RESEARCH PAPER

ARSENIC IN SURFACE WATERS IN THE CENTRAL PART OF THE NORTH CAUCASUS AND CORRESPONDENT HEALTH RISK ASSESSMENT

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ABSTRACT. Arsenic is ranked as a significant global health hazard associated with potable water. The present study assesses the arsenic pollution of the surface waters in the mountainous regions of the central part of the North Caucasus due to the presence of geochemical anomalies and the potential health risk by its consumption for the residents. The studies were carried out from 2016 to 2022. The surface waters of 5 main rivers of the region (Kuban, Malka, Baksan, Chegem and Cherek) with their main tributaries have been studied. Samples were taken during the period of intensive melting of glaciers (summer). The determination of the soluble form of arsenic was carried out using the method of atomic absorption spectrometry. In general, arsenic concentrations in this region are lower than Clark values for river waters. Along with this, watercourses with high and very high concentrations of arsenic have been identified. Elevated concentrations of arsenic in surface waters spatially coincide with the location of geochemical anomalies. The most polluted is the Baksan River. The levels of surface waters pollution from natural and anthropogenic sources are almost the same (up to 100 μg/dm^3). In this regard, an assessment of the health hazard was carried out. For residents receiving drinking water from wells located at the southern foot of Elbrus, the carcinogenic risk for adults was 4.51×10^{-4}, which is unacceptable for the general population. The non–carcinogenic risk was 1.00 - the maximum permissible risk causing concern.

KEYWORDS: arsenic geochemical anomalies, carcinogenic risk, non-carcinogenic risk, North Caucasus, surface waters

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INTRODUCTION

The role of environmental geochemistry in the etiology of many types of cancer and other non-communicable diseases in some countries reaches 70% of cancer deaths worldwide. Their dependence on local geochemistry for drinking water and growing crops is still widespread (Middleton et al. 2020). Water pollution by heavy metals and metalloids is one of the global problems of our time. The problems of arsenic in the environment are recognized and identified in many countries of the world, in a wide range of geological and climatic conditions (Ahamad et al. 2020; Goswami et al. 2020; Murtaza et al. 2020; Wang et al. 2020). Drinking water is the highest single source of exposure to high arsenic levels by humans (Aderibigbe 2018). Arsenic is ranked as a significant global health hazard associated with potable water. This element is considered one of the most toxic to humans and can cause both carcinogenic and non-carcinogenic diseases. Thus, high concentrations of arsenic in potable water (≥50 μg/l) are the cause of lung, liver, kidney, bladder and skin cancers (Saint-Jacques et al. 2014; Goswami et al. 2020; Middleton et al. 2020). Children are more susceptible than adults to As poisoning (Ahamad et al. 2020; Goswami et al. 2020). There is a growing body of evidence that prenatal and early childhood exposure to arsenic from drinking water can have serious long-term health implications (Dauphine et al. 2011; Smith et al. 2012; Farzan et al. 2013). The presence of arsenic in potable water at concentrations ≥5 μg/l pose a threat to child development (Wasserman et al. 2014) and leads to arsenic neuropathy in adults (Chakraborti et al. 2003). A high correlation was found between the presence of arsenic in drinking water and its content in urine, blood (Kladsomboon et al. 2020), nails and hair (Goswami et al. 2020), which indicates the accumulation of this element in the human body.

The dependence of the chemical composition of soils, surface and groundwater on the geochemical characteristics of the region is well known. The chemical composition of these environmental components has a significant impact on public health (Aderibigbe et al. 2018; Middleton et al. 2020). In this regard, the study of the chemical composition of surface waters, which are the main source of potable water, is an urgent task.

The waters of mountain rivers are traditionally considered very clean. But mountains are areas of modern and ancient volcanism, which affects the chemical composition of these waters. The aim of this work is to study the arsenic pollution of the surface waters in the mountainous regions of the central part of the North Caucasus due to the presence of geochemical anomalies and to assess the potential health risk by its consumption for the residents.

The chemical composition of the waters of the Terek and the Kuban has been studied by a number of authors – Reshetnyak O.S., Komarov R.S. (2021), Lurie P.M., Panov V.D., Bazelyuk A.A. (2015), etc. Such data are summarized in the yearbooks "Quality of surface waters of the Russian Federation". But all these data relate only to the low-mountain zone and assess the anthropogenic impact. There are a small number of works with the results of surveys of the Baksan, Chegem and Cherek rivers in the high and mid-mountain zone (Central Caucasus) by a number of authors (Gazaev et al. 2014: Reutova T. et al. 2018; Ermakov et al. 2020), as well as the Kuban and Teberda rivers (Western Caucasus) (Degas et al. 2016; Onishchenko et al. 2016). But in all these works there is no data on the content of arsenic in the waters under study. The only works that provide data on arsenic are studies in the area of the Tyrnyauz tungsten-molybdenum factory (Bortnikov et al, 2013; Vinokurov et al. 2016). Thus, we studied the features of arsenic content in the surface waters of the mountainous zone of the Central and Western Caucasus for the first time.

