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Hydrochemical Study of Artesian and Spring Waters of Racha-Lechkhumi and Kvemo Svaneti Region in 2022-2024

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ABSTRACT

Hydrochemical characteristic of artesian and spring (drinking) waters available at the territory adjacent to arsenic processing enterprises of Racha-Lechkhumi and Kvemo Svaneti region in 2022-2024 has been considered in the work. There have been identified artesian and spring waters polluted with different ingredients.
The following conclusions have been made based on the carried-out studies:

- *in some cases, among ingredients polluting artesian and spring waters there has been registered increase of some components (mineral forms of nitrogen, water hardness, sulfates, mineralization, microbiological indicators) compared to respective MPCs; these waters belong to the category of medium-salt (average mineralization) waters, while an acid water of the spring located below Lentekhi is ranked among highly mineralized waters;*
- *total arsenic content in the spring waters flowing towards Tsana in 2022-2024 has surpassed the MPC and arsenic hazard quotient $HQ_{Dw} > 1$, so these waters are at risk;*
- *arsenic concentration in other spring waters is within the norm.*

Key words: *artesian waters, spring waters, hydrochemistry, arsenic, pollution.*

Introduction

Arsenic ore extraction, processing and arsenic-containing compounds production took place for several decades in Tsana and Uravi villages of Racha-Lechkhumi and Kvemo Svaneti region. As of today, both deposits are temporarily closed down and there is no more arsenic production there. But a large amount of toxic waste remained due to arsenic production (more than 130 000 ton of waste containing 4-9% of white arsenic) is still stored at the territory of mining and chemical plant and is not safely disposed there [1; 2]. For years, the basic mechanism of arsenic waste propagation is related to washing-out of toxic waste by atmospheric precipitations and waters of overflowing rivers and their transfer that leads to high risk of ecological catastrophe for artesian waters and soils [3-5].

Arsenic is a natural component of the Earth crust and is spread in any ecosystem. It is represented in the nature by organic and inorganic forms, and the latter is very toxic [6]. Despite the fact that generally arsenic may penetrate the human organism through skin, respiratory passages, it mainly hit the organism from food and drinking water. Organic arsenic varieties are most common in sea products, while in the land products they are basically represented by inorganic forms of 3-5-valent arsenic. Based on this fact, arsenic mainly enters the food chain from polluted soil and water.

Materials and methods

Physical-chemical and hydrochemical characteristic of artesian and spring waters available at the territory adjacent to arsenic processing enterprises of Racha-Lechkhumi and Kvemo Svaneti region in 2022-2024 is given in the work. With the purpose of solution of assigned tasks, sampling points for artesian and spring waters have been selected from background and contaminated places of the Racha-Lechkhumi and Kvemo Svaneti region.

The following indicators have been identified in the water samples taken: physical-chemical and hydrochemical parameters, in particular: pH, electric conductivity; biogenic substances: NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, principal ions, mineralization, general total forms of arsenic [7], total Coliforms, E-coli and fecal streptococci [8].

The following formula has been used for calculation of the hazard quotient [9]:

Hazard quotient (HQ) = Measured concentration (MC)/Environment quality standards EQS_{DW}

In case of HQ >1.0, arsenic is considered as a potential hazard for water medium and, respectively, for population health.

The following EQS boundary values have been used:

drinking water: 0.01 mg/l (maximum permissible concentrations according to the Decree no. 58 on Approval of Technical Regulations for Drinking Water protection from Pollution in Georgia) [10].

Analyses have been conducted using the up-to-date methods and equipment, which meet the requirements and comply with European standards, in particular:

1. Spectrophotometric method - SPECORD 205;   ISO 7150-1: 2010;
2. Ion-chromatographic method IC-1000; ISO 10304-1:2007
3. Plasma-emission spectrometer - ICP-OES; Epa method 200.8;
4. Field portable apparatus - Hanna Combo pH/EC/TDS/PPM Tester HI98129;
5. IDEXX-Apparatus - ISO 9308-3
6. pH-meter - Milwaukee-Mi 150.

Results and discussion

Results of hydrochemical and microbiological analyses of artesian and spring drinking waters are given in Table 1.

