
**WATER QUALITY AND PROTECTION:
ENVIRONMENTAL ASPECTS**

Assessing the Quality of Water of the Araks Basin Rivers in Armenia¹

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Abstract—This article deals with the quality of water of tributaries of transboundary River Araks. The performed river water research was underpinned by monthly monitoring data for 2004–2007. As a result of the research, a general characteristic of water quality by basic quality indices and the contents of common ions were given. The impact sources and water quality formation-determining factors were indicated. Geochemical series of heavy metals streams were made up and studied, and dominating elements indicated. As a result of statistical data analysis, correlation dependence between concentrations of a different parameters was indicated.

Keywords: water quality, common ions, heavy metals, ore regions.

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INTRODUCTION

River Araks—the largest tributary of River Kura—is one of the most essential water arteries to the Caucasus. The total length of the river is 1072 km, with the covering an area over one hundred thousand square kilometers, with around a quarter of that flowing into Armenian territory. Mean annual runoff is 9 km³. The Araks River forms in Turkey and flows a distance of 638 km before entering the wide Ararat Valley. The river waters are used predominantly for irrigation.

This article covers an investigation of water quality of 8 rivers belonging to the Araks basin: the Hrazdan, Marmarik, Sevjur, Voghchi, Meghriget, Gorisget, Arpa and Vorotan (Fig. 1).

In the present paper the results for key water parameters, common ions, heavy metals obtained in the Armenian part of Araks River basin of the network during four years of operation are summarized and discussed in relation to geology, hydrology and hydro-geochemistry of the river catchments, and potential sources of water pollution.

EXPERIMENTAL

The article highlights the outcomes of monitoring performed in a period from 2004 to 2007. Data on monthly river water quality monitoring on 8 stations Ar-4, Ar-5, Ar-6, Ar-7, Ar-8, Ar-9, Ar-12, Ar-13 (Fig. 1) were used for interpretation of the character, level and inclinations of the studied water quality indices.

Samples were collected, conserved, transported and stored following Standard Operational Proce-

dures (SOPs) developed based on the methods of International Standardization Organization (ISO) [7].

Field measurements were done on a monthly basis. In-situ measurements included hydrogen index (pH), conductivity, turbidity, dissolved oxygen, temperature and salinity and were done on a portable analyzer U-10 (Horiba). Water discharge was measured on a USGS-type AA Current Meter using a Data Storage Computer of AquaCala 500 model (Ricky Hydrological Co) (Table 1).

Common ions Na, K, Mg, Ca, SO₄, Cl, HCO₃, CO₃, N_{total}, P_{total} were studied on a quarterly basis and were determined in non-acidified and filtered samples. Common ions are determined through ISO methods in untreated natural water samples in the shortest interval after transmission to the lab, this being registered in protocols for sample check-in and checkout.

Sulfates are determined through the accepted gravimetric method ISO-9280 as it allows expansion of detection, from 0.2 to 500 mg/L. To determine chlorides, SOPs were developed based on ISO method 9297—argentometric titration method MDL—1.0 mg/L.

To determine cations, both chemical and physico-chemical methods of determination are applicable. For instance, we determine Ca and Mg through titration (ISO-6058, 6059), whereas the control method is that of flame photometry and atomic-absorption spectrophotometry. The accuracy of determination is high, varies 0.4–0.6 mg/L and is in error by max. 0.5%. K and Na are determined through the ISO method 9964-3 and keeping the developed SOPs for determination through the flame photometry method. The applied

