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ASSESSMENT OF HEAVY METAL POLLUTION IN THE SOTK AND DZKNAGET RIVERS (ARMENIA)

G. A. KHACHATRYAN *

Scientific Center of Zoology and Hydroecology, NAS of RA, Armenia

This study examines the spatial and temporal variability of heavy metal contamination in the Dzknaget and Sotk Rivers in 2023 and 2024, applying the Heavy Metal Pollution Index (HMPI) and the Metal Index (MI). The concentrations of seven heavy metals (Al, Cd, Fe, Pb, Cr, Ni, Zn) were assessed in three river sections: the upper (Dzk-1) and lower (Dzk-2) reaches of the Dzknaget River, and the lower reach of the Sotk River (Sot-2). The results show consistently low contamination levels at Dzk-1, indicating limited human impact, whereas significantly higher HMPI and MI values at Dzk-2 and Sot-2 point to substantial pollution. Comparative analysis according to World Health Organization (WHO), Food and Agriculture Organization (FAO), and local standards reveals notable differences in contamination classification. Based on FAO criteria, the irrigation risk is considered low, while WHO and local standards indicate more serious ecological and health risks. The observed decrease in contamination in the Sot-2 section in 2024 may suggest some improvement in water quality. Overall, the results emphasize the need for multi-layered assessment frameworks, continuous monitoring, targeted pollution control, and stricter environmental regulations to protect aquatic ecosystems and water resources.

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***Keywords*:** Sotk River, Dzknaget River, heavy metal pollution index (HIP), metal index (MI), water quality assessment, heavy metals.

Introduction. Water is one of the most vital natural resources that sustain life on Earth. Its significance extends beyond mere availability; its quality is crucial for various uses, such as drinking, irrigation, and domestic needs [1]. The quality of water bodies can vary greatly, influenced by geographical conditions, pollution sources, and environmental factors. “Water quality” encompasses the chemical, physical, and biological characteristics of water, reflecting its suitability for intended uses [2]. In the modern era, water pollution by heavy metals (HMs) has become an urgent global environmental issue. When the levels of certain HMs exceed acceptable thresholds, they can have harmful effects on both human health and ecosystems [3]. HMs primarily enter water systems through significant discharges of domestic and industrial wastewater, as well as agricultural runoff [4]. In addition to anthropogenic sources, natural processes such as volcanic eruptions, weathering

* E-mail: gor.khachatryan2@edu.ysu.am

of bedrock, and erosion of mineral-rich soils also contribute to the presence of HMs in water bodies [5].

Among all water sources, surface waters are the most susceptible to pollution, as they are directly exposed to various forms of wastewater discharge. As a result, rivers and lakes around the world face increasing threats from HM pollution, primarily due to rapid urbanization, industrial growth, and inadequate sanitation infrastructure [6]. HMs are considered some of the most dangerous environmental pollutants due to their high toxicity, chemical stability, and non-biodegradable nature [7]. Although some metals, such as Zn, Cu, Fe, and Mn, play important roles in the metabolic functions of living organisms, their accumulation in high concentrations can pose serious threats to biological systems [8]. Given their potential for bioaccumulation and biomagnification through aquatic food chains, monitoring HMs in rivers and lakes is essential [9].

Effective water resource management, therefore, requires regular assessments to identify the sources of HMs and their ecological impacts. In this context, water quality assessment is a key component of sustainable environmental management.

The Dzknaget and Sotk Rivers are among the most important rivers flowing into Lake Sevan, with their waters used for irrigation, industry, and supporting aquatic life. However, few studies have been conducted to assess their quality concerning HMs. This study aims to evaluate water quality pollution by HMs using methods such as the Heavy Metal Pollution Index (HPI) and the Metal Index (MI). The results of this research are expected to attract the attention of local and federal authorities.

Materials and Methods.

