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AN INVESTIGATION OF HYDROCHEMICAL CONTAMINATION IN THE HRAZDAN RIVER, ARMENIA

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Hydrochemical investigations in the Hrazdan River, Armenia, were conducted. Water samples for pH, EC, K^+, Ca^{2+}, SO_4^{2-}, Mg^{2+}, Cr^{6+}, Fe, and Zn analyses were taken from the river midstream in May and July 2019 and the downstream in June, August, and September 2020. The results of this study revealed the current hydrochemical status of the Hrazdan River, as well as the ecological and agorecological risks and potential sources of hydrochemical pollution in the river ecosystem.

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***Keywords*:** Hrazdan River, hydrochemical status, hydroecological hazards, agroecological risks, pollution sources.

Introduction. Chemical, physical, and biological properties of water determine whether water is suitable for consumption or safe for the environment [1]. Human activities affect water quality which limits its availability for humans and ecosystems [2]. Surface waters are most vulnerable to anthropogenic influence. Global surface water quality is governed by complex anthropogenic activities (e.g., household, industrial, and agricultural activities) and natural processes (i.e., weathering, hydrological features) [3]. Rapid development of economy and urbanization has intensified the river pollution, which changes the hydrochemical regime of the rivers and harms the ecosystems seriously [4].

Similar is the situation for Armenian rivers. The Hrazdan River is considered one of the longest (141 *km*) in Armenia. It originates from Lake Sevan, passes through 3 provinces (Gegharkunik, Kotayk, and Ararat) of Armenia and capital city of Yerevan and flows into the transboundary Araks River. The water of the Hrazdan River is used for irrigation, energetic, recreational, industrial and other purposes [5, 6]. Having such economic importance for Armenia, the Hrazdan River is endangered by anthropogenic pollution due to insufficient management of discharges from human activities [5, 6, 7]. Hydrochemical assessment is, therefore, essential for evidence-informed decision-making on the best pollution management and control. The present study aimed to investigate the level and potential anthropogenic sources of chemical contamination in the Hrazdan River water.

Materials and Methods. Sampling and measurements were done in 8 locations of the midstream (M-1, M-2, M-3, and M-4) and downstream (D-5, D-6,

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D-7, and D-8) of the Hrazdan River as outlined in Table 1. Water samples from the midstream locations including "Yerevanyan Lich" Reservoir site were collected in May and July 2019, and the samples from the downstream locations in June, August, and September 2020. The water samples in most of cases before measurement were evaporated to increase the density of major ions and heavy metals in the water, which made it possible to increase the sensitivity of major ion and heavy metal measurements. Due to the limited measurement range of an analyzer (photometer), the water samples in some cases were diluted to decrease the density of major ions in the water. The water samples were analysed for K^+ (turbidimetric tetraphenylborate method), Ca^{2+} (oxalate method), SO_4^{2-} (sulfate is precipitated with barium chloride crystals), Mg^{2+} (calmagite method), Cr^{6+} (diphenylcarbohydrazide method), Fe (TPTZ method), and Zn (zincon method) using a multi-parameter photometer (HI83200, Hanna Instruments) [8]. Water electrical conductivity (EC) and pH were determined using a multiparameter tester (HI98129, Hanna Instruments). Hydrochemical contamination levels in terms of the investigated ions, elements, and parameters were assessed according to the Armenian ecological norms for the rivers of the Hrazdan River basin [9]. Hazards in the case of water use for irrigation purposes were assessed according to the USDA classification of irrigation water based on EC values [10] and magnesium adsorption ratio (MAR) [11].

Table 1

Coordinates of investigated sites.