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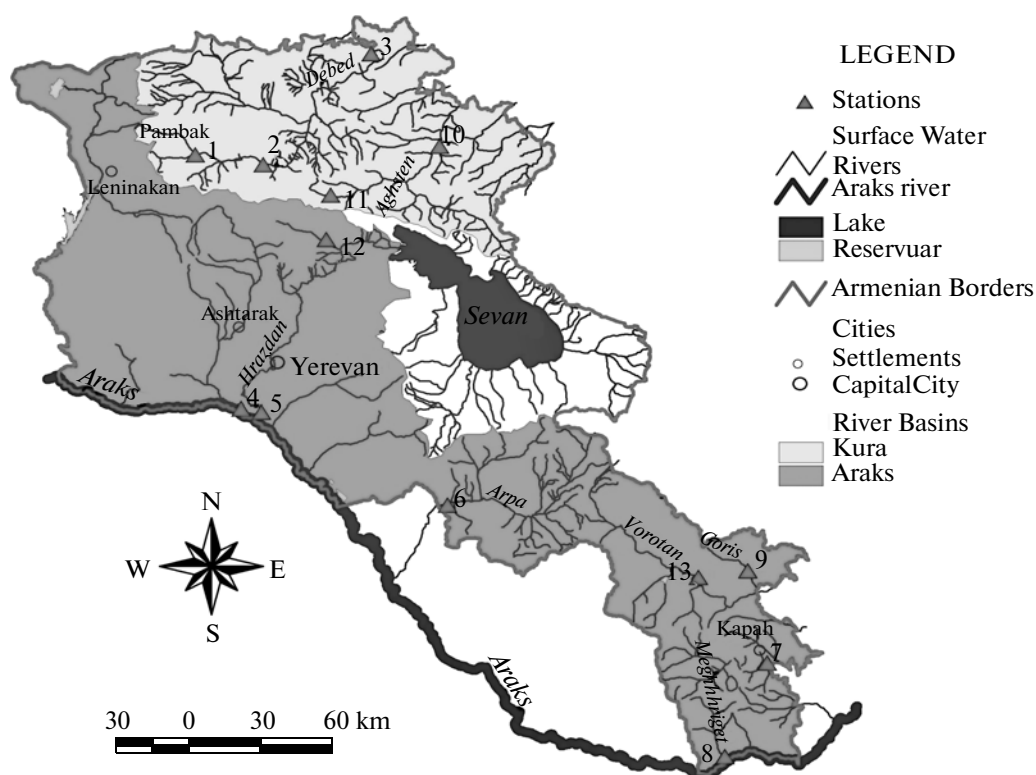


Fig. 1. A Map of River Network and Monitoring Stations in Armenia.

method is as accurate as that of determining emission variant of atomic-absorption photometry.

The quantity of ions was determined in lab conditions on a SF-46, a portable spectrophotometer DR/2400 Hach.

On a monthly basis, determined were soluble forms of heavy metals: Cu, Mo, Zn, Cr, Ni, Mn, Cd, As, Hg, Co, Pb, Ag. Samples for determination of mercury were collected into a glass container, acidified by HNO_3 until reaching $\text{pH} < 2$, and then $\text{K}_2\text{Cr}_2\text{O}_7$ was added. While determining concentrations of other HMs, the samples were filtered through membrane filters with a pore diameter $0.45 \mu\text{m}$, then acidified by HNO_3 (1 : 1) until reaching $\text{pH} \sim 2$ and stored in polyethylene containers. HMs were determined on a RE Aanalist 800 through the atomic-absorption method with graphite atomizer, and flame photometry. Analyte concentrations were measured following the developed ISO-based SOPs [1, 2].

To characterize the level of abnormality of chemical element distribution in the study mediums, Man-made Concentration Coefficient (C_c) was applied. It means relation of element contents in the study anomalous object (C_i) to its background contents (C_b): $C_c = C_i/C_b$. To obtain the integral characteristic of poly-element pollution, a Summary Concentration Index (Z_c) is calculated, which represents the sum of elements

contents in the sample standardized by the background [5]: $Z_c = \sum C_c - (n - 1)$, where n is the number of elements with $C_c > 1$.

Statistical data treatment was performed based on non-parametric Spearman correlation, statistical program Statistica 6.0.

RESULTS AND DISCUSSION

Studying Basic Water Quality Parameters

To the waters of basin rivers weak-alkaline reaction is common. pH values vary 7.3 to 7.7. The indices of DO contents are relatively high this being typical of mountain-region rivers with intense fall, high current velocity and active turnover. Redox potential values (Eh) vary 211.3–245.8 mB. Oxygen as universal oxidizer impacts the Eh value. The role of organic compounds that use oxygen for oxidation allows to justify relatively low Eh values. They are specific of sampling points located in the vicinities of cities where untreated waste waters contain large amounts of organic substances and compounds. Such sampling sites are: 5—city of Masis, 7—Kapan, 9—Goris (Table 2). The values of water conductivity indices (Ec) for the studied period indicate mean water mineralization level for most rivers except the Sevjur and the Hrazdan.