MATERIALS AND METHODS

Study area

In the Western Caucasus region, we examined the upper reaches of the Kuban River and its main tributaries in mountainous areas. In the Central Caucasus region, the rivers Malka, Baksan, Chegem and Cherek, which are tributaries of the Terek River, were examined. The location of sampling points and As ore mineralization are shown in Fig. 1 and 2. The numbers of sampling points in the figures and in all tables are the same.

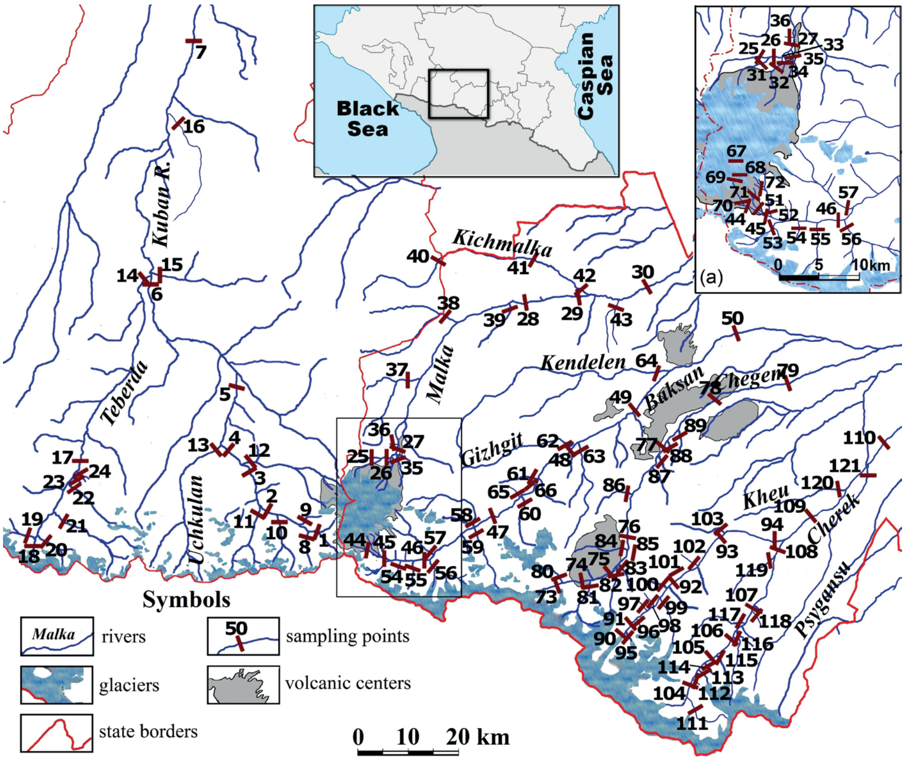

Fig. 1. Schematic map of sampling points

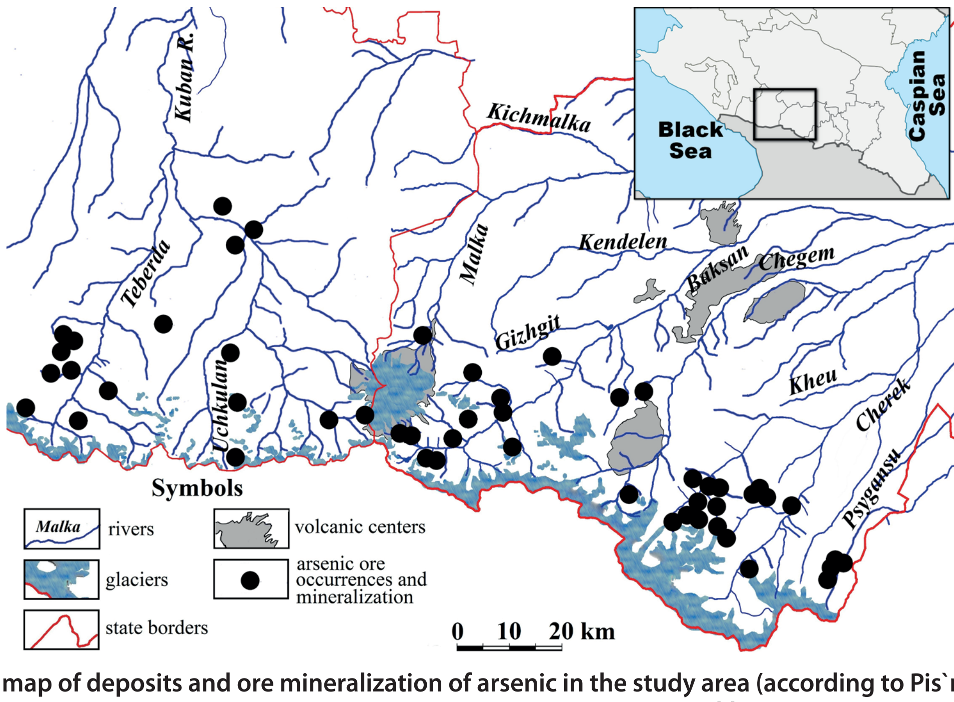

Fig. 2. Schematic map of deposits and ore mineralization of arsenic in the study area (according to Pis`menny`j et al. 2002; Pis`menny`j et al. 2013; Pis`menny`j et al. 2021; Semenukha et al. 2021)

