	Cd-Se (0.88), Mo-Cd (0.84), Mo-Se (0.81), Pb-Ti (0.79), Mo-As (0.78), Fe-Mn (0.78), V-Ti (0.75) Se-As (0.74), V-As (0.72), Cd-As (0.70), V-Co (0.70), Pb-Fe (0.70)
3	Mo-As (0.88), Mo-Cd (0.76), Ti-Fe (0.74), Cu-Fe (0.72), Cd-As (0.70)
4	Mo-As (0.95), Cu-Zn (0.89), Sb-As (0.88), Mo-V (0.86), Mo-Sb (0.86), As-V (0.85), Cu-Co (0.82), Co-Zn (0.81), Cd-Zn (0.79), Co-Mn (0.77), Cd-Sb (0.73), Cd-Co (0.72), Sb-V (0.71)
5	Mn-Fe (0.74), Mn-Ti (0.71)
6	As-V (0.76), Pb-Co (0.73), Zn-Cu (0.73), Cu-V (0.70), Cu-Co (0.70), Fe-Cr (0.70), Fe-Ti (0.70), Ti-Cr (0.70)
7	Fe-Ti (0.87), Fe-Co (0.85), Fe-V (0.84), Sb-Co (0.82), V-Ti (0.80), Pb-Ti (0.77), Co-V (0.75), Fe-Pb (0.72), Fe-Sb (0.72), Fe-Cu (0.72), Co-Ti (0.71), Mo-Cr (0.70)
8	Cd-Mo (0.93), As-Mo (0.86), Fe-Pb (0.85), Cu-V (0.84), Fe-Ti (0.83), Cd-As (0.79), Cu-Ti (0.79), Pb-Ti (0.75), Cu-Co (0.75), Cu-Cr (0.73), Fe-Cu (0.72), Cr-Mn (0.72), Ti-V (0.71), Cr-V (0.70), Co-V (0.70), Co-Ti (0.70), Fe-V (0.70), Mn-Ti (0.70), Pb-Ti (0.70)

Table 5: Heavy metals in sediments (mean value in mg/kg) in the Voghji River basin in 2014–2016.

SS	Fe	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Cd	Sb	Pb
1	8962	840	25.4	8.89	450	5.34	11.3	119	41.4	6.93	24.0	0.32	0.23	11.5
2	4674	2037	45.9	9.42	239	8.12	14.8	620	99.6	9.41	109	0.44	1.54	30.1
3	20018	4203	121	11.1	245	13.8	17.0	494	54.4	29.7	80.0	0.33	2.96	40.5
4	4471	1499	35.3	1.95	75.4	4.36	3.22	137	67.2	11.8	25.4	0.97	1.62	18.4
5	2053	2094	39.3	11.8	172	6.73	18.8	15.4	26.9	2.50	0.27	0.09	0.12	3.52
6	13674	3176	84.6	7.16	176	7.76	5.78	126	92.3	13.1	33.1	0.84	1.46	13.8
8	6537	1382	36.5	7.17	200	5.51	8.14	192	36.8	8.21	12.3	0.14	0.79	15.5
ISQG	-	-	-	37.3	-	-	-	35.7	123	5.9	-	0.6	-	35.0

Pb > Ni > Cr > As > Co > Sb > Cd. In spite of the increase in metal contents at the SS-2, the order of average concentration values of metals remains almost the same.

At the SS-3, Fe, Ti, V, As, and Sb were accumulated in the sediment leading to the highest concentration of these metals in the whole river basin.

The sediments of Norashenik River are polluted with heavy metals because of inflowing wastewater of the Artsvanik tailings dam. This can be seen from the comparison of heavy metal content in sediments of SS-5 (source of Norashenik River) and SS-6 (mouth of Norashenik River). The only difference was observed at the SS-3 where the metals content is inexplicably high. The spatial distribution of metals in sediments, in general, is similar to the distribution of water. As the results demonstrated, the concentration values of Mo, Sb, Cd, Cu, and Fe in the sediments at the mouth of Norashenik River (SS-6) increased sharply. The slight increase in concentrations was observed in the case of Ti, V, Co, Zn, As, and Pb. In the case of Cr and Ni, conversely, the concentrations decreased.

The specific distribution pattern of Mn showed that the concentration in sediments is higher only at SS-1 and lower at SS-4. In the other sites, the concentration range of Mn was not changed indicating that Mn distribution in sediments is not directly related to the mining activities.

The concentrations of Cu and As in sediments exceeded ISQG in all sites besides SS-5. The concentrations of Cd exceeded ISQG in sediments of SS-4 and SS-6. It is noteworthy that cadmium concentration exceeded corresponding ISQG only in the sediments of SS-3.

3.3. Relationship of Heavy Metals Content in Water and Sediment. Waters and sediments surrounding the mining area bear the brunt of industrial discharges and destruct environmental natural balance. To identify changes in the natural chemical composition of heavy metals in water and sediments as a result of mining operations, the ratio of heavy metals in water and sediment and correlation between the ratio of heavy metals in water and sediment were estimated.