Study Area. There are 993 rivers and streams in the Lake Sevan basin, with a total length of approximately 2.687 *km*. The source of the Dzknaget River (length: 22 *km*, area: 86.3 km^2, average basin elevation: 2202 *m*, average annual discharge: 1.08 m^3/s, flow modulus: 13.08 $l/s{\cdot}km^2$) is located at an altitude of 2310 *m*, originates at the junction of the Pambak and Areguni Mountains and flows in a southeasterly direction. In the local drainage zone of the upper river basin, middle-to-upper Quaternary andesite-dacite, andesite, and andesite-basalt formations are widespread. In the lower reaches, the river traverses Paleogene terrigenous and volcanic-sedimentary formations, including sandstones, conglomerates, porphyrites, tuff breccias, and tuff conglomerates, which are locally hydrothermally altered. The Sotk River (length: 20 *km*, area: 59.5 km^2, average basin elevation: 2390 *m*, average annual discharge: 0.55 m^3/s) originates on the western slope of the Sevan Mountain range at an altitude of 2400 *m* and flows from east to west. The Sotk River in its upper reaches (mainly in the mine area) forms typical V-shaped canyons with steep sides, which are mainly composed of ultramafic rocks. The circulation of groundwater mainly occurs through a complex of rocks of basal and ultramafic composition. These rocks occupy approximately two-thirds of the study area [10, 11].

The locations of the sampling points are shown in Fig. 1, with detailed information summarized in Tab. 1.

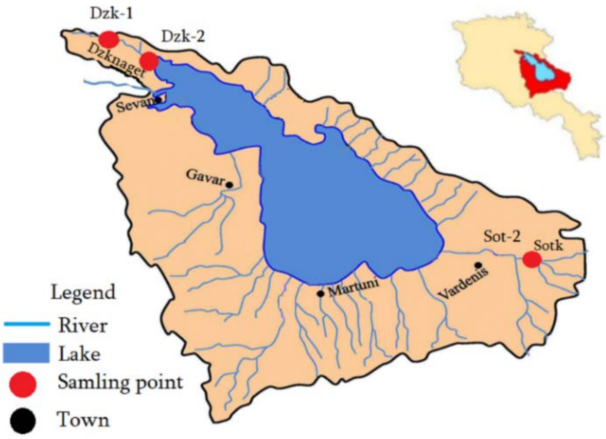

Fig. 1. The locations of the sampling sites along the Sotk and Dzknaget Rivers, identified by their respective codes, are provided in Tab. 1.

Table 1

Summary of the sampling points

River name	Sampling point	The location of the sampling point	Geographic coordinates
Dzknaget	Dzk-1	Upstream, 0.5 *km* above v. Semyonovka	E44.89219, N40.65306
Dzknaget	Dzk-2	Downstream	E44.96272, N40.61709
Sotk	Sot-2	Downstream	E45.85186, N40.20072

Sampling of River Water. A total of 47 water samples were collected on a monthly basis during 2023–2024 from both the upper and lower reaches of the Dzknaget River, as well as the lower reaches of the Sotk River. Sampling procedures followed the guidelines established in ISO 5667-3:2016 [12]. Water samples were collected in disposable polypropylene containers, which were pre-rinsed 2–3 times with the sampled water to minimize contamination. To remove suspended particulates, the samples were filtered through 0.45 μm membrane filters (Supor® 450 Membrane Disc Filter, Port Washington, NY, USA). Immediately after collection, samples were acidified to pH<2 using nitric acid (HNO_3) to prevent alterations in trace element (TE) concentrations due to adsorption or precipitation.

Sample Preparation and Analysis. Water samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS; ELAN® 9000, PerkinElmer, Waltham, MA, USA). The analyses were conducted in accordance with the analytical protocols outlined in ISO 17294-1:2004 [13] and ISO 17294-2:2016 [14]. To ensure the accuracy and reliability of the results, stringent quality control measures were implemented, including blank tests, the use of certified reference materials, quality control samples, and routine performance checks of analytical instruments. The validity of calibration curves was regularly verified using standard solutions to maintain data precision and repeatability. Additionally, to enhance the credibility of the results, qualification tests and interlaboratory comparisons were conducted in collaboration with Umweltbundesamt GmbH

(Vienna, Austria) as part of the "Proficiency Testing (PT) and Interlaboratory Comparison (ILC) Participation Plan."

This monitoring was carried out by the Hydrometeorology and Monitoring Center of the Ministry of Environment of the Republic of Armenia. The laboratory is accredited in accordance with the requirements of GOST ISO/IEC 17025-2019 [15], ensuring compliance with internationally recognized quality standards.

