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RESEARCH ARTICLE

ARSENIC POLLUTION STUDY OF THE RIVERS AND SOILS IN SOME OF THE REGIONS OF GEORGIA

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ABSTRACT

In Georgia there are many sources, whether natural or anthropogenic, which causes environmental pollution by arsenic compounds. Arsenic sulfide ore mining, processing and production of arsenic-containing drugs was carried out for decades (Racha-Lechkhumi and lower Svaneti). In the Article is presented studies of eco-chemical conditions for soils contaminated areas with arsenic industrial wastes (in the village Uravi - Ambrolauri Municipality, village Tsana - Lentekhi Municipality) and surface water (River Tskhenistskali and Lukhuni) 2014-2016years. The sampling of the soil and water, conservation, labeling, storage and transportation were produced in the accordance with the International Standard Organization (ISO) standard methodology. The study was conducted in laboratory by the ISO standards and USEPA methods in soil samples arsenic will be determined by plasma–emission spectrometer. The survey results shows that the arsenic maximum content in 2014 were observed in the vicinity of Uravi white arsenic treatment plant, where the arsenic maximum concentration was 61814.9 mg/kg and in the settling of the surrounding area - 36373.7 mg/kg; According to the 2015 data a high value was observed only in the samples from the 3rd site and settling in the village Tsana. The results were the following 59025.0 mg/kg and 55795.0 mg/kg. Ecologically most polluted rivers are: Tskhenistskali and Lukhuni. River Tskhenistskali (upper Tsana) arsenic concentracion in 2014 exeded the MPC. While in 2016 the concentrations were in the norms and in most cases it has been a declining trend. In 2014-2016 years the project "Arsenic Containing Mining Waste Management in Georgia", was ongoing between the Ministry of the Environment and Natural Resources Protection of Georgia and the Ministry of Economic Affairs of the Netherlands. The project was carried out in bilateral financing, which aims first urgent works to be carried out near the territory of the former arsenic hazardous plants, resulting in decreased concentrations of arsenic in the study areas.

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INTRODUCTION

It is long time known that Arsenic and its compounds have a toxic character. In seventies of the last century their carcinogenic properties has been established. However, arsenic compounds are widely used in technology, agriculture, medicine and so on, which is one of the reasons of their emissions in the environment. Therefore, Study of the arsenic content and distribution in natural waters, soils, food products and other objects is problematic issue. The problem is particularly relevant in Georgia, where there are sources, whether natural or anthropogenic, which causes environmental pollution by arsenic and its compounds. In Georgia Arsenic sulfide ore mining, processing and production of arsenic-containing drugs was carried out for decades (Racha-Lechkhumi and lower Svaneti). As a result of Arsenic production remaining toxic waste at a number of points that have not yet been safely placed are creating real possibilities of contamination for rivers, ground water and soils, especially during the natural disaster conditions (Aleksidze and Lolishvili, 2016). Arsenic and arsenic compounds are included in the list of 10 toxic elements (Hg, Pb, Cd, As, Ni etc.), which are posing serious problems for public health from the harmful effects on human health multilateral aspects (WHO) (Gvakharia *et al*., 1997; Tkhelidze *et al*., 2009). It is approved that Arsenic and arsenic compounds are I category hazard carcinogens (IARC) (Гагошидзе *et al*., 2004; Гагошидзе *et al*., 2005; Skalnaya *et al*., 2001; Arsenic and arsenic compounds iarc monographs, 2004). Those toxic elements, including arsenic compounds, are subject to the international food products trade essential control (SCIENTIFIC REPORT OF EFSA Dietary exposure to inorganic arsenic in the