Table 1. Results of hydrochemical and microbiological analyses of artesian and drinking waters June, October 2022.

#	Ingredients	Spring water in the territory of Uravi 2 (150-200 m away)	Spring water from the mountain in the direction of Tsana	Acidic water (spring) above Lentekhi	MPC *
		X-359777 Y-4722474	X-316809 Y-4741183	X-313288 Y-4741009	
		June			
1	pH	8.0	7.1	6.5	6-9
2	Electrical conductivity, μsms/cm	89	345	1125	
3	BOD_5, mg/l	1.25	2,10	0,95	
4	Hardness, mg.seq./l	0.97	5,53	18,57	7-10
5	Ammonium, mgN/l	0.221	0,098	0,469	0,39
6	Nitrites, mgN/l	0.022	0.075	132.05	1.0
7	Nitrates, mgN/l	0.113	0.029	0.070	10
8	Phosphates, mg/l	0.072	0.196	0.156	3.5

9	Sulfates, mg/l	1.29	53.67	12.51	250
10	Chlorides, mg/l	0.46	0.06	81.99	250
11	Bromine, mg/l	0.170	0.101	0.667	
12	Fluoride, mg/l	0.072	0.041	0.040	0.7
13	Hydrocarbons, mg/l	74.42	189,10	502,64	
14	Potassium, mg/l	0.88	0,95	80,5	
15	Sodium, mg/l				
16	Calcium, mg/l	10.44	84,27	220,15	
17	Magnesium, mg/l	5.52	16,19	10,98	
18	Mineralization, mg/l	93.14	341,28	921,76	1000-1500
19	Arsenic-As, mg/l	0.0097	0.0123	0.0013	0.01
20	E-Coli, in 250 ml	8	10	N.D	not allowed
21	Total coliforms in 250 ml	25	32	N.D	
22	Fecal streptococci, in 300 ml	5	3	N.D	
			October		
1	Arsenic-As, mg/l	0.0016	0.0111	0.0024	0.01

MPC* - maximum permissible concentrations according to Technical Regulations for Drinking Water (Decree №58 of the Georgian government as of 15th January of 2014, Tbilisi) [10]

As is seen from Table 1, pH of artesian and spring drinking waters varies within the limits of 6.5-8.0. pH (medium reaction) equal to 6.5 is peculiar for spring acid water. It should be especially noted an increase of hardness of spring acid water (18.57 mg.eq/l) compared to MPC. Content of hydrocarbonates is 502.64, $Ca^{++} - 220.15$, $Na^{+} + K^{+} - 80.5$ and $Mg^{++} - 10.98$ mg/l.

Biogenic elements (nitrogen, phosphorus), which reflect surface water pollution degree and are indicators of anthropogenic load, are important components. It is especially important to control the content of their separate forms (NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}) in water, which point at the intensification of such processes as fecal contamination induced by discharge of household and agricultural waste waters. Among nitrogen mineral forms there are identified high contents of ammonia (0.469/1.2 MPC) and nitrite forms (132.05/132.1 MPC) that is presumably stipulated by the impact of fecal waste waters, causing pollution of the mentioned spring water. Nitrate and phosphate values don't exceed the respective MPCs. Mineralization of this spring comprises 921.76 mg/l so it is ranked among the waters with moderate mineralization (500-1000 mg/l) [11], while a spring water flowing from mountains towards Tsana, belongs to the category of medium-salt (average mineralization) waters (341.28 mg/l).

In samples taken from the spring waters in June (Table 1), arsenic content at the territory of Uravi 2 (at 150-200 m distance) almost equals to one MPC, while in the spring water flowing from mountains towards Tsana, arsenic concentration is 0.0123 mg/l and its ratio to MPC is 1.2, i.e. arsenic concentration 1.2-times exceeds MPC. It should be mentioned the fact that this water is heavily used for drinking by population. Arsenic content in the spring's acid water above Lentekhi is low and its concentration comprises 0.0013 mg/l. Arsenic concentration higher than MPC in the spring water flowing from mountains towards Tsana was recorded again in October (0.0111 mg/l), and in other cases arsenic concentration is within the norm.