Heavy Metal Pollution Index (HPI). The HPI method is a widely used approach for the comprehensive assessment of water quality contamination resulting from multiple HMs. It is based on the weighted arithmetic mean and can be calculated using Eqs. (1)–(3) [16]:

$$W_i = \frac{k}{S_i}, \quad (1)$$

$$Q_i = \frac{100C_i}{S_i}, \quad (2)$$

$$\text{HPI} = \frac{\sum_{i=1}^{n}(Q_i W_i)}{\sum_{i=1}^{n} W_i}. \quad (3)$$

In these equations, S_i represents the standard permissible concentration of HM i in the water body (*mg*/*L*), and C_i is the corresponding measured concentration (*mg*/*L*). The proportionality constant k is taken as 1. The quality rating Q_i indicates the relative pollution level of metal i, while HPI denotes the overall HPI. The parameter n refers to the total number of HMs considered in the evaluation. The weight factor W_i for each metal is calculated as an inverse function of its standard value S_i, reflecting its relative significance in the overall index.

The suitability of water from the Dzknaget and Sotk Rivers for drinking, agricultural, and ecological purposes was assessed based on guidelines provided by the World Health Organization (WHO) [17], the Food and Agriculture Organization (FAO) of the United Nations [18], and the Republic of Armenia Surface Water Quality Standards (ARLIS) [19], respectively (Tab. 2). The reference values presented in Tab. 1 were used as the standard concentrations (S_i) in the HPI calculation formulas described above.

Table 2

Global and National Determinants for Drinking Water, Irrigation, and Ecological Suitability [17–19]

No.	Heavy metals	Unit	FAO	WHO	ARLIS	
					Dzknaget	Sotk
1	Al	*mg*/*L*	5	0.2	0.28	0.12
2	Cd	*mg*/*L*	0.01	0.003	0.00101	0.00101
3	Fe	*mg*/*L*	5	0.3	0.42	0.24
4	Pb	*mg*/*L*	5	0.01	0.0101	0.01018
5	Cr	*mg*/*L*	0.1	0.05	0.0108	0.014
6	Ni	*mg*/*L*	0.2	0.02	0.011	0.0218
7	Zn	*mg*/*L*	2	3	0.1	0.1

The classification of HPI levels in this study follows the criteria proposed by Tiwari et al. [20], where HPI values are categorized into low, medium, and high pollution levels, as summarized in Tab. 3.

Table 3

HPI pollution index classes

No.	HPI	Pollution levels
1	< 5	low contamination with heavy elements
2	15–30	moderate contamination with heavy elements
3	30 <	high contamination with heavy elements

Metal Index. The Metal Index (MI) is defined as the ratio of the concentration of each metal in the water sample to its corresponding maximum allowable concentration, as expressed in Equation (4) [21]:

$$\text{MI}=\sum_{i=1}^{n}\frac{\text{C}_\text{i}}{(\text{MAC})_i}. \quad (4)$$

In this context, MI represents the Metal Index, where C_i is the concentration of the ***i***-th metal in the water sample, and MAC denotes the maximum allowable concentration for each corresponding element. The subscript iii refers to the specific parameter being evaluated. The MAC values used in the calculation were derived from the reference standards listed in Tab. 2. The classification of MI values into pollution categories is presented in Tab. 4.

Table 4

MI pollution index classes

No.	MI	Pollution levels
1	< 0.3	very pure
2	0.3–1.0	pure
3	1.0–2.0	slightly affected
4	2.0–4.0	moderately affected
5	4.0–6.0	strongly affected
6	> 6.0	seriously affected

Statistical Analysis. Data visualization and graph generation were performed using Origin (version 2018; OriginLab Corporation, Northampton, MA, USA). One-way statistical calculations were conducted in Excel (version 2016; Microsoft Corporation, Redmond, WA, USA). The spatial map was created using ArcGIS (version 10.3; Esri, Redlands, CA, USA).

Results and Discussion.

Heavy Metal Pollution Index. The average concentrations of seven HMs – Al, Cd, Fe, Pb, Cr, Ni, and Zn – were used to calculate the HPI. Fig. 2 presents the detailed HPI values obtained. To evaluate pollution levels and assess water quality for drinking, irrigation, and ecological purposes, the HPI was calculated individually for each sampling station, as illustrated in Fig. 2.

In 2023, the HPI values for the upper (Dzk-1) and lower (Dzk-2) reaches of the Dzknaget River were 4.5 and 11.0, respectively, according to WHO standards [17], both falling within the low pollution category. In contrast, the lower reach of the Sotk River (Sot-2) recorded an HPI of 17.1, placing it in the medium pollution range. This elevated pollution level in the Sotk River is likely associated with mining activities at the Sotk gold mine [3]. In 2024, the HPI value at Sot-2 decreased to 12.3, resulting in a reclassification to the low pollution category. The HPI values at Dzk-1 and Dzk-2 remained within the low pollution range in both years, indicating relative stability in HMs contamination in the Dzknaget River.