Table 1. Applied analytical methods and detection limits (DL) for waters

Variable	Extraction	Methods	Detection limit and unit
pH	n/a	Water checker U-10	—
Temperature	n/a	Water checker U-10	°C
Dissolved oxygen (DO)	n/a	Water checker U-10	mg/L
Salinity	n/a	Water checker U-10	%
Conductivity	n/a	Water checker U-10	Sm/cm
Turbidity	n/a	Water checker U-10	NTU
Ca	Dissolved	Complexometric	0.05 mg/L
Mg	Dissolved	Complexometric	0.05 mg/L
K	Dissolved	Flame photometry	0.02 mg/L
Na	Dissolved	Flame photometry	0.02 mg/L
SO ₄	Dissolved	Gravimetric	0.2 mg/L
NO ₃	Dissolved	Spectrometry	0.005 mg/L
NO ₂	Dissolved	Spectrometry	0.005 mg/L
N	Total	Spectrometry	0.05 mg/L
P	Total	Spectrometry	0.005 mg/L
HCO ₃	Dissolved	Potentiometric, Titration	0.5 mg/L
Cl	Dissolved	Argentometric	1.0 mg/L
Mo	Dissolved	Atomic absorption	0.5 µg/L
Hg	Dissolved	Atomic absorption with mercury—hydride system	0.6 µg/L
Ag	Dissolved	Atomic absorption	0.1 µg/L
Co	Dissolved	Atomic absorption	0.7 µg/L
Cr	Dissolved	Atomic absorption	0.06 µg/L
Ni	Dissolved	Atomic absorption	0.3 µg/L
Cu	Dissolved	Atomic absorption	0.5 µg/L
Cd	Dissolved	Atomic absorption	0.02 µg/L
Pb	Dissolved	Atomic absorption	0.3 µg/L
As	Dissolved	Atomic absorption	0.7 µg/L
Mn	Dissolved	Flame photometry	0.5 µg/L
Zn	Dissolved	Flame photometry	1.6 µg/L

Relatively high Ec values for the noted rivers are predetermined by high contents of basic ions in water which are known to be strong electrolytes (Table 3). High values of water mineralization of the 2 noted rivers were proved both by Ec indices and water salinity measurements (Table 2).

Studying Common Ions

Table 3 gives data on ion contents in the basin rivers. As a result of the assessment of total contents of ions in the water and basing on river water classification by mineralization level [3], the waters of Rivers Arpa, Voghchi, Meghriget, Gorisget, Marmarik, Vorotan are characterized as “hydrocarbonate”, and those of Rivers Sevjur and Hrazdan—as “hydrocarbonate-sulfate” (Fig. 2d). Total water hardness corresponds to carbonate and varies 1.98–4.98 mg/L. Basing on the

accepted classification of waters by hardness [4], the waters of Rivers Arpa, Voghchi, Meghriget, Gorisget, Marmarik, Vorotan are characterized as “soft” and those of Rivers Sevjur and Hrazdan—as “medium hard”.

High values of River Hrazdan water mineralization is predetermined by the impact of waste- and sewage waters from city of Yerevan and numerous settlements located in the Ararat Valley. As for River Sevjur water quality, it forms under the impact of both natural and man-made factors. The river is fed predominantly by ground waters, this influencing formation of salt composition of the water.