Based on this fact, a hazard quotient (HQ_{dw}) in both months varies in artesian drinking waters from 0.0013 to 0.0123 mg/l and create a hazard, since all measured concentrations were not lower than MPC.
Pollution is resulted not only in change of physical properties of water (color, odour, muddiness), but also chemical composition (organic, biogenic substances, heavy metals etc.) and microflora. River water bacteriological purity is evaluated by means of intestinal bacteria (E-coli) quantity per 1 liter of water (Coli index). High value of Coli index is an indicator of fecal contamination of water (MPC - not allowed), (Table 1), [11].

In Tables 2 and 3 there are given the results of hydrochemical analyses of artesian and spring drinking waters in 2023-2024.

As is seen from Table 2, a srping's acid water above Lentekhi stands out here too, according to its hydrochemical parameters. Water hardness comprises 18.44 that exceeds MPC. Chloride content is high, as well, and surpasses MPC, spring water mineralization is 2612.22 mg/l and this water belongs to the category of highly mineralized waters.

Among mineral forms it should be noted high content of ammonia (0.44 mg/l) and nitrite nitrogen (11.70 mg/l), which equals 1.1 and 58.5 MPC, respectively.

Arsenic content is high in the spring water flowing from mountains towards Tsana, where arsenic content 1.3- and 1.9-times surpasses MPC.

As can be seen from the conducted results, similarly to Table 1, in the month of October (Table 2, Fig. 1), a spring water at the Uravi 2 territory and towards Tsana contains E-coli, total coliforms and fecal streptococci, which are not permitted according to Georgian legislation, while for acid waters pollution in terms of microbiological parameters was not registered.

Table 2. Results of hydrochemical analyses of artesian and spring waters, May, 2023.

#	Ingredients	Spring water above Uravi 1	Spring water in the territory of Uravi 2 (150-200 m away)	Spring water from the mountain in the direction of Tsana	Spring water from the mountain (in the middle)	Spring water from the mountain (in last)	Acidic water (spring) above Lentekhi	MPC *
			X-359777 Y-4722474	X-316809 Y-4741183	X-316833 Y-4741198	X-316930 Y-4741232	X-313288 Y-4741009	
		May						
1	pH	7.9	7.8	8.2	7.9	8.1	7.0	6-9
2	Electrical conductivity, μsms/cm	105	85	350	170	190	2558	
3	BOD_5, mg/l	0.98	1.45	2.25	0.75	1.35	0.78	
4	Hardness, mg.seq./l	1.30	1.03	4.49	1.93	2.07	18.44	7-10
5	Ammonium, mgN/l	0.44	0.053	0.058	0.059	0.054	0.212	0.39
6	Nitrites, mgN/l	0.021	0.095	0.216	0.052	0.126	11.70	0.2
7	Nitrates, mgN/l	1.072	0.320	0.237	1.304	1.202	0.084	50
8	Phosphates, mg/l	0.085	0.142	0.153	0.112	0.241	0.094	3.5
9	Sulfates, mg/l	2.94	2.86	78.89	4.22	12.28	24.40	250
10	Chlorides, mg/l	3.77	2.29	2.27	3.38	3.30	376,84	250
11	Bromine, mg/l	0.120	0.142	0.381	0.210	0.059	0.910	
12	Fluoride, mg/l	0.111	0.016	0.200	0.023	0.060	0.042	0.7
13	Hydrocarbons, mg/l	75.64	59.78	180.56	124.44	136.64	1526.22	
14	Potassium, mg/l	3.08	2.05	4.5	6.0	4.0	333.88	
15	Sodium, mg/l							
16	Calcium, mg/l	13.17	10.61	71.81	26.63	26.51	291.71	
17	Magnesium, mg/l	7.85	6.04	10.99	7.33	9.07	47.26	
18	Mineralization, mg/l	107.62	84.03	349.56	172.18	192.01	2612.22	1000-1500
19	Arsenic-As, mg/l	0.0072	0.0086	0.0133	0.0092	0.0190	0.0022	0.01
		October						
1	Arsenic-As, mg/l		0.0004	0.0025	0.0144	0.0093	0.0149	0.01
2	E-Coli, in 250 ml		5	3	4	11	N.D	not allowed
3	Total coliforms in 250 ml		11	8	10	21	N.D	
4	Fecal streptococci, in 300 ml		N.D	N.D	2	7	N.D	