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European population1 European Food Safety Authority, 2014; EN Official Journal of the European Union L 213/9, 2015; SCIENTIFIC OPINION Scientific Opinion on Arsenic in Food1 EFSA Panel on Contaminants in the Food Chain (CONTAM) 2, 3 European Food Safety Authority (EFSA), 2009). According to the Basel Convention the arsenic belongs to the category of controlled waste (The Basel Convention on the "Control of Transboundary Movements of Hazardous Wastes and their Disposal", 1989). All the aforesaid conditions, the arsenic should be in the normalized list of substances. Besides that arsenic ingestion ways may be the skin, respiratory tract, it is still mainly occurring in the human body from food and drinking water. Organic arsenic species most often can be occurred in seafood, and terrestrial products mostly 3-5 units and organic forms of arsenic valence. Therefore, in the food chain arsenic is involved mainly by contaminated soil and water (https://en.wikipedia.org/wiki/ Arsenic_contamination_ of_groundwater; http://www.ncbi. nlm.nih.gov/pmc/articles/ PMC35641 29/; http://www.who.int/ bulletin/archives/78(9) 1093. pdf; http://www.hindawi.com/ journals/tswj/2014/3045/; http:// www.scientificamerican.com/ article/ us-drinking-water-wells-contaminated-with-arsenic-other-elements/; http://well. blogs. nytimes.com/2013/09/20/ the-arsenic-in-our-drinking-water/? _r=0; https://www.research gate.net/publication/22669 5937_ Arsnic_and_Heavy_Metal_ Pollution_of_Soil_Water_and_Sediments_in_a_Semi-Arid_ Climate_Mining_Area_in_ Mexico; http://scialert.net/ fulltext/?doi=rjet.2015.231.240& org=10; http://www.science direct.com/science/article/pii/S026 9749107005222; https://en. wikipedia.org/wiki/Soil_contamina tion; http://journal.fron tiersin.org/article/10.3389/fenvs.2014. 00050/full; http://bmb. oxfordjournals.org/content/68/1/167.full; http:// www.ncbi. nlm.nih.gov/pmc/articles/PMC3128386/; http://www.ncbi.nlm. nih.gov/pmc/articles/PMC3013251/; http:// www.sciencedirect. com/science/article/pii/S1878029 613001345; ttps://www.jstor. org/stable/23499433?seq=1#page _scan_ tab _contents; http:// stud.epsilon.slu.se/1180/1/ahmed_b_100517.pdf; http://www. irinnews.org/report/80476/ bangladesh-arsenic-food-chain-raises-health-concerns; https://ijer.ut.ac.ir/pdf_370_1d66491 78b58411238004871c6e232ec.html; http://www.tand fonline. com/doi/abs/10.1081/ESE-120016881?journalCode=lesa20; http://www.bioline.org. br/pdf?hn10075). In Racha and Svaneti regions environmental problems occur due to the anthropogenic impact of arsenic-contamination. Without any management toxic arsenic-containing waste are located in the above mentioned regions. Industrial waste are usually mixed in the soil and water. As a result of the accumulation of toxic substances in the soil is gradually changing the chemical composition of the soil, geochemical and violated the integrity of living organisms. At present acute problem is toxic effects of arsenic waste in Lower Svaneti and Racha uncontrolled dumped sites near the rivers due to washing. Arsenic has ability of bioaccumulation so the real risk to the natural environment and human health and life, which is complicating from year to year. Dying livestock, destroyed flora and fauna. Waste management has become one of the priority issues in Georgia. The law "Waste Management Code" become in force (http://www.moe.gov.ge), which clearly presents the problems and ways for their resolving. Many scientific researches were carried out on the problem of the Racha and Svaneti region's industrial waste, environmental pollution and waste management issues (Мышьяк, 2006; Gvakharia *et al*., 2011; Bagrationi *et al*., 2015). Therefore it is strategically important in Racha and Svaneti to assess ecosystem ecological condition, assessment of negative factors on the environment, eco-toxicological risk, arsenic industrial pollution spreading possibilities, as well as development of the mitigation measures and reconciliation from scientific and practical point of view.