Sample collection and processing

Samples were taken annually, during the summer floods (July – early August). During this period there is an intense melting of glaciers. In this regard, the differences between water bodies of various origins are well expressed. In addition, during the cold season, most of the objects in the highlands are inaccessible. All tables show the average values for 7 years (2016-2022). We determined only the dissolved form of arsenic. Sampling, processing and preservation of samples were carried out in accordance with GOST 17.1.5.05-85, GOST 31861-2012 and GOST R 59024-2020. Samples from a polyethylene sampler with a volume of 1 dm^3 were filtered *in situ* through membrane filters with a pore size of 0.45 microns (using syringe filter cartridges) into polypropylene tubes (15 ml) with screw caps. Preservation of samples for the determination of heavy metals was carried out with nitric acid (High Purity) at the rate of 0.5%. The samples were transported and stored at a temperature of 2°C - 5 °C.

Analysis methods

The hydrogen ion exponent in the samples was measured using a portable pH meter on the day of sampling. Arsenic concentrations were determined using the atomic absorption spectrometry (AAS) in accordance with GOST R 57162-2016. This method is widely used to determine concentrations of potentially toxic elements in natural waters (Ahamad et al. 2020; Brindha et al. 2020; Mallongi et al. 2022).

Statistical data processing was carried out using the Excel 2016 program to calculate the average values and coefficients of variation.

RESULTS AND DISCUSSION

Western Caucasus

Mountain region of the Kuban River basin.

For the Kuban River basin, we provide data on 24 sampling points (Table A.1). Of these, 7 samples were taken directly along the riverbed. For tributaries, data on the arsenic content in their mouth zone are given.

In the rivers waters the pH changes from neutral to weakly alkaline with increasing distance from the sources. We present the pH value in the tables due to the fact that it has a significant effect on the solubility and migration of arsenic in surface waters. Under oxidizing conditions (pH 5.7), As(III) migrates faster than As(V); under neutral conditions, migration of As(V) increases, but As(III) is still more mobile; at pH 8.3, migration of both forms of As increases significantly (Putilina et al. 2011).

Arsenic concentrations both along the riverbed of the Kuban River and its tributaries are lower than Clark for river waters (2 μg/dm^3) (Nikanorov 2008). Only two sampling points have high and very high concentrations of arsenic. These are the waters of the Shumka River (No. 24) and a water pipe on the highway (No. 23). In the latter, the concentration of arsenic is 15 times higher than the MPC for drinking water (10 μg/dm^3). This sampling point is a popular source of drinking water for the residents. In both of these objects, arsenic concentrations are very stable over the years, as evidenced by the low values of the coefficients of variation. Such stability is characteristic of waters of underground origin. The water flow in the water pipe is small. The Shumka River is also a small river. After the confluence of these tributaries, the concentration of arsenic in the waters of the Teberda river does not increase. In this zone there are mineralization points and geochemical arsenic halos associated with hydrothermal gold-arsenic mineralization (As up to 5.74%) (Semenukha et al. 2021). The main ore mineral is arsenopyrite.

Central Caucasus

Mountain region of the Malka river basin

There are 19 sampling points located in the area, 6 of them directly along the riverbed. The data is given in Table A.2.

Most of the river waters in the Malka River basin are neutral and slightly alkaline. There is a tendency to latch down the Malka River. This is typical not only for the waters of the river itself, but also for its tributaries.

Some geochemical anomalies of arsenic are located in the basin of the Malka River. This is the point of mineralization of the arsenic-polymetallic formation of the Sirkh and stream sediment sample with single signs of arsenic in the upper reaches of the Kichmalki River. In the surface waters of the studied area, arsenic concentrations were very low and ranged within 1 μg/dm^3 which is lower than the Clark value. Only in the water of the drinking spring (No. 33) and the Sultangarasu river (No. 34), located near the Sirkh mineralization point (Fig. 1,2), the concentration of arsenic was almost 4 μg/dm^3. We found no elevated concentrations of arsenic in the waters of the Kichmalka River (Reutova et al. 2021). But we took samples starting from the 22nd kilometer, and stream sediment sample with single signs of arsenic were detected in the upper reaches of this river.

Mountain region of the Baksan river basin.

There are 29 sampling points in the Baksan River basin. Table A.3 shows the average values of arsenic concentrations. This table also shows data on the arsenic content in meltwater flowing down the southern slopes of Elbrus.