Sampling site code	N/Lat	E/Long	Sampling site location
M-1	40°16'51.1"	44°35'21.1"	Hrazdan River site located in Getamej Village
M-2	40°09'31.6"	44°29'33.5"	Hrazdan River site located in Yerevan City, upstream of "Yerevanyan Lich" Reservoir
M-3	40°09'34.2"	44°28'23.2"	"Yerevanyan Lich" Reservoir site located near the dam
M-4	40°08'57.0"	44°27'50.7"	Hrazdan River site located in Yerevan City, downstream of "Yerevanyan Lich" Reservoir
D-5	40°07'53.7"	44°25'07.5"	Hrazdan River site located in Yerevan City, downstream of the Aeratsia sewage treatment plant
D-6	40°06'17.8"	44°22'49.5"	Hrazdan River site located in Darbnik Village
D-7	40°02'26.6"	44°24'33.7"	Hrazdan River site located downstream of Sis Village
D-8	40°01'22.8"	44°26'28.4"	Hrazdan River site located near Hovtashen Village

Results and Discussion. Based on pH values, natural waters are divided into groups [12], according to which, the Hrazdan River mid- and downstream waters with pH values between 7.5 and 8.4 and between 7.1 and 7.4, respectively (Tables 2, 3), belonged to the groups of weakly alkaline (7.5–8.5) and neutral (6.5–7.5) waters, accordingly. pH is of high importance for chemical and biological processes in natural waters. The growth of hydrobionts and the toxicity of contaminants are dependent on the water pH value [12]. The pH values in all the investigated sites during the whole investigation period were within the ecologically safe level (see Tables 2, 3).

EC is a measure of the amount of total dissolved ions in water [13] and, therefore, it is used as a salinity indicator [14]. Freshwater salinization can affect basic functions such as osmoregulation and reproduction and, therefore, reduce survival [15]. The EC value in the Hrazdan River during the investigation period varied from 374 to 1050 $\mu S/cm$ (Tables 2, 3) indicating the lowest total soluble salt concentrations in the sampling site M-3 and the highest contents in the sampling site D-8. The total soluble salt level expressed by EC exceeded the ecological norm in all the investigated sites during the whole investigation period (see Tables 2, 3). All of this indicated that the Hrazdan River mid- and downstream sites were under pressures from urban (Yerevan City) and rural household activities as well as agricultural land use. According to the USDA classification for irrigation water based on EC values [10], in the case of waters used for irrigation purposes, the total soluble salt content (see Tables 2, 3) in some cases may have caused stress for sensitive plants (250–750 $\mu S/cm$), however, it in most of the cases may have adversely affected most plants (750–2250 $\mu S/cm$).

Although inorganic ions such as Mg^{2+}, Ca^{2+}, K^+, and SO_4^{2-} have physiological roles for aquatic organisms, however, they can cause aquatic toxicity when present in excessive concentrations [16]. The Mg^{2+} concentrations in the Hrazdan River downstream sites were noticeably higher than in the midstream sites, however, they were much lower than the unallowable level for the hydroecosystem health (see Tables 2 and 3). MAR is used to specify the magnesium hazard of irrigation water [17]. The MAR value in the waters of the investigated sites varied from 3.9 to 15.3 (Tables 2, 3) indicating no magnesium hazard for irrigation water use (≤ 50). The Ca^{2+} concentrations between 170 and 230 *mg*/*l* in the Hrazdan River downstream sites were about 2–12 times higher than the concentrations in the midstream sites (see Tables 2 and 3), indicating water quality deterioration from the II class (good) in the midstream to the III–IV class (moderate-bad) in the downstream [9]. The Ca^{2+} level exceeded the ecological norm in all the downstream sites during the whole investigation period (see Tables 2, 3). The K^+ concentrations between 7 and 36 *mg*/*l* and the SO_4^{2-} concentrations between 63 and 200 *mg*/*l* exceeded the ecological norms in all the investigated sites during almost the whole investigation period (see Tables 2, 3). It is worth to mention that the K^+ and SO_4^{2-} concentrations in the river downstream sites were noticeably higher than in the midstream sites (see Tables 2, 3).