At the same time, the river takes the discharging untreated waste- and sewage waters from industrial enterprises and settlements located within the river basin. The noted factors play a considerable role in

Table 2. Mean values of basic water parameters for the Araks basin rivers for 2004–2007

StN	Monitoring station	pH	Eh, mV	Ec, mS/sm	Turbidity (NTU)	DO, mg/l	Temperature, °C	Salinity, %
4	r. Sevjur–v. Ranchpar	7.50	243.51	1.18	25.86	10.55	16.04	0.05
5	r. Hrazdan–t. Masis	7.29	211.31	1.04	37.29	10.76	14.86	0.04
6	r. Arpa–v. Areni	7.70	235.54	0.39	43.36	11.08	12.39	0.01
7	r. Vokhchi–c. Kapan	7.52	225.46	0.35	43.19	11.04	11.88	0.01
8	r. Meghriget–c. Meghri	7.71	226.72	0.33	31.29	10.81	13.11	0.01
9	r. Gorisget–c. Goris	7.34	223.28	0.26	40.60	10.92	12.38	0.01
12	r. Marmarik–v. Aghavnadzor	7.39	242.97	0.25	37.38	11.66	9.08	0.00
13	r. Vorotan–v. Vorotan	7.31	245.85	0.30	19.12	10.78	12.61	0.01

Table 3. Mean contents of common ions for River Araks basin for 2004–2007 (mg/L)

N	Monitoring station	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	N _{total}	P _{total}	Total miner.
4	r. Sevjur–v. Ranchpar	190.22	104.67	304.01	85.86	5.98	81.81	48.51	15.82	0.19	837.07
5	r. Hrazdan –t. Masis	169.77	99.29	255.15	93.54	6.84	71.64	34.57	25.75	0.34	756.89
6	r. Arpa–v. Areni	50.99	19.25	175.78	24.04	3.26	46.59	11.82	8.30	0.09	340.12
7	r. Vokhchi–c. Kapan	72.51	24.67	177.95	19.41	2.36	50.68	12.98	9.04	0.19	369.79
8	r. Meghriget–c. Meghri	41.66	13.84	147.79	10.26	2.29	40.72	9.29	5.77	0.14	271.76
9	r. Gorisget–c. Goris	38.04	16.35	157.90	22.16	5.62	33.22	12.51	14.76	0.32	300.88
12	r. Marmarik–v. Aghavnadzor	23.82	18.03	121.03	15.94	2.79	24.48	9.29	9.66	0.10	225.14
13	r. Vorotan–v. Vorotan	37.96	15.33	158.29	16.30	3.34	39.08	9.80	7.29	0.49	287.88

water quality formation, this explaining high contents of anions and cations in the waters (Figs. 2a, 2b).

To assess water pollution level, a comparative analysis was performed for anion and cation composition of River Hrazdan water collected from a sampling point nearby city of Masis and at the headwaters. As a result of the analysis, rather a specific picture was obtained. As River Hrazdan flows out from Lake Sevan, so at the riverhead the quality of river water is similar to that of lake water. As seen from Fig. 2 the riverhead water is high in HCO₃ and Mg. The picture is quite different for the point Hrazdan-Masis: a decrease of HCO₃ and Mg and increase in Na, K, Ca and SO₄ (Figs. 2a, 2b).

The type of the Sevan waters HCO₃-Mg is characterized by high contents of Mg, which is typical of carbonate waters forming in ultra-basic rocks. Of all sources the most essential is the Sevan ophiolite belt. The increase in Na and SO₄ in the water is associated

with their transfer from erupted and volcanogenic-sedimentary rocks through which the river flows. The increase in Ca is provoked by calcium-containing aluminosilicates [3].

The river crosses a number of cities, which sewage waters are discharged into the waters after mechanic treatment only. So alongside with natural factors, sewage waters, too, add to water enrichment with the noted ions.

Rivers Hrazdan and Sevjur are high in biogenic elements. In particular, the indicated levels of nitrogen contents prove the presence of man-made load (household pollution) on water objects (Figs. 2c).