An excess of 1.4-40.0 times in comparison with Clark values was noted in the water of 10 out of 29 sampling points. This indicates the enrichment of the surface waters with this element, which is due to the presence the rocks with a high arsenic content. One of them is the arsenic ore occurrence "Azau arsenic", which is located on the right, steep side of the Azau River valley, 2 km below the village Terskol. This ore occurrence is represented by three ore zones: Northern, Central and Eastern (Fig. 2). According to the Pis`menny`j (2013), the arsenic content reaches 9.52-10%. The main ore minerals are realgar, auripigment, galena, sphalerite, rarely cinnabar.

During the summer, it is possible to conduct a comparative analysis of arsenic concentrations in thawed streams flowing down from the southern slopes of Elbrus and in the rivers waters originating from these glaciers. Thus, in the meltwater flowing down the snowy slope near of "Priyut 11" (No. 67, Garabashi glacier, altitude 4000 m above sea level), arsenic concentrations ranged from 0.33-1.21 μg/dm^3. In the area of the Garabashi cable car station (No. 68, altitude 3800 m above sea level), where there is snow in summer, arsenic concentrations in meltwater were 0.7-1.69 μg/dm^3. And at the "Mir" station (No. 69, altitude 3500 m above sea level), where meltwater flows directly through the ground, arsenic concentrations become higher – 0.9-9.15 μg/dm^3. The Azau waterfall (No. 70), the waters of which are in contact with the rocks of the southern slopes of Elbrus for about 2 km, is also characterized by high concentrations of arsenic. This distribution of concentrations indicates that the rocks are the main source of arsenic in surface waters. This zone of arsenic mineralization causes extremely high natural arsenic contamination of the Garabashi River waters, originating from the southern slopes of Elbrus, and pollution to a lesser extent of the Terskol River, whose sources are located on the eastern slopes of Elbrus. One of the tributaries of the Garabashi River is the waterfall "Devich`i kosy" (No.

71), located on the southeastern slopes of Elbrus and having an underground origin. The water of this waterfall is characterized by high and very high concentrations of arsenic (2.01-107.78 μg/dm^3).

The sources of the Terskol River are located on the eastern slopes of Elbrus. The right tributary of this river is the waterfall "Terskol". It is located on the other side of the same offshoot of Elbrus mountain range as the waterfall "Devich`i kosy" and is characterized by a relatively high content of arsenic (Table A.3). After the confluence of these rivers into the Baksan River, arsenic concentrations in it also increase (No. 45).

Arsenic mineralization of Alpine age is also represented by the mineralization point "Irikskoye" (Fig. 2) (Pis`menny`j et al., 2013). But we did not find elevated concentrations of arsenic in the water of the Irik River.

Two points of mineralization are located in the area of the Kyrtyk river (Fig.2) (Pis`menny`j et al. 2013). In the water of the Kyrtyk river, we did not detect elevated concentrations of arsenic (Table A.3).

The highest arsenic content in rocks is characterized by the Gitche–Tyrnyauz deposit, where its content reaches 23.1% (Fig.2) (Pis`menny`j et al. 2013). The Tyrnyauz tungsten-molybdenum factory is located here. The extremely high arsenic pollution of the watercourses of this area is anthropogenic. These are the Kamyksu River (No. 61), the Bolshoy Mukulan (No. 65), the "Rudnik" stream (No. 66). Flowing into the Baksan River above the 60th kilometer (No. 48), they lead to an increase in the concentration of arsenic in the waters of the Baksan River (Table A.3).

Thus, the arsenic content in the surface waters of the Baksan River basin is due to its content in rocks and its sources are both natural and anthropogenic. The levels of surface waters pollution from natural and anthropogenic sources are almost the same (up to 100 μg/dm^3).

Mountain region of the Chegem river basin.

For the surface waters of the Chegem river basin, we provide data on 17 sampling points, of which seven are located directly along the riverbed (Table A.4).

All glacial rivers and most non-glacial rivers in the high-altitude zone of the Chegem River basin had a neutral or slightly alkaline reaction. Unlike the Baksan River basin, there are almost no geochemical anomalies with a high arsenic content in the Chegem River basin. Only the Kektash mineralization point in the upper reaches of the left tributary of the Chegem river (As content – 1%) (Pis`menny`j et al. 2021) and the Gubuchhan (Pis`menny`j et al. 2002), located in the basin of the Gara-Aususu river, were noted (Fig. 2). The concentrations of this element in the surface waters of this region are at the level of Clark values (Table A.4.).

A few dozen kilometers east of Elbrus is the ancient Verkhnechegem caldera with an age of about 2.8 million years (Chernyshev et al. 2014; Myshenkova and Koronovsky 2015). In the area of this caldera, the Chegem River flows up to the 30th kilometer. After the 30th to the 88th kilometer, the area of the Nizhnechegemsky plateau is located. It is characterized by the presence of acidic volcanites (tuffs), which are either aerally transferred products of the activity of the Verkhnechegem caldera, or they are associated with an independent center of Pliocene volcanism in this area (Chernyshev et al. 2014). Thus, this part of the Chegem riverbed flows through an area of ancient volcanism. But this did not affect the arsenic content in the surface waters in this region.