Some inorganic substances such as heavy metals are often highly toxic and may cause undesirable hydroecological effects when accumulated to a toxic concentration [18]. The Fe concentrations in the river midstream sites and the downstream sites D-7 and D-8 during the whole investigation period were within the allowable level (see Tables 2, 3), while the concentrations in the downstream sites D-5 and D-6 in some cases exceeded the ecological norm (see Table 3). The Cr^{6+} and Zn concentrations in all the investigated sites during the whole investigation period were within the ecologically safe levels (see Tables 2, 3).

Thus, the concentrations of almost all the investigated contaminants in the Hrazdan River downstream sites were noticeably higher than in the midstream sites which can be explained by the impact of Yerevan City household wastewaters from the non-operational Aeratsia sewage treatment plant on the river sites D-5 and D-6 and the influence of rural household and agricultural discharges on the sites D-6, D-7, and D-8. However, the river midstream sites also showed pollution but only with some contaminants such as K^+ and SO_4^{2-} which was supposedly caused by the impact of Yerevan City household and rural discharges.

Table 2

The results of the investigation of some physicochemical parameters in the Hrazdan River midstream in 2019.

Sampling site code	pH	EC (*μS/cm*)	MAR	Mg^{2+} (*mg/l*)	Ca^{2+} (*mg/l*)	K^+ (*mg/l*)	SO_4^{2-} (*mg/l*)	Cr^{6+} (*μg/l*)	Fe (*μg/l*)	Zn (*μg/l*)
	May									
M-1	7.6	756.0	9.8	3.3	50	6.0	30.0	1.7	75	3
M-2	7.7	528.0	3.9	1.7	70	4.0	35.0	2.7	88	4
M-3	8.4	368.0	8.6	1.7	30	3.5	25.0	2.0	75	3
M-4	7.5	374.0	12.3	1.7	20	3.0	20.0	2.2	80	4
	July									
M-1	7.9	762.0	15.3	3.3	30	6.5	35.0	1.2	85	4
M-2	7.8	832.0	10.8	3.3	45	7.0	75.0	2.3	102	6
M-3	8.4	710.0	13.4	3.3	35	6.5	65.0	1.2	89	2
M-4	7.9	760.0	9.8	3.3	50	6.0	65.0	3.0	85	3
Norm [9]	6.5–9.0	227.4	–	50.0	100.0	3.0	20.7	11.0*	160	100

Table 3

The results of the investigation of some physicochemical parameters in the Hrazdan River downstream in 2020.

Sampling site code	pH	EC (*μS/cm*)	MAR	Mg^{2+} (*mg/l*)	Ca^{2+} (*mg/l*)	K^+ (*mg/l*)	SO_4^{2-} (*mg/l*)	Cr^{6+} (*μg/l*)	Fe (*μg/l*)	Zn (*μg/l*)
	June									
D-5	7.2	800.0	10.1	15.0	220	21	90.0	1.2	83	6
D-6	7.1	862.0	9.7	15.0	230	36	65.0	1.0	75	6
D-7	7.1	980.0	7.6	10.0	200	7	140.0	2.2	78	3
D-8	7.2	1050.0	8.8	10.0	170	9	200.0	3.0	91	5
	August									
D-5	7.3	938.0	10.7	16.7	230	31	85.0	0.5	130	5
D-6	7.3	946.0	10.5	15.0	210	26	70.0	0.7	87	8
D-7	7.3	1010.0	7.6	10.0	200	9	150.0	3.5	68	6
D-8	7.3	1012.0	8.4	10.0	180	9	150.0	2.5	100	6
	September									
D-5	7.1	886.0	10.1	15.0	220	23	80.0	3.0	200	6
D-6	7.1	916.0	9.5	13.3	210	24	70.0	1.2	180	5
D-7	7.3	990.0	9.9	13.3	200	10	170.0	1.5	85	3
D-8	7.4	1012.0	8.8	10.0	170	10	140.0	2.5	79	3
Norm [9]	6.5–9.0	227.4	–	50.0	100	3	20.7	11.0*	160	100