Statistical Data Processing

The statistical analysis was performed for the general database on the all rivers of the Araks basin. As a result, indicated was stable correlation dependence of

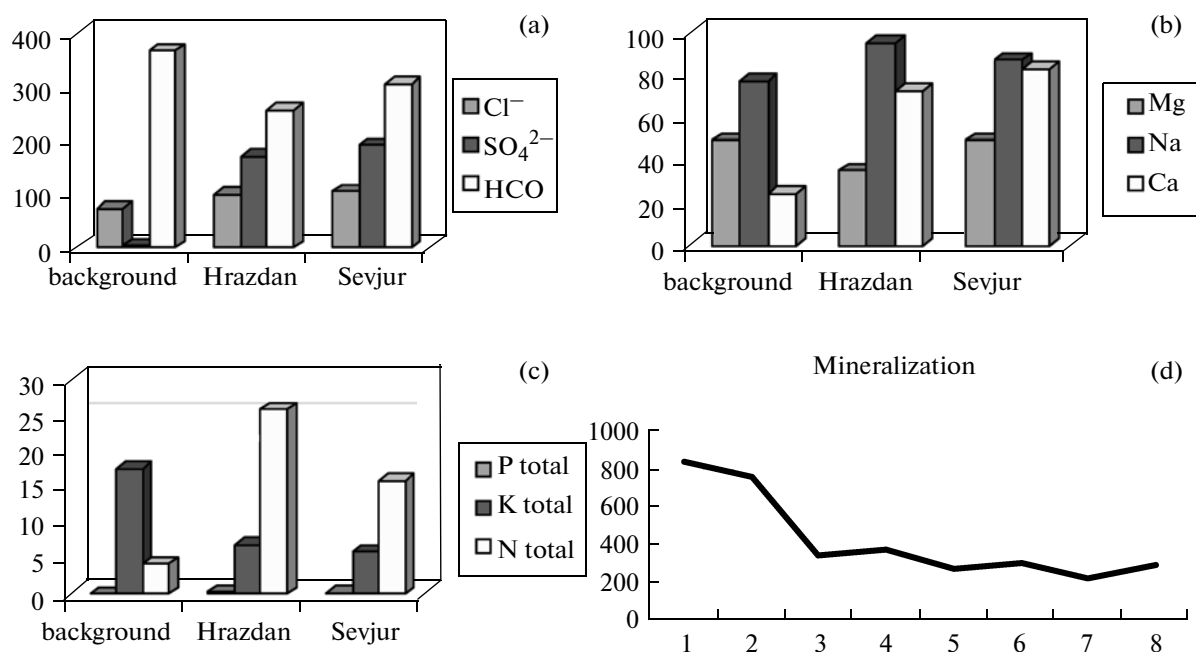


Fig. 2. The level of anion-cation composition and total mineralization in the waters of the Araks basin rivers, mg/L.

different ions as well as of electroconductivity and ions.

Heavy Metals

Hydrogeochemical characteristic of heavy metals contents in the river water. As indicated above, the contents of heavy metals in the studied river waters are not excessive vs. MAC. However, the contents of separate metals show a manifold excess vs. the background. So for determining the degree of the impact of geochemical landscape upon water quality formation we assessed the contents of heavy metals from hydrogeochemical viewpoint.

For this purpose calculated were concentration coefficients (C_c) (the element contents excess vs. the background) and summary indices of heavy metals concentrations (Table 4).

Based on the obtained C_c values, ranged qualitative series of geochemical stream were made up (Table 5).

Assessing hydrogeochemical peculiarities of HM contents for 2005–2007 indicated that

for River Hrazdan dominating was nickel in 2005 and arsenic—in 2006 and 2007. The river is exposed to both natural and man-made sources of heavy metals, thus experiencing the impact of a whole set of factors. Domination of metals in geochemical series was indicated with regard for basic factors: agricultural runoffs and industrial waste water;

river Vogchi was characterized by high indices of copper in 2005, 2006, 2007. Such high concentration

coefficients (Table 5) are linked to presence of copper and copper-molybdenum deposits within the river basin [6] as well as to active operation of mining enterprises. For the rest rivers chromium was dominant in 2005, 2006, 2007, which could be presumably induced by a soil-washout factor dominating over other quality formation sources.

Assessing the total value of summary concentration index for the basin as a whole indicates that the dynamics of its variations positively correlates to that of the value of annual water runoffs from the watershed (Fig. 5). This allows a conclusion that priority in formation of total geochemical stream of heavy metals is given to chemical runoff from watershed river basins through both surface and surface-slope washout. Therefore, though point pollution sources exert a strong local impact, nonetheless in formation of total geochemical stream of heavy metals in the basin scattered source is dominant, which is manifested as a washout from the watershed.