Mountain region of the Cherek river basin.

Since the Cherek River has two equivalent sources – the Bezengi Cherek and the Balkar Cherek –we present both of these rivers with their tributaries in Table A.5. There are 14 sampling points located on the Cherek Bezengiysky River, 5 of them along the riverbed. In the basin of the Balkar Cherek and the Cherek River itself, we provide data on 18 sampling points, 7 of which are located along the riverbed.

The majority of river waters are neutral or slightly alkaline, in the high-altitude zone, pH<8, in the lower zones, pH>8, but does not reach 8.5.

Many manifestations of arsenic locate in the upper reaches of the Cherek River basin from the interfluve of the Chegem River and the Bezengiysky Cherek River to the Psygansu (Fig. 2) (Pis`menny`j et al. 2002). There are also polymetallic ore represented by minerals such as chalcopyrite, pyrite, sphalerite, arsenopyrite, etc. (Kaigorodova and Petrov 2016). It affected the distribution of arsenic concentrations in the surface waters of the area. Thus, in two sampling points of the Chegem river basin, the sources of which are located on the border of the Chegem and Cherek Bezengiysky river basins (Nos. 82 and 83), arsenic concentrations are higher than in all other sampling points (Table A.4, Fig. 1,2). From the tributaries of the Cherek Bezengiysky River, higher concentrations of arsenic are characteristic of Nos. 97-99 (Table A.5). But they do not lead to a noticeable increase in arsenic concentrations in the waters of the Bezengiysky Cherek River.

In the basin of the Cherek Balkarsky river, the highest concentrations of arsenic were detected in the waters of a small stream (No. 112). In the waters of the river itself, the arsenic content increases from 33 to 58 km. In two tributaries flowing in this interval (Nos. 117 and 118), arsenic concentrations are also higher (Table A.5, Fig. 1,2). In general, the arsenic content in the surface waters of the Cherek river basin is higher than in the basins of the Kuban, Malka and Chegem rivers, but lower than in the Baksan River basin, which well reflects the geochemical features of these areas.

Thus, the dependence of arsenic concentrations in surface waters on the presence of geochemical anomalies is clearly traced in the mountainous areas of the river basins of the central part of the North Caucasus.

There is another region in the North Caucasus with a high arsenic content in drinking water. This is the Republic of Dagestan, where groundwater is used for water supply. The arsenic content in them ranged from 10-500 μg/l, which is significantly higher than in the study area. But in Dagestan, the arsenic content was estimated in groundwater, not in surface waters (Abdulmutalimova 2019).

Health risk assessment

According to S.F. Vinokurov and co-authors (2016), arsenic (as well as tungsten and molybdenum), unlike other trace elements, is found in the surface waters of this region in dissolved form. Consequently, it enters potable water in the same concentration as in surface waters.

As – code CAS 7440-38-2. According to the classification of carcinogens by the International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency (EPA), arsenic is a carcinogen for humans. The affected organs and systems are the skin, central nervous system, nervous system, cardiovascular system, immune system, hormonal system (diabetes) and the gastrointestinal tract. To quantify the impact of drinking water with a high arsenic content on the health of the population, a methodology for assessing the risk to public health was used, within which an algorithm recommended by WHO and other leading international organizations was used.

The risk assessment for public health was carried out in accordance with the Human Health Risk Assessment from Environmental Chemicals. Manual P 2.1.10.1920—04.

For the mountainous region of the Kuban River basin, very high concentrations are characteristic of the sampling point No. 23 (Table A.1). Although this spring is popular among residents, it is not the main source of potable water. For the residents of the Tyrnyauz tungsten-molybdenum factory, the main source of potable water is the Baksan river. Arsenic concentrations in the river waters are not high, and the water intakes for the city of Tyrnyauz are located above the ore body. Therefore, we did not calculate the health risks to the population in these regions.

Potable water in the geologists' camp located at the Gitche-Tyrnyauz deposit contains 156 μg/dm^3 of arsenic. Potable water in the village Azau is obtained from water pipelines located directly on the southern slope of Elbrus, and the concentration of arsenic in it is about 35 μg / dm^3. Potable water from the well of the village Terskol is received by all hotels located below, contains 6.27-15.41 μg/ dm^3 (on average 11 μg/ dm^3). Therefore, for these areas with a high natural level of arsenic pollution, we calculated the risks to public health in accordance with the Human Health Risk Assessment from Environmental Chemicals. Manual P 2.1.10.1920—04.