*Ecological norm for total Cr

Conclusion. In general, it can be stated that the anthropogenic activities caused such salinity degrees in the Hrazdan River mid- and downstream sites that may have had negative hydroecological effects and may have posed agroecological risks in the case of waters used for irrigation. The potential sources of this pollution were the irregular urban (Yerevan City) household and rural discharges. The concentrations of some contaminants such as Ca^{2+}, K^{+}, and SO_4^{2-} in the Hrazdan River downstream sites were mostly formed by the potential impact of discharges from the non-operational Aeratsia sewage treatment plant in Yerevan City as well as rural household and agricultural activities and may have adversely affected the hydroecosystem health. The river downstream occasionally also showed ecologically unfavorable conditions in terms of Fe content which can also be explained by the potential impact of discharges from the non-operational Aeratsia sewage treatment plant. The ecologically unsafe levels of K^{+} and SO_4^{2-} were also observed in the river midstream sites potentially affected by Yerevan City household and rural discharges.

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REFERENCES

1. Khatri N., Tyagi S. Influences of Natural and Anthropogenic Factors on Surface and Groundwater Quality in Rural and Urban Areas. *Fron. Life Sci.* **8** (2015), 23–29. https://doi.org/10.1080/21553769.2014.933716
2. Singh J., Yadav P., et al. Water Pollutants: Origin and Status. In Pooja D., Kumar P. et al. (Eds) *Sensors in Water Pollutants Monitoring: Role of Material.* Singapore: Springer, (2020), 5–20. https://doi.org/10.1007/978-981-15-0671-0_2
3. Bhat S.A., Pandit A.K. Surface Water Quality Assessment of Wular Lake, a Ramsar Site in Kashmir Himalaya, Using Discriminant Analysis & WQI. *J. Ecosyst.* (2014), Article ID: 724728. https://doi.org/10.1155/2014/724728
4. Wang J., Liu X.D., Lu J. Urban River Pollution Control and Remediation. *Procedia Environ. Sci.* **13** (2012), 1856–1862. https://doi.org/10.1016/j.proenv.2012.01.179
5. Gevorgyan G.A., Gabrielyan B.K. Assessment of the Ecologo-Sanitary State of the Hrazdan River and “Yerevanyan Lich” Reservoir by Bacteriological Parameters. *Electron. J. Nat. Sci. NAS RA* **26** (2016), 20–23.
6. Kobelyan H.H. Assessment of the Water Quality of the River Hrazdan by Microbiological Indicators. *Biol. J. Armenia* **69** (2017), 35–38.
7. Kobelyan H.H., Gevorgyan G.A. Hydrochemical Investigation of the Hrazdan River and “Yerevanyan Lich” Reservoir, Armenia. *Biol. J. Armenia* **71** (2019), 93–99.
8. Instruction manual: HI 83200, Multiparameter Bench Photometer. Retrieved from http://www.pewa.de/DATENBLATT/DBL_HA_HA83200-02_MANUAL_ENGLISCH.PDF
9. Armenian Legal Information System (ARLIS) Ecological Norms Recommended for the Surface Waters of the Republic of Armenia (RA Government Resolution №75-N as of January 27, 2011). Retrieved from https://www.arlis.am/DocumentView.aspx?DocID=65705
10. Allison L.E., Bernstein L., et al. Diagnosis and Improvement of Saline and Alkali Soils. USDA Handbook No. 60. Washington, DC, USA: US Government Printing Office (1954).
11. Raghunath I.I.M. Groundwater. 2nd edition. New Delhi, India: Wiley Eastern Ltd. (1987)
12. Guseva T.V., Molchanova Ya.P., et al. Hydrochemical Indicators of the State of the Environment: Reference Materials. Moscow, Russia: SoES (2020). (in Russian)