MPC* - maximum permissible concentrations according to Technical Regulations for Drinking Water. (Decree №58 of the Georgian government as of 15th January of 2014, Tbilisi) [10]

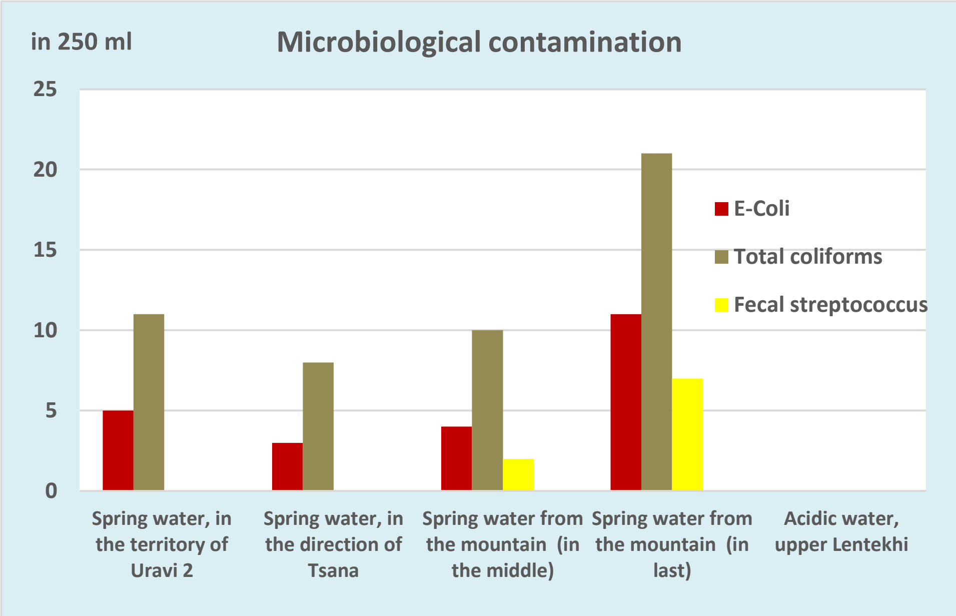

Fig. 1. Microbiological pollution in spring water, October, 2023
(MPC – is not permitted).

Table 3. Results of hydrochemical analysis of artesian and drinking waters, April, 2024.

#	Ingredients	Spring water above Uravi 1	Spring water in the territory of Uravi 2 (150-200 m away)	Spring water from the mountain in the direction of Tsana	Spring water from the mountain (in the middle)	Spring water from the mou-ntain (in last)	Acidic water (spring) above Lentekhi	MPC*
1	pH	7.6	7.8	8.0	8,1	8.3	6.9	6-9
2	Electrical conductivity, µsms/cm	135	98	365	220	310	390	
3	BOD_5, mg/l	1.32	1.52	1.95	1.25	0.95	5.27	
4	Hardness, mg.seq./l	1.53	1.09	2.93	3.15	2.45	3.58	7-10
5	Ammonium, mgN/l	0.226	0.217	0.252	0.236	0.302	0.318	0.39
6	Nitrites, mgN/l	0.170	0.051	0.044	0.111	0.124	0.050	0.2
7	Nitrates, mgN/l	0.624	0.756	2.114	1.326	3.321	0.203	50
8	Phosphates, mg/l	0.171	0.084	0.147	0.139	0.088	0.018	3.5
9	Sulfates, mg/l	4.63	6.46	58.65	8.24	52.34	28.55	250
10	Chlorides, mg/l	2.66	2.97	3.23	2.78	3.09	12.22	250
11	Bromine, mg/l	0.046	0.016	0.036	0.048	0.015	0.092	
12	Fluoride, mg/l	0.237	0.488	0.108	0.131	0.178	0.321	0.7
13	Hydrocarbons, mg/l	96.16	65.88	0.178	0.205	0.269	239.12	
14	Potassium, mg/l	4.5	5.0	5.5	4.0	4.5	36.25	
15	Sodium, mg/l							
16	Calcium, mg/l	17.82	11.24	65.42	52.25	32.86	51.42	
17	Magnesium, mg/l	7.82	6.49	9.133	10.02	8.53	11.89	
18	Mineralization, mg/l	133.23	99.14	345.55	238.60	345.88	380.12	1000-1500
19	Arsenic-As, mg/l	0.0093	0.0023	0.0123	0.0140	0.0152	0.0072	0.01