The standard values of exposure factors for oral intake of chemicals with potable water for the geologists' camp were: exposure frequency (EF) 180 days/year, since the field season lasts from May to November, and exposure duration (ED) is 5 years (approximate average working time of one employee). The remaining values are standard (average body weight 70 kg and water ingestion rate 2.0 litre for adults). For this contingent, the carcinogenic risk (CR) was 2.35×10^{-4}, which corresponds to the third range (individual lifetime risk of more than 1×10^{-4}, but less than 1×10^{-3}) acceptable for occupational groups and unacceptable for the general population. This is a hazard risk. The non-carcinogenic risk (HQ) for this contingent was 1.22. If HQ > 1, this is a hazard risk. We reported the results to the head of the geologists' camp, the employees began to use bottled water.

For hotels and cafes located in the Azau glade, potable water comes from water pipelines located on the southern slopes of Elbrus. There is no health hazard for tourists living here for a short time. This drinking water can only pose a danger to employees of hotels and cable cars, who are mostly local residents. To calculate individual risks, we used standard values of exposure factors for oral intake of chemicals with drinking water according to Human Health Risk Assessment from Environmental Chemicals (365 days/year, 70 lifetime year for carcinogen and 30 year for adult and 6 years for children for non-carcinogen, average body weight 70 kg for adults and 15 kg for children, water ingestion rate 2.0 litre for adults and 1 litre for children). The carcinogenic risk (CR) for adults was 1.44×10^{-3}, which is unacceptable neither for the population nor for professional groups (extremely hazard, unacceptable risk). The non-carcinogenic risk (HQ) for this contingent was 3.20, which is significantly more than 1. But it should be noted that there are very few people who have been permanently residing in this village for many years.

For Terskol villagers receiving drinking water from the well, the carcinogenic risk for adults was 4.51×10^{-4}, which is unacceptable for the general population. The non–carcinogenic risk was 1.00 - the maximum permissible risk causing concern. Children are more vulnerable to As exposure than adults (Dauphine et al. 2011) and are therefore central to any such assessment. For children, the carcinogenic risk was 1.05×10^{-3}, which is unacceptable neither for the population nor for professional groups. The non-carcinogenic risk was 2.34. If we take into account that in this region there is also aluminum pollution associated with the presence of the Elbrus Neovolcanic Center (Reutova N. et al. 2018), the total risks to public health may be higher. This problem requires further study.

CONCLUSIONS

This study is novel in three ways: (a) it studies As concentrations in the surface waters of mountainous regions of the Central and Western Caucasus; (b) it examines the sources of arsenic entering surface waters; and (c) it evaluates health hazard of natural arsenic pollution for residents.

Arsenic content in surface waters depends on the presence of geochemical anomalies. Concentrations of arsenic in the waters of the rivers are two times lower than Clark values in those areas where there are no arsenic ore. The presence of ancient paleovolcanoes has no effect on arsenic concentrations in surface waters. Natural levels of surface water pollution are the same as anthropogenic. The intake of arsenic is not associated with atmospheric precipitation, but is entirely due to its intake from rocks.

The carcinogenic risk for adult residents of this region was unacceptable for the general population. The non–carcinogenic risk was the maximum permissible risk causing concern. For children, the carcinogenic risk was unacceptable neither for the population nor for professional groups.

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APPENDIX

Table A.1. Arsenic in surface waters of the mountainous area of the Kuban River basin

No	Sampling points	Distance from the source, km	$pH_{min} – pH_{max}$	As μg/dm^3 (coefficient of variation)
1	Kuban River	7.5	7.15-7.50	0.81 (1.13)
2	Kuban River	20.7	7.19-7.68	1.03 (1.18)
3	Kuban River	31.1	7.16-7.55	2.11 (0.87)
4	Kuban River	38.3	7.23-7.54	1.91 (1.09)
5	Kuban River	54.5	7.24-7.61	2.30 (1.04)
6	Kuban River	89.0	7.47-7.73	1.45 (0.93)
7	Kuban River	150.0	7.37-7.90	1.52 (1.13)
The main tributaries of the Kuban river				
8	R. Kichkinekol	8.0	7.20-7.66	1.40 (1.28)
9	R. Akbash	6.0	7.65-7.89	0.66 (1.56)
10	R. Chirinkol	14.3	6.92-7.50	1.41 (1.11)
11	R. Uzunkol	18.1	6.95-7.42	3.18 (0.47)
12	R. Ullukhurzuk	21.9	7.40-7.80	1.53 (1.08)
13	R. Uchkulan	36.0	7.20-7.35	2.27 (0.96)
14	R. Teberda	72.0	7.15-7.66	1.35 (1.15)
15	R. Mara	31.7	8.23-8.52	1.06 (1.31)
16	R. Dzheguta	30.8	8.12-8.21	1.50 (1.24)
Teberda river, left tributary of the Kuban River at 89 km				
17	R. Teberda	22.6	6.85-7.75	1.61 (1.15)
14	R. Teberda	72.0	7.15-7.66	1.35 (1.15)
Tributaries of the Teberda river				
18	R. Amanauz	3.9	6.66-6.92	0.97 (2.09)
19	R Alibek	8.6	6.64-7.05	1.15 (1.52)
20	R. Dombay Ulgen	8.7	6.77-7.80	1.70 (0.94)
21	R. Gonachhir	20.4	7.01-7.28	1.28 (1.54)
22	R. Ulu-Muruju	15.0	7.18-7.20	5.20 (0.37)
23	water pipe on the highway	0	7.71-7.82	142.00 (0.06)
24	R. Shumka	3.1	7.18-7.35	30.57 (0.16)