CONCLUSIONS

The outcome of research indicated that in respect to total mineralization the waters of all the studied rivers except the Hrazdan and the Sevjur are characterized by predominantly hydrocarbonate and the noted 2 rivers—by transitive to sulfate composition. Collating derived conclusions with situation prior to the research and literature data of historic period indi-

Table 4. Concentration coefficients (C_c) and summary indices (Z_c) of heavy metals contents for 2005–2007

Elements	Ni	Cr	Mn	Zn	Cu	Hg	Cd	Mo	Z_c^*
R. Hrazdan–t. Masis									
background	1.027	1.182	16.00	15.00	0.732	0.548	0.018	2.312	
C_c									
2005	8.05	1.33	3.86	2.86	2.36	7.82	2.50	0.46	22.4
2006	2.45	1.13	3.50	3.81	3.38	1.31	2.00	0.59	20.9
2007	2.36	1.26	3.32	2.16	9.84	1.34	2.50	0.63	45.0
R. Arpa–v. Aren									
background	0.574	0.001	20.28	22.28	1.646	0.000	0.052	0.000	
C_c									
2005	4.18	12.50	1.17	1.18	0.65	0.76	0.80	1.82	16.3
2006	1.61	12.00	0.70	0.89	0.70	0.66	0.60	1.18	11.7
2007	2.36	14.68	1.02	1.13	2.22	0.67	0.92	1.17	17.5
R. Vokhchi–1. Kapan									
background	2.95	0.06	24.2	39.0	1.096	0.6	0.02	0.5	
C_c									
2005	1.19	20.33	2.22	2.01	20.08	–	10.00	12.86	62.5
2006	0.42	11.00	4.30	3.65	23.63	–	10.50	8.26	58.3
2007	0.51	22.25	1.95	1.91	23.96	–	7.61	8.31	64.4
R. Meghri get–v. Meghri									
background	0.368	0.000	15.62	15.62	2.045	0.418	0.068	3.060	
C_c									
2005	4.86	12.83	1.56	2.24	0.95	2.38	0.57	1.15	19.0
2006	3.16	8.50	1.88	2.02	1.33	1.76	0.43	0.27	12.3
2007	3.14	13.13	1.72	1.28	3.20	1.43	0.61	1.44	18.8
R. Gorisget–t. Goris									
background	0.378	0.083	20.00	20.00	1.275	0.197	0.029	0.000	
C_c									
2005	6.97	12.00	2.10	1.72	1.06	4.30	1.33	1.50	23.9
2006	3.08	8.13	1.46	1.50	1.78	4.15	1.67	1.88	16.8
2007	3.15	16.45	1.51	1.13	4.06	5.90	0.94	2.09	28.1
R. Vorotan–t. Vorotan									
background	0.576	0.085	11.26	11.29	0.926	1.015	0.053	0.000	
C_c									
2005	3.98	13.75	2.53	2.78	2.29	1.02	0.80	2.96	2.31
2006	2.90	6.13	2.43	2.47	3.30	0.81	0.60	2.18	18.9
2007	2.03	9.99	2.26	1.80	7.61	0.63	0.56	1.88	28.9

* Summary Index of Concentration.

	Valid	Spearman	t(N-2)	p-level
HCO ₃ & Ca	182	0.785726	17.04182	0.000000
HCO ₃ & Mg	182	0.673985	12.24031	0.000000
Na & HCO ₃	182	0.701281	13.19803	0.000000
Na & K	182	0.631602	10.92985	0.000000
Na & Ca	182	0.701999	13.22466	0.000000
Na & Mg	182	0.643582	11.28144	0.000000
Ca & Mg	182	0.634682	11.01896	0.000000