MPC* - maximum permissible concentrations according to Technical Regulations for Drinking Water (Decree №58 of the Georgian government as of 15th January of 2014, Tbilisi) [10]

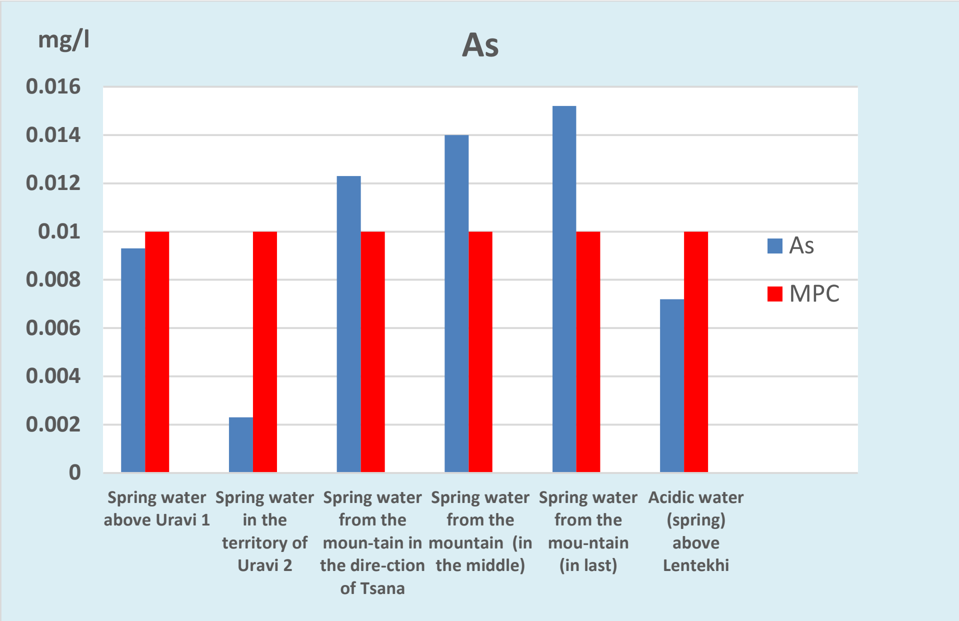

Fig. 2. Arsenic concentration content in artesian and drinking waters, April 2024.

According to hydrochemical parameters, a spring acid water, which is located above Uravi 1, with observed water hardness increase (3.58 mg.eq/l), stands out again (Table 3). Hydrocarbonate content comprises 239.12; $Ca^{++} -$ 51.42, $Na^{+} + K^{+} -$ 36.25 and $Mg^{++} -$ 11.89 mg/l, though none of these parameters surpasses MPC.

Among mineral forms of nitrogen, high contents of ammonia and nitrite forms are not registered, and nitrate and phosphate values don't exceed respective MPCs.

In the spring water flowing from the mountains towards Tsana, arsenic concentration comprises 0.0123-0.0140 and 0.0152 mg/l and its ratio to MPC is equal to 1.2, 1.4 and 1.5, i.e. arsenic concentration 1.2-1.5-times surpasses MPC (Fig. 2). It should be mentioned the fact that waters of all three springs are used for drinking by population. Proceeding from this fact, hazard quotient (HQ_{dw}) of spring water flowing from mountains towards Tsana exceeds permissible standards in April and poses a danger, since all measured concentration were not lower than MPC. In other cases, arsenic concentration is within the norm.