13. Han T., Li X., et al. Electrical Conductivity during the Ablation Process of the Glacier No. 1 at the Headwaters of the Urumqi River in the Tianshan Mountains. *Arct. Antarct. Alp. Res.* **47** (2015), 327–334.
https://doi.org/10.1657/AAAR00C-13-138
14. Oyem H.H., Oyem I.M., Ezeweali D. Temperature, pH, Electrical Conductivity, Total Dissolved Solids and Chemical Oxygen Demand of Groundwater in Boji-Bojiagbor/Owa Area and Immediate Suburbs. *Res. J. Environ. Sci.* **8** (2014), 444–450.
https://doi.org/10.3923/rjes.2014.444.450
15. Castillo A.M., Sharpe D.M.T., et al. Exploring the Effects of Salinization on Trophic Diversity in Freshwater Ecosystems: a Quantitative Review. *Hydrobiologia* **807** (2018), 1–17.
https://doi.org/10.1007/s10750-017-3403-0
16. Mount D.R., Erickson R.J., et al. The Acute Toxicity of Major Ion Salts to *Ceriodaphnia dubia*: I. Influence of Background Water Chemistry. *Environ. Toxicol. Chem.* **35** (2016), 3039–3057.
https://doi.org/10.1002/etc.3487
17. Varagyan A.L., Gevorgyan G.A., Varagyan V.M. Mineral Salt Content in the Water of the Voghji River Catchment Basin (Armenia): Assessment of Potential Effects on Irrigated Soils and Crops. *Proc. YSU B: Chem. Biol. Sci.* **52** (2018), 204–210.
https://doi.org/10.46991/PYSU:B/2018.54.2.204
18. Gevorgyan G.A., Boshyan T.V. Investigation of river macrozoobenthos community in the Debed River catchment area under the risk of mining impact. *Electron. J. Nat. Sci.* **32** (2019), 9–11.

Գ.Ա. ԳԵՎՈՐԳՅԱՆ

ՀԱՅԱՍՏԱՆԻ ՀՐԱԶԴԱՆ ԳԵՏԻ ՀԻԴՐՈՔԻՄԻԱԿԱՆ ԱՂՏՈՏՄԱՆ ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆ

Իրականացվել են Հայաստանի Հրազդան գետի հիդրոքիմիական հետազոտություններ: pH-ի, էլեկտրահաղորդականության, K^+, Ca^{2+}, SO_4^{2-}, Mg^{2+} և Cr^{6+} իոնների, Fe և Zn տարրերի անալիզների համար ջրանմուշները վերցվել են գետի միջին հոսանքից 2019 թ. մայիս և հուլիս ամիսներին ու ստորին հոսանքից 2020 թ. հունիս, օգոստոս և սեպտեմբեր ամիսներին: Այս ուսումնասիրության արդյունքները բացահայտել են Հրազդան գետի ներկայիս հիդրոքիմիական վիճակը, ինչպես նաև գետի էկոհամակարգի հիդրոքիմիական աղտոտման էկոլոգիական և ագրոէկոլոգիական ռիսկերը ու հնարավոր աղբյուրները:

Г.А. ГЕВОРГЯН

ИССЛЕДОВАНИЕ ГИДРОХИМИЧЕСКОГО ЗАГРЯЗНЕНИЯ РЕКИ РАЗДАН В АРМЕНИИ

Проведены гидрохимические исследования реки Раздан в Армении. Пробы воды для анализов pH, электропроводности, K^+, Ca^{2+}, SO_4^{2-}, Mg^{2+}, Cr^{6+}, Fe и Zn были взяты из среднего течения реки в мае и июле 2019 года и из нижнего течения в июне, августе и сентябре 2020 года. Результаты этого исследования выявили текущее гидрохимическое состояние реки Раздан, а также экологические и агроэкологические риски и потенциальные источники гидрохимического загрязнения экосистемы реки.