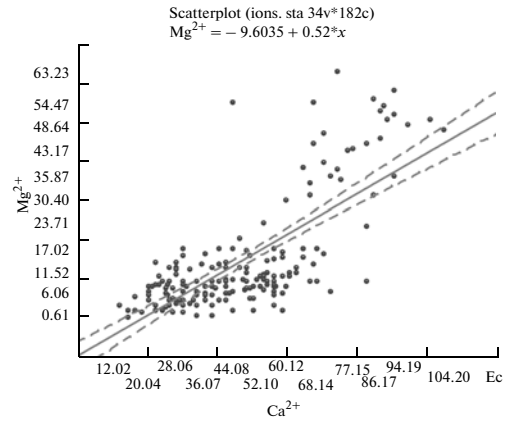


Fig. 3. The results of the Spearman correlation of electroconductivity and ions between 2004 and 2007 (to the right: one of plots displaying relations between Ec and SO₄²⁻).

	Valid	Spearman	t(N-2)	p-level
Ec & SO ₄ ²⁻	182	0.668742	12.06749	0.000000
Ec & HCO ₃	182	0.749624	15.19536	0.000000
Ec & Na	182	0.717426	13.81682	0.000000
Ec & Ca	182	0.813262	18.75082	0.000000
Ec & Mg	182	0.691097	12.82861	0.000000

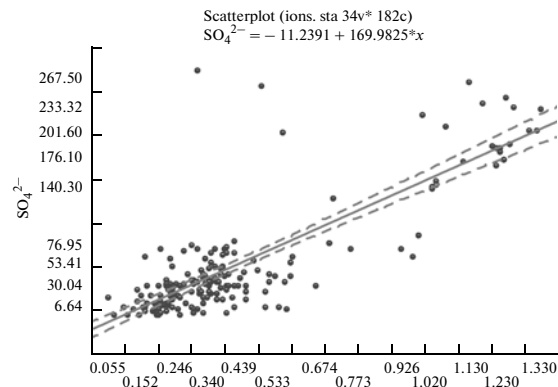


Fig. 4. The results of the Spearman correlation of different ions between 2004 and 2007 (to the right: one of plots displaying relations between Ca and Mg).

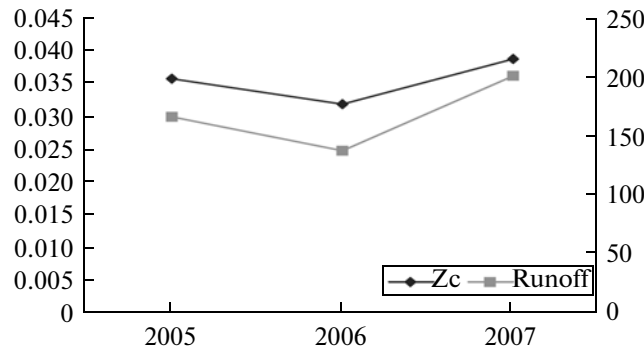


Fig. 5. Variations in the value of total summary index of HM concentration and water runoff from the watershed for 2005–2007.

cated that the rivers belong to the same classes as earlier.

Statistical treatment of water quality data allowed indication of good correlation dependence of different ions as well as of electroconductivity and ions for all the rivers of the Araks basins. As a result of the analysis

of data on heavy metals, transfer sources and impact factors were revealed.

Despite a substantial impact of industrial, household and agricultural runoffs, the dominating role of geochemical landscape of watershed in river water quality formation is evident. The transport of this or that heavy metals of the river water is predetermined

Table 5. Qualitative series of geochemical stream of HMs in River Araks basin rivers