According to the FAO-based criteria [18], HPI values remained consistently low across all sampling sites and throughout both years, falling within the low contamination range. This uniformly low HPI under FAO guidelines may reflect either less stringent thresholds or lower weighting of HM concentrations in the FAO methodology. These results suggest that the water quality at the studied sites does not present a significant risk for agricultural use.

According to the ARLIS [19], the HPI values in 2023 for the upper (Dzk-1) and lower (Dzk-2) reaches of the Dzknaget River were 9.2 and 12.0, respectively, both within the low pollution category. In contrast, Sot-2 exhibited a higher HPI value of 17.9, reaching the threshold for moderate pollution. In 2024, the HPI at Sot-2 decreased to 13.6, bringing it back into the low pollution range. Meanwhile, Dzk-2 experienced a slight increase in HPI from 12.0 to 13.4, although it remained within the low contamination category. The HPI at Dzk-1 remained relatively stable, with values of 9.1 and 9.2 in 2023 and 2024, respectively, indicating consistent environmental conditions in the upper reaches of the Dzknaget River.

Overall, the comparison between 2023 and 2024 indicates a general trend of stabilization or improvement in HPI values across the monitored sites. The most notable improvement was observed at Sot-2, where HPI levels decreased under both WHO [17] and ARLIS [19] standards, suggesting either a reduction in heavy metal inputs or the influence of natural attenuation processes. Dzk-1 consistently maintained low HPI values across all standards and years, reinforcing the assumption that the upper reaches of the Dzknaget River are relatively unaffected by anthropogenic influences. In contrast, Dzk-2, located in the lower reaches of the Dzknaget River, demonstrated greater variability in HPI values, likely reflecting its increased exposure to human activities.

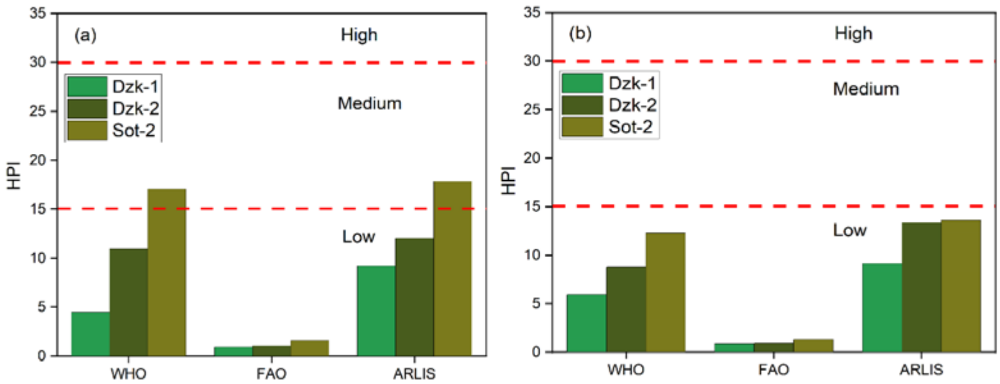

Fig. 2. Heavy Metal Pollution Index (HPI) for Dzknaget and Sotk River sites : (a) 2023; (b) 2024.

Metal Index. The MI is a valuable tool for assessing the extent of HM contamination in aquatic environments. This study evaluates MI values based on international and national water quality standards, including those from the WHO

[17], FAO [18], and ARLIS [19]. The analysis focuses on three monitoring points: Dzk-1, Dzk-2, and Sot-2 across two consecutive years, 2023 and 2024 (Fig. 3).

According to WHO guidelines [17], MI values reveal a clear increase in pollution levels in the lower reaches of the river. In 2023, Dzk-1 was classified as slightly affected (MI = 1.89), while Dzk-2 and Sot-2 exhibited MI values of 6.81 and 6.74, respectively, both falling into the seriously affected category. In 2024, a slight improvement was observed in the lower reaches, with Dzk-2 showing an MI of 5.34 and Sot-2 an MI of 4.21, reclassifying them as strongly affected. Meanwhile, Dzk-1 transitioned to the moderately affected category (MI = 3.38). These trends reflect the influence of anthropogenic pressures on the lower reaches of the rivers.