Results & Analysis

Lukhuni Arsenic ore processing, ore enrichment, roasting and white arsenic (As_2O_3) was refined into a chemical plant in the village of Uravi Racha in 27 km away from mining ore. From 1993 year the industrial complex were not operational and near the plant and the surrounding areas were dumped 100-110 thousand tons of arsenic compounds waste with arsenic common content 4-5 thousand tons (Gvakharia *et al*., 2011). According to the observations carried out since 2013 the regional mining-chemical plant, the old sarcophagus, industrial sites and complex of buildings, tombs, treatment facilities, sedimentation ponds of acidic water, as well as all buildings and structures of Mepischala tomb have been destroyed or seriously damaged (Bagrationi *et al*., 2015), in result arsenic-containing substances freely overflows pollute the surrounding environment and objects near the tomb (Photo 1-7). On the old factory territory is located a sarcophagus, the old factory buildings and facilities, as well as 55 - 60 thousand tons of soot, white arsenic and other toxic substances imported from the former Soviet Union. Waterproofing of the sarcophagus is violated and due to the precipitation occurs pollution of the surrounding area.

Photo 1

Photo 2

A similar situation is in Mepischala tomb, which is in the north-western part, it is damaged, due to the arsenic-containing substances freely overflows pollute the surrounding environment and the burial objects. Near the Lentekhi areas were operated two mining-chemical plants – Tsana and Qoruldashi, which stopped functioning in 1993. Now no one plant in Svaneti area have waste disposal single tomb or temporary storage.

Photo 3

Photo 4

Especially dangerous is the factory northwest 500 tons of metal waste, which is left unattended, placed in barrels. Almost the whole of the barrel as a result of corrosion has been violated (broken), and the residuals pollute the environment.

Photo 5

Soil pollution is high risk for pasture and other agricultural lands, resulting that food products become useless, danger to the environment, human health and the lives of thousands.

Photo 6

Photo 7

Now, Uravi cemented crypt, which covers 60 thousand tons of arsenic residue, cracked down on the river and along its sides substances directly are flown into the river that increases the risks. River Lukhuni passes Uravi, then running through several regions and joins the river Rioni. Rioni deliveries arsenic from Lukhuni and at the end may pollute the Black Sea (1). In 2014-2016 by us were studied the soils contaminated with arsenic industrial wastes (in the village Uravi - 0-20 cm layer. Table 1 and 2 shows soil sampling sites, Ambrolauri Municipality, village Tsana - Lentekhi Municipality) and surface water (River Tskhenistskali and Lukhuni) eco-chemical condition. Soils and wastes mixed samples were taken from the average depth of the coordinates in the village Uravi arsenic industrial wastes contaminated area and results of the analysis (the concentrations of arsenic) in 2014-2015. The survey results shows that the arsenic maximum content in 2014 were observed in the vicinity of Uravi white arsenic treatment plant (Sample # 589), where the arsenic maximum concentration was 61814.9 mg/kg and in the settling of the surrounding area (Sample # 591) - 36373.7 mg/kg (Figure 1). According to the 2015 data (Table 2 and Figure 2) a high value was observed only in the samples from the 3rd site and settling. The results were the following 59025.0 mg/kg and 55795.0 mg/kg. Table 3. shows the concentrations of Arsenic in the soil samples from the village Tsana on the territory of the former arsenic industry.

Table 1. Results of soil samples analyzes in village Uravi, 2014

#	Sampling point	Sample #	Latitude	Longitude	Date	As mg/kg
1	Uravi, white arsenic processing factory	589	N42038'14,9''	EO 43017'16,3''	21.07.2014	61814.9
2	Uravi 1- concreted	590	N 42038'34,9''	EO 43017'27,8''	21.07.2014	267.4
3	Uravi 1 - old ruins area	595	N 42038'14,3''	EO 43017'18,6''	21.07.2014	4530.3
4	1- Uravi old ruins area	593	N 42038'15,6''	EO 43017'19,4''	21.07.2014	2515.5
5	1- Uravi old ruins area	597	N $42^0$38'19,5''	E$_O$ $43^0$17'19,1''	21.07.2014	1620.9
6	Uravi-metallic building	598	N $42^0$38'18,2''	E$_O$ $43^0$17'17,5''	21.07.2014	815.5
7	Uravi 3	592	N $42^0$40'32,5''	E$_O$ $43^0$18'02,3''	21.07.2014	2369.9
8	Uravi 3-laboratory	596	N $42^0$40'05,0''	E$_O$ $43^0$18'02,3''	21.07.2014	75.9
9	Uravi 3-settling	591	N $42^0$40'07,2''	E$_O$ $43^0$18'04,1''	21.07.2014	36373.7
10	Uravi- riv.Lukhunis bank	594	N $42^0$32'38,9''	E$_O$ $43^0$13'15,8''	21.07.2014	23.5