N	Sampling stations	Qualitative series of geochemical flow
2005		
St. 5	r. Hrazdan–t. Masis	Ni ₍₈₎ -Hg _(7.8) -Mn _(3.8) -Zn _(2.9) -Cd _(2.5) -Cu _(2.3) -Cr _(1.3) -Mo _(0.5)
St. 6	r. Arpa–v. Areni	Cr _(12.5) -Ni _(4.2) -Mo _(1.8) -Zn _(1.2) -Mn _(1.2) -Hg ₍₁₎ -Cd _(0.8) -Cu _(0.6)
St. 7	r. Vokhchi–c. Kapan	Cu _(20.1) -Cr ₍₂₀₎ -Mo ₍₁₂₎ -Cd ₍₁₀₎ -Mn _(2.2) -Zn ₍₂₎ -As ₍₂₎ -Ni _(1.2)
St. 8	r. Meghriget–c. Meghri	Cr _(12.8) -Ni _(4.9) -Hg _(2.4) -Zn _(2.2) -Mo _(1.5) -Mo _(1.1) -Cd _(0.6) -Cu _(0.5)
St. 9	r. Gorisget–c. Goris	Cr ₍₁₂₎ -Ni ₍₇₎ -Hg _(4.3) -Mn _(2.1) -Zn _(1.7) -Mo _(1.5) -Cd _(1.3) -Cu ₍₁₎
St. 13	r. Vorotan–v. Vorotan	Cr _(13.7) -Ni ₍₄₎ -Mo ₍₃₎ -Zn _(2.8) -Mn _(2.5) -Cu _(2.3) -Hg ₍₁₎ -Cd _(0.8)
2006		
St. 5	r. Hrazdan–t. Masis	As _(10.3) -Zn _(3.8) -Mn _(3.5) -Cu _(3.4) -Ni _(2.5) -Cd ₍₂₎ -Hg ₍₂₎ -Cr _(1.1)
St. 6	r. Arpa–v. Areni	Cr ₍₁₂₎ -Ni _(1.6) -Mo _(1.1) -Zn _(0.9) -Mn _(0.7) -Hg ₍₁₎ -Cd _(0.7) -Cu _(0.7)
St. 7	r. Vokhchi–c. Kapan	Cu _(23.6) -Cr ₍₁₁₎ -Cd _(10.5) -Mo _(8.3) -Mn _(4.3) -Zn _(3.6) -As _(3.6) -Ni _(0.4)
St. 8	r. Meghriget–c. Meghri	Cr _(8.5) -Ni _(3.2) -Zn ₍₂₎ -Mn _(1.9) -Hg _(1.7) -Cu _(1.3) -Cd _(0.4) -Mo _(0.3)
St. 9	r. Gorisget–c. Goris	Cr _(8.1) -Hg _(4.1) -Ni _(3.1) -Cu _(1.8) -Cd _(1.7) -Mo _(1.9) -Mn _(1.5) -Zn _(1.5)
St. 13	r. Vorotan–v. Vorotan	Cr _(6.1) -As _(5.7) -Cu _(3.3) -Ni ₍₃₎ -Zn _(2.5) -Mn _(2.5) -Mo _(2.2) -Cd _(0.6)
2007		
St. 5	r. Hrazdan–t. Masis	As _(29.2) -Cu _(9.8) -Mn _(3.3) -Cd _(2.5) -Ni _(2.4) -Zn _(2.2) -Cr _(1.3) -Hg _(1.3)
St. 6	r. Arpa–v. Areni	Cr _(14.7) -Ni _(2.4) -Cu _(2.2) -Mo _(1.2) -Zn _(1.1) -Mn ₍₁₎ -Cd ₍₁₎ -As _(0.9)
St. 7	r. Vokhchi–c. Kapan	Cu ₍₂₄₎ -Cr _(22.2) -Mo _(8.3) -Cd _(7.6) -As _(5.8) -Mn _(1.9) -Zn _(1.1) -Ni _(0.5)
St. 8	r. Meghriget–c. Meghri	Cr _(13.1) -Cu _(3.2) -Ni _(3.1) -Mn _(1.7) -Hg _(1.4) -Mo _(1.4) -Zn _(1.3) -Cd _(0.6)
St. 9	r. Gorisget–c. Goris	Cr _(16.4) -Hg _(5.9) -Cu _(4.1) -Ni _(3.1) -Mo _(2.1) -Mn _(1.5) -Zn _(1.1) -Cd _(0.9)
St. 13	r. Vorotan–v. Vorotan	Cr _(9.9) -As _(9.8) -Cu _(7.6) -Mn _(2.3) -Ni ₍₂₎ -Mo _(1.9) -Zn _(1.8) -Cd _(0.6)

by geogenic factors of ore regions, ore water, peculiarities of soil washout and so on. Exploitation of ore deposits located within river basins adds to water enrichment with metals.

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