In the upper part of the Voghji River (WS-1), the median Cu/Zn ratio in the water samples of background sites varied between 0.8 and 1.6. Then, after ZCMC the ratio of Cu/Zn was 3.5, and after the city of Kapan the ratio was again 1 despite the sharp growth of Cu and Zn. In the sediment samples of upper part of the Voghji River, the ratio of Cu/Zn was 3. After ZCMC, the ratio increased to the same extent and was 6–9.

The ratio of Mo/Zn in the water of sampling sites 1 and 5 was 1.5 and 1.9, respectively. Then, after the influence of ZCMC (below Kajaran city) the ratio of Mo/Zn was 21.5. Due to the inefficient processing, the large amount of Mo remains in the processed rocks and enters into the waters.

The ratio of Ti/V, Ti/Cr, V/Cr, and Ti/Ni changed slightly after the influence of ZCMC in waters of both Voghji and Norashenik Rivers.

Table 6: Water quality of the Voghji River basin based on only heavy metals.

Sampling sites	Main indicator metals	Water quality parameter class	Overall water quality class
1	-	-	Good
2	Fe, Mn, Co Mo	Moderate Poor	Poor
3	Mo	Moderate	Moderate
4	Mo, Fe Cu Mn, Co	Moderate Poor Bad	Bad
5	Fe, Co	Moderate	Moderate
6	Fe, Cd Co Mn, Mo, Sb	Moderate Poor Bad	Bad
7	Fe	Moderate	Moderate
8	Mn	Moderate	Moderate

The ratio of Fe/Al in the water of sampling sites 1, 5, and 7 was 2.5, 2.9, and 2.7, respectively. After the influence of mining, the natural composition was changed in the range 1.2–1.9.

The Mo/Ti ratio increased to 6.8 in the upper part (site 1) which increased to 13 after the city of Kajaran, and a sharp growth was observed after the city of Kapan, about 28 in water of river. The Pb/Cd ratio increased from 1.3 to 1.7 after the city of Kajaran, and then a slow decrease was observed before the city of Kapan, reaching the minimum values after ZCMC, which is an evidence that enterprise wastes contain large amounts of toxic metals. Due to diffusion, heavy metal abundant waste and tailings penetrate into the river, becoming pollution sources. In the process of mining, the spatial distribution of metals concentrations is disturbed.

3.4. Assessment of Heavy Metal Pollution in the Voghji River Basin. The assessment of the contents of heavy metals was done based on mean concentrations value for the period of 2014–2016 (see Table 3). The mean values of heavy metals are compared to the national water quality standards (see Section 2.3) and derived quality class. The results of the assessment are presented in Table 6. According to the results (Table 6), in the upper reaches of the Voghji River (WS-1), the water quality corresponds to the “good” quality. Then, in the river receiving drainage wastewater from ZCMC, the water quality was worsened gradually to “poor” class at downstream of Kajaran. The “poor” water quality in the section downstream of Kajaran (site 2) was associated with the high concentration of Mo. Then, after mixing with Geghi River, the water quality of Voghji River was getting better and water quality was classified as “moderate” (WS-3) connected with elevated concentration of Mo. After the influence of KPM and mixing of the Norashenik River, the water quality of the Voghji River worsened to the “bad” quality due to elevated Mn and Co levels. The water quality of the Geghi tributary was classified as “moderate” due to iron. The water quality of the Norashenik tributary was classified as “bad” connected to Mn, Mo, and Sb.

4. Conclusions

Our results indicated a high degree of mining-derived pollution in the Voghji River. Both ZCMC and KPM mining districts with their ore processing center leachate, operated tailings dams, the abandoned mine, and other enterprises located in the Voghji River basin are the major sources of heavy metals pollution. The water quality is worsening after the influence of mining waters from the “good” to the “bad” state.

The research revealed the pollution sources of each metal. ZCMC with its wastewater and diffuse water pollutes the Voghji River mostly with Mo and Sb. The content of other metals increases slightly (less than 10 times) after the influence of ZCMC. The wastewater of Artsvanik tailings dam polluted the Norashenik River and then Voghji River mostly with Mn, Zn, Se, Mo, Cd, As, and Sb. KPM and the abounded mining area Kavart were mainly responsible for the elevated concentrations of Cu, Zn, and Co in the Voghji River (below Kapan city). Both ZCMC and KPM were responsible for the increase in concentrations of Fe, Mn, Zn, Pb, and Cd in Voghji River (below Kapan city). The concentrations of Ti, V, Cr, Ni, and As in the Voghji River changed slightly. The high concentration of V in the waters of the source of Norashenik River was mostly due to natural sources indicating the peculiarities of geohydrochemistry of Norashenik River.

The spatial distribution of metals in sediments, in general, is similar to the distribution of water. The only difference was observed at the SS-3 where the metals content is inexplicably high. The concentration values of Mo, Sb, Cd, Cu, and Fe in the sediments at the mouth of Norashenik River increased sharply. The slight increase in concentrations was observed in the case of Ti, V, Co, Zn, As, and Pb. In the case of Cr and Ni, conversely, the concentrations decreased.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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