Table A.2. Arsenic in surface waters of the mountain region of the Malka river basin

No	Sampling points	Distance from the source, km	$pH_{min} – pH_{max}$	As µg/dm³ (coefficient of variation)
25	R. Malka (R. Kyzylkol)	10.6	6.53-7.89	0.58 (1.28)
26	R. Malka	12.4	7.26-7.66	0.84 (1.07)
27	R. Malka	15.7	7.53-7.93	1.26 (0.50)
28	R. Malka	65.6	7.84-8.14	2.42 (1.12)
29	R. Malka	79.1	7.83-8.05	1.89 (1.31)
30	R. Malka	93.9	7.91-8.17	2.15 (1.29)
The main tributaries				
31	R.Ullukol	8.6	6.78-7.38	2.03 (0.87)
32	R. Birjaly	6.3	6.70-7.21	0.49 (1.01)
33	Spring-drinking water	0	7.27-7.56	3.74(0.32)
34	R. Sultangarasu	1.9	6.94-7.60	3.61 (0.20)
35	R. Karakayasu	8.0	6.97-7.75	1.13 (0.38)
36	R. Sirkh	1.2	7.95-8.52	0.79 (0.38)
37	R. Harbaz	13.8	7.34-7.94	0.30 (1.20)
38	R. Khasaut	21.7	7.94-8.40	1.89 (1.17)
39	R. Gedmysh	12.8	8.02-8.31	0.75 (0.89)
40	R. Kichmalka	22.0	7.87-8.41	1.12(0.73)
41	R. Kichmalka	45.6	7.82-8.10	0.79(0.62)
42	R. Kichmalka	61.6	7.59-8.39	2.00 (1.13)
43	R. Ekiptsoko	11.5	8.08-8.21	2.78 (0.93)

Table A.3. Arsenic in surface waters of the mountainous region of the Baksan river basin

No	Sampling points	Distance from the source, km	$pH_{min} - pH_{max}$	As µg/dm³ (coefficient of variation)
67	Meltwater "Priyut 11"	0	6.32-6.60	0.77 (0.81)
68	Meltwater on the ground of Garabashi station	0	6.22-8.54	2.09 (1.16)
69	Meltwater on the ground of station "Mir"	0	6.37-7.52	1.25(0.87)
44	R. Baksan (Azau)	3.3	6.60-7.08	2.08 (1.24)
45	R. Baksan	8.1	7.07-7.53	3.67 (0.73)
46	R. Baksan	17.7	7.15-7.55	3.12 (0.95)
47	R. Baksan	35.3	7.07-7.80	1.52 (0.65)
48	R. Baksan	59.4	7.58-7.95	2.96 (0.62)
49	R. Baksan	76.2	7.63-8.14	2.31 (0.56)
50	R. Baksan	112.3	7.70-8.20	2.99 (0.51)
The main tributaries				
70	Azau Waterfall	3.0	6.91-7.03	14.47 (0.84)
51	R. Garabashi	4.3	7.04-7.69	66.38 (0.29)
71	Waterfall «Devich`i kosy`»	1.6	6.85-7.67	79.81 (0,40)
72	Terskol Waterfall	0.8	6.99-7.09	10.06 (0.49)
52	R. Terskol	4.2	6.66-7.73	5.87 (0.61)
53	R. Donguz-Orun	8.0	6.93-7.34	2.71 (0.87)
54	R. Kogutai	3.5	1.15-7.55	2.16 (0.65)
55	R. Yusengi	7.6	7.50-7.59	1.66 (0.71)
56	R. Adylsu	11.8	6.89-7.77	2.35 (1.31)
57	R. Irik	11.8	7.30-7.90	1.62 (0.53)
58	R. Kyrtyk	22.2	7.79-7.88	1.45 (0.92)
59	R. Adyrsu	16.1	7.32-7.80	1.54 (0.70)
60	R. Tyutyusu	11.2	7.06-7.85	1.33 (0.79)
65	Bolshoy Mukulan Stream	4.5	7.76-7.99	70.19 (0.57)
66	"Rudnik" Stream	2.0	7.63-8.24	47.18 (0.15)
61	R. Kamyksu	10.2	8.06-8.41	29.43 (0.67)
62	R. Gizhgit	28.5	8.17-8.45	1.66 (0.67)
63	R. Kestanty	27.6	7.87-8.29	1.77 (0.89)
64	R. Kendelen	58.7	7.88-8.16	2.31 (1.12)