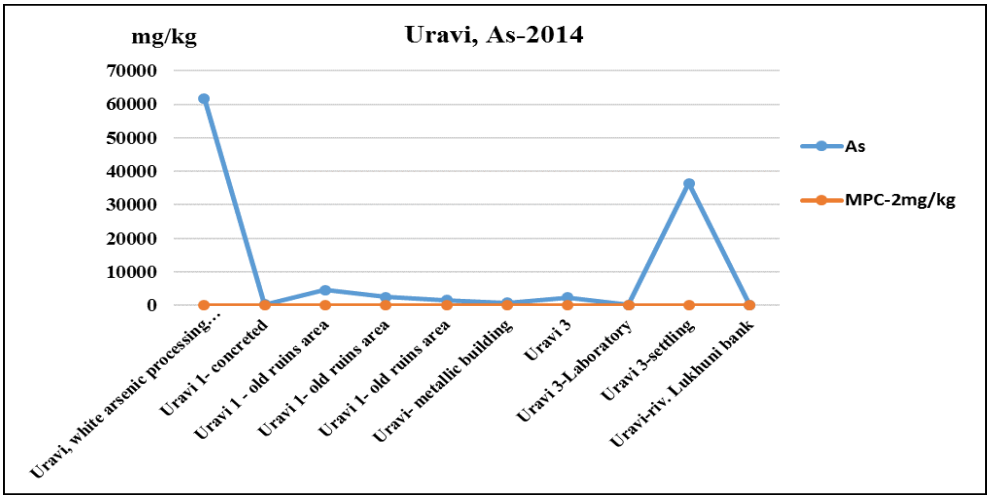

Figure 1. Arsenic concentrations in the soil samples in village Uravi, 2014

Table 2. Rresults of soil samples analyzes in village Uravi, 2015

#	Sampling point	Sample #	Latitude	Longitude	Date	As mg/kg
1	Uravi 1, old tailings	517	X 0359722	Y 4722043	10.06.2015	683,0
2	Uravi 1, old ruins	518	X 0359667	Y 4722067	10.06.2015	548,0
3	Uravi, #2	519	X 0359627	Y 4722005	10.06.2015	857,0
4	Uravi, #2	520	X 0359639	Y 4722060	10.06.2015	35327,0
5	Uravi, #2	521	X 0359820	Y 4721985	10.06.2015	2989,0
6	Uravi, #2	522	X 0359510	Y 4722213	10.06.2015	961,0
7	Uravi #2, former territory of Arsenic enterprise	528	X 0359826	Y 4722577	10.06.2015	6907,0
8	Uravi	523	X 0359839	Y 4722220	10.06.2015	5001,0
9	Uravi, 3 site	524	X 0360720	Y 4725248	10.06.2015	1530,0
10	Uravi, 3 site	525	X 0360735	Y 4725252	10.06.2015	1884,0
11	Uravi, 3 site	526	X 0360724	Y 4725301	10.06.2015	59025,0
12	Uravi, from settling	527	X 0360771	Y 4725406	10.06.2015	55795,0