Conclusions

- in some cases, among ingredients polluting artesian and spring waters there has been registered increase of some components (mineral forms of nitrogen, water hardness, sulfates, mineralization, microbiological indicators) compared to respective MPCs, these waters belong to the category of medium-salt (average mineralization) waters, while an acid water of the spring located below Lentekhi belongs to the category of highly mineralized waters;
- in spring water flowing towards Tsana, arsenic concent in 2022-2024 has exceeded MPC and arsenic hazard quotient $HQ_{Dw} > 1$, so these waters are at risk;
- arsenic concentration in other spring waters is within the norm.

Acknowledgments

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რაჭა-ლეჩხუმის და ქვემო სვანეთის რეგიონის 2022-2024 წწ. არტეზიული და წყაროს წყლების ჰიდროქიმიური კვლევა

ლ. შავლიაშვილი, გ. კუჭავა, ე. შუბლაძე, მ. ტაბატაძე

რეზიუმე

ნაშრომში განხილულია 2022-2024 წწ რაჭა-ლეჩხუმი და ქვემო სვანეთის რეგიონის დარიშხანის გადამამუშავებელი საწარმოების მიმდებარე ტერიტორიებზე არსებული არტეზიული და წყაროს (სასმელი) წყლების ჰიდროქიმიური დახასიათება.
გამოვლენილია სხვადასხვა ინგრედიენტებით დაბინძურებული არტეზიული და წყაროს წყლები.

ჩატარებული კვლევების საუძველზე მიღებულია შემდეგი დასკვნები:

- არტეზიულ და წყაროს წყლებში დამაბინძურებელი ინგრედიენტებიდან ზოგიერთ შემთხვევაში აღინიშნება კომპონენტების (აზოტის მინერალური ფორმები, წყლის სიხისტე, სულფატები, მინერალიზაცია, მიკრობიოლოგიური მაჩვენებლები) მატება შესაბამის ზდკ-სთან. ისინი მიეკუთვნებიან საშუალო მინერალიზირებული წყლების კატეგორიას, ხოლო მჟავე წყაროს წყალი ლენტეხის ქვევით, მიეკუთვნება მაღალ მინერალიზირებულ წყლების კატეგორიას;

- წყაროს წყლებში ცანას მიმართულებით 2022-2024 წწ დარიშხანის საერთო შემცველობა აღემატება ზდკ-ს და დარიშხანის საშიშროების ინდექსი (HQ_{Dw} >1), ამრიგად, ეს წყლები არის რისკის ქვეშ;
- დანარჩენ წყაროს წყლებში დარიშხანის კონცენტრაცია ნორმის ფარგლებშია.

საკვანძო სიტყვები: არტეზიული წყლები, წყაროს წყლები, ჰიდროქიმია, დარიშხანი, დაბინძურება.

Гидрохимическое исследование артезианских и родниковых вод региона Рача-Лечхуми и Квемо Сванети за 2022-2024 гг.

Л. Шавлиашвили, Г. Кучава, Е. Шубладзе, М. Табатадзе

Резюме

В работе рассмотрена гидрохимическая характеристика артезианских и родниковых (питьевых) вод, имеющихся на территории, прилегающей к предприятиям по переработке мышьяка региона Рача-Лечхуми и Квемо Сванети за 2022-2024 гг. Выявлены артезианские и родниковые воды, загрязненные различными ингредиентами.

На основании проведенных исследований сделаны следующие выводы:

- среди ингредиентов, загрязняющих артезианские и родниковые воды, в некоторых случаях отмечено превышение компонентов (минеральные формы азота, жесткость воды, сульфаты, микробиологические показатели) по сравнению с соответствующими ПДК; данные воды относятся к категории вод средней минерализации, а кислая родниковая вода ниже Лентехи относится к категории высокоминерализованных вод;
- в родниковой воде, текущей в направлении Цана, общее содержание мышьяка в 2022-2024 гг. превышает ПДК, а индекс опасности мышьяка HQ_{Dw} >1, т.е. данные воды находятся под угрозой;
- в остальных родниковых водах концентрация мышьяка находится в пределах нормы.

Ключевые слова: артезианские воды, родниковые воды, гидрохимия, мышьяк, загрязнение.