In contrast, the MI values based on FAO irrigation standards [18] were significantly lower, with all sites falling within the very pure to pure categories. In both years, Dzk-1 remained in the very pure category (MI = 0.10 (2023); MI = 0.17 (2024)), while Dzk-2 and Sot-2 were classified as pure or very pure, with MI values not exceeding 0.34. These results suggest that the water remains suitable for agricultural use.

Based on the ARLIS [19], the MI assessments provided intermediate insights between those of WHO and FAO. In 2023, Dzk-1 was classified as slightly affected (MI = 1.57), which escalated to moderately affected in 2024 (MI = 2.66). Both Dzk-2 and Sot-2 fell within the strongly affected to seriously affected range, with Sot-2 reaching the highest MI value of 9.84 in 2023. Although a slight decline was observed in 2024 (MI = 5.93), it remained in the strongly affected category. These findings suggest ongoing contamination challenges, particularly in the downstream segments of the rivers.

Overall, this assessment demonstrates a consistent trend of increasing pollution along the river courses, with the most significant impacts observed in the lower reaches, particularly in Dzk-2 and Sot-2. The discrepancies between the standards emphasize the importance of a multidimensional approach to water quality evaluation. While the results based on FAO standards [18] indicate minimal concern for irrigation purposes, the assessments derived from WHO [17] and national standards [19] highlight substantial ecological and health risks.

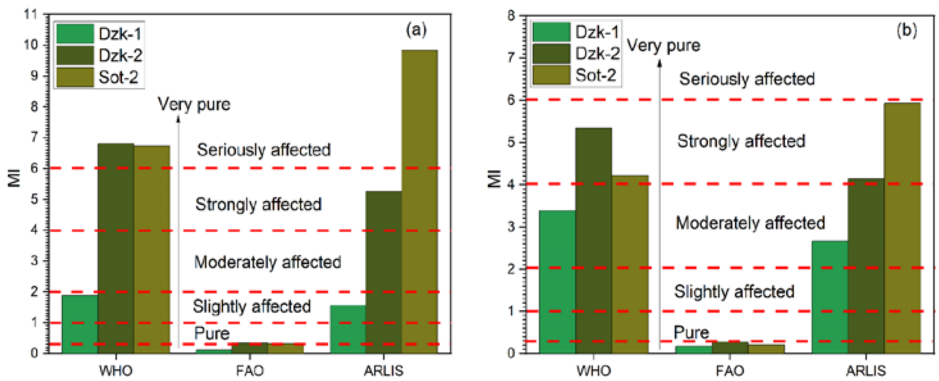

Fig. 3. Spatiotemporal Variation of MI in the Dzknaget and Sotk Rivers: (a) 2023; (b) 2024.

The improvements in water quality observed at certain locations in 2024 may be attributed to seasonal variability or a reduction in human activity. However, pollution levels still remain concerning. Ongoing long-term monitoring, alongside the implementation of effective pollution control measures, is crucial to ensure the sustainability of these freshwater systems.

Conclusion. This study underscores the effectiveness of the HPI and the MI as valuable tools for evaluating the spatial and temporal dynamics of HM contamination in river systems. Analysis of 2023–2024 data reveals significant spatial variability in pollution levels, particularly between upstream (Dzk-1) and downstream (Dzk-2, Sot-2) sampling sites. The upper reach of the Dzknaget River (Dzk-1) consistently exhibited low pollution levels, indicative of minimal anthropogenic influence. In contrast, higher contamination levels were observed in the lower reaches, especially at Dzk-2 and Sot-2, likely linked to intensified human activity, including mining operations near the Sotk River.

While HPI and MI values assessed according to FAO standards [18] suggest that water quality remains suitable for irrigation, evaluations based on WHO [17] and national standards [19] present a more concerning scenario, with Dzk-2 and Sot-2 classified as moderately to severely polluted. These discrepancies highlight the necessity of employing multiple water quality criteria to achieve a more nuanced and comprehensive understanding of potential environmental and public health risks.

Encouragingly, the observed reduction in HPI and MI values at certain sites – most notably Sot-2 – in 2024 suggests potential improvements in water quality, possibly due to mitigation measures or natural attenuation processes. Nevertheless, the continued presence of HM pollution in downstream areas underscores the urgent need for sustained long-term monitoring, the implementation of targeted pollution reduction strategies, and the enforcement of stricter environmental regulations to safeguard freshwater ecosystems and ensure the safety of water resources for diverse uses.