Table A.4. Arsenic in surface waters of the Chegem river basin

No	Sampling points	Distance from the source, km	$pH_{min} - pH_{max}$	As µg/dm^3 (coefficient of variation)
73	R. Chegem (Bashil)	8.9	7.30-7.55	0.80 (0.58)
74	R. Chegem (Bashil)	14.7	7.32-7.75	0.51 (0.43)
75	R. Chegem	19.3	7.32-7.61	0.60 (0.82)
76	R. Chegem	29.1	7.36-7.72	1.11 (0.56)
77	R. Chegem	55.8	7.68-8.17	0.99 (0.43)
78	R. Chegem	70.2	7.67-8.18	1.13 (0.47)
79	R. Chegem	88.7	7.62-8.14	2.93 (1.16)
The main tributaries				
80	R. Jailyk	7.9	7.45-7.80	1.55(0.65)
81	R. Gara-Aususu	7.7	7.30-7.52	0.83 (0.11)
82	R. Bulungusu	8.5	7.39-7.95	2,98 (0.19)
83	R. Sylyksu	6.4	7.54-7.98	3.22(0.15)
84	R. Jylgysu	11.4	7.15-7.68	1.91 (0.43)
85	R. Cardan	8.4	7.95-8.51	1.92 (0.55)
86	R. Kektash	10.6	8.28-8.59	1.28(0.70)
87	R. Chatysu	6.3	7.96-8.38	1.16 (0.08)
88	R. Adaysu	3.8	7.94-8.45	2.20 (0.33)
89	R. Kiyikchisu	8.0	8.08-8.41	1.99 (0.15)

Table A.5. Arsenic in the surface waters of the Cherek river basin

No	Sampling points	Distance from the source, km	$pH_{min} - pH_{max}$	As μg/dm³ (coefficient of variation)
Cherek Bezengiysky River				
90	R. Cherek Bezengiysky	9.05	7.04-7.51	2.50 (0.73)
91	R. Cherek Bezengiysky	11.0	7.23-7.59	3.71 (0.63)
92	R. Cherek Bezengiysky	24.5	7.19-7.79	2.34 (0.51)
93	R. Cherek Bezengiysky	40.8	7.74-7.80	3.18 (0.63)
94	R. Cherek Bezengiysky	53.3	7.91-8.17	3.66 (0.48)
The main tributaries of the Cherek Bezengiysky River				
95	R. Mizhirgi	3.2	7.06-7.52	2.16 (1.15)
96	Stream Gitche-Naratli	1.9	7.82-7.89	3.12 (0.87)
97	R. Bashkamsu	4.0	8.02-8.20	6.48 (0.84)
98	R. Akkusu	5.3	7.85-7.90	15.30 (1.06)
99	R. Dumala	12.1	7.75*	8.27*
100	Stream Shiki	4.75	7.29-7.66	2.83 (0.19)
101	R. Kishlyksu	6.8	8.25-8.33	1.47 (0.74)
102	R. Shoudorsu	5.9	8.37-8.38	2.49 (0.03)
103	R. Karasu (Bezengi)	15.7	7.98-8.23	2.04 (1.02)
Cherek Balkarsky River				
104	R. Cherek Balkarsky	11.1	7.35-7.58	2.96 (0.78)
105	R. Cherek Balkarsky	17.8	7.38-7.58	3.31 (0.90)
106	R. Cherek Balkarsky	25.6	7.11-7.94	2.80 (0.70)
107	R. Cherek Balkarsky	32.7	7.10-7.76	3.47 (0.65)
108	R. Cherek Balkarsky	47.2	7.07-7.92	4.75 (0.06)
109	R. Cherek	58.0	7.69-8.30	4.05 (0.70)
110	R. Cherek	82.2	7.95-8.13	2.71 (0.71)
The main tributaries of the Cherek River (Balkarsky)				
111	R. Karasu	9.3	7.57-7.57	3.91 (0.53)
112	Stream	2.0	7.72-7.96	10.44 (0.23)
113	R. Zerklisu	4.0	7.30-7.66	2.70 (0.54)
114	stream from Mount Sabalah	2.6	7.88-7.93	5.58 (0.04)
115	R. Gulchisu	4.5	7.35-7.89	3.35 (0.47)
116	R. Ishkirty	16.2	7.47-7.91	2.45 (0.85)
117	R. Chinashki	16.4	7.60-7.88	6.27 (0.93)
118	R. Kurungusu	3.8	8.25-8.47	8.89 (1.03)
119	R. Karasu (Balkarsky)	15.8	7.90-8.34	2.69 (0.87)
120	R. Kheu	28.2	8.05-8.56	2.75 (0.65)
121	R. Psygansu	55.6	8.05-8.26	2.06 (1.21)

*- Arsenic was determined once.