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Գ. Ա. ԽԱՉԱՏՐՅԱՆ

ՍՈԹՔ ԵՎ ՁԿՆԱԳԵՏ ԳԵՏԵՐՈՒՄ ԾԱՆՐ ՄԵՏԱՂՆԵՐՈՎ ԱՂՏՈՏՎԱԾՈՒԹՅԱՆ ԳՆԱՀԱՏՈՒՄ (ՀԱՅԱՍՏԱՆ)

Այս ուսումնասիրությունը դիտարկում է ծանր մետաղներով աղտոտվածության տարածական և ժամանակային փոփոխականությունը Ձկնագետ և Սոթք գետերում 2023 և 2024 թվականներին՝ կիրառելով Ծանր Մետաղների Աղտոտման Ցուցիչը (ԾՄԱՑ) և Մետաղների Ցուցիչը (ՄՑ): Յոթ ծանր մետաղների (Al, Cd, Fe, Pb, Cr, Ni, Zn) արժեքները գնահատվել են երեք գետահատվածներում՝ Ձկնակետ գետի վերին (Ձկ-1) և ստորին (Ձկ-2), ինչպես նաև Սոթք գետի ստորին հոսանքում (Սոթ-2): Արդյունքները ցույց են տալիս կայունորեն ցածր աղտոտման մակարդակ Ձկ-1-ում, ինչը վկայում է մարդկային ազդեցության սահմանափակ լինելու մասին, մինչդեռ էականորեն բարձր ԾՄԱՑ և ՄՑ արժեքներ՝ Ձկ-2-ում և Սոթ-2-ում, ինչը վկայում է զգալի աղտոտման մասին: Համեմատական վերլուծությունը՝ ըստ ԱՀԿ, ՊԳԿ և տեղական նորմերի, բացահայտում է աղտոտման դասակարգման մեջ զգալի տարբերություններ: ՊԳԿ չափանիշներով ոռոգման համար ռիսկը համարվում է նվազ, մինչդեռ ԱՀԿ և տեղական ստանդարտները մատնանշում են ավելի լուրջ էկոլոգիական և առողջական ռիսկեր: Սոթ-2 գետահատվածում 2024 թ.-ի դրությամբ արձանագրված աղտոտման նվազումը կարող է վկայել ջրի որակի որոշակի բարելավման մասին: Ընդհանուր առմամբ, արդյունքներն ընդգծում են բազմաշերտ գնահատման շրջանակների կիրառման, մշտադիտարկման, թիրախավորված աղտոտման վերահսկման և բնապահպանական կարգավորումների խստացման անհրաժեշտությունը՝ ջրային էկոհամակարգերն ու ջրային ռեսուրսները պահպանելու համար:

Г. А. ХАЧАТРЯН

ОЦЕНКА ЗАГРЯЗНЕНИЯ ТЯЖЕЛЫМИ МЕТАЛЛАМИ В РЕКАХ СОТК И ДЗКНАГЕТ (АРМЕНИЯ)

Данное исследование рассматривает пространственную и временную изменчивость загрязнения тяжелыми металлами рек Дзкнагет и Сотк в 2023 и 2024 гг. с применением индекса загрязнения тяжелыми металлами (ИЗТМ) и металлического индекса (МИ). Концентрации семи тяжелых металлов (Al, Cd, Fe, Pb, Cr, Ni и Zn) были оценены в трех участках рек: в верхнем (Дзк-1) и нижнем (Дзк-2) течении реки Дзкнагет, а также в нижнем течении реки Сотк (Сот-2). Результаты показывают стабильно низкий уровень загрязнения на участке Дзк-1, что свидетельствует о ограниченном антропогенном воздействии, тогда как значительно более высокие значения ИЗТМ и МИ на участках Дзк-2 и Сот-2 указывают на существенное загрязнение. Сравнительный анализ в соответствии со стандартами ВОЗ, ООН и местными нормативами выявляет

заметные различия в классификации уровня загрязнения. Согласно критериям ООН, риск для орошения оценивается как низкий, тогда как стандарты ВОЗ и местные нормативы указывают на более серьезные экологические риски и риски для здоровья населения. Зафиксированное снижение уровня загрязнения на участке Сот-2 в 2024 г. может свидетельствовать о некотором улучшении качества воды. В целом результаты подчеркивают необходимость применения многоуровневых подходов к оценке, постоянного мониторинга, целенаправленного контроля загрязнения и ужесточения природоохранного регулирования для защиты водных экосистем и водных ресурсов.