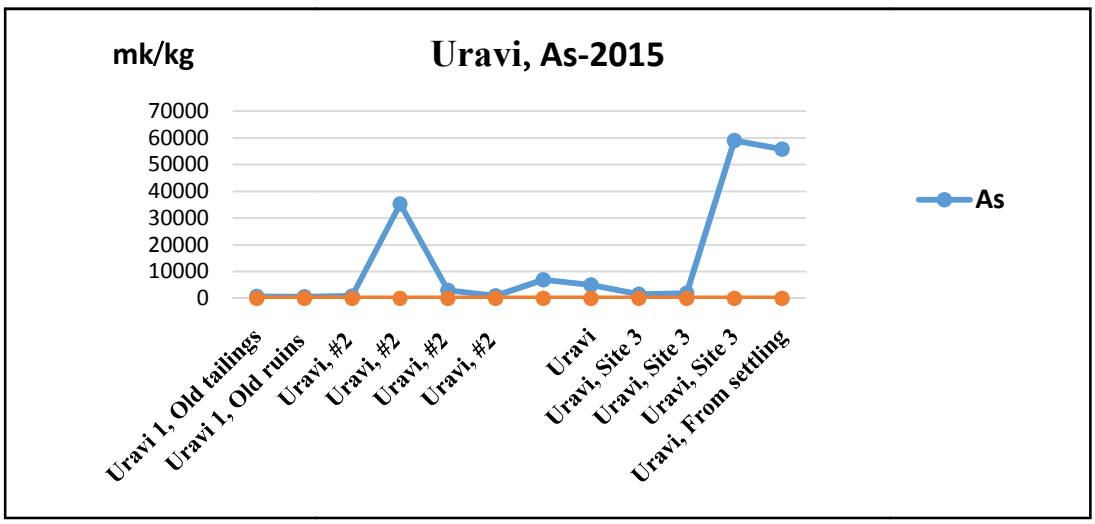

Figure 2. Arsenic concentrations in the soil samples in village Uravi, 2015

Table 3. The results of analyzes of soil samples in village Tsana

#	Sampling point	# Sample	Latitude	Longitude	Data	As
						mg/kg
1	#1, 2, 3, 4, 5 Upper Tsana	1291	X-0345560	Y-4741473	24.11.2015	21.52
2	#6, 7, 8, 9, 10 Lower Tsana	1292	X-0345480	Y-4741380	24.11.2015	48.55

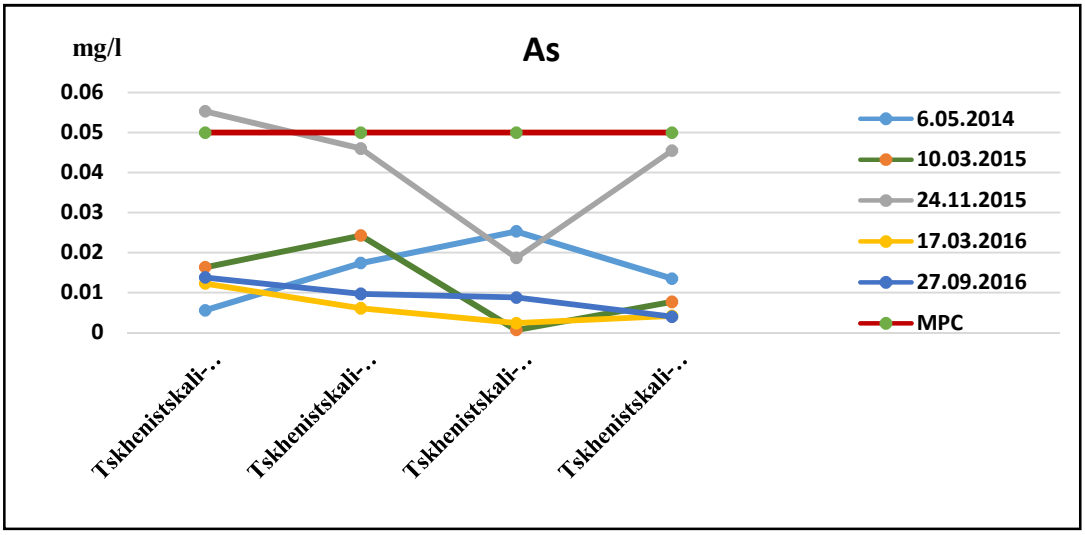

Figure 3. Arsenic concentration in the river Tskhenistkali in village Tsana, 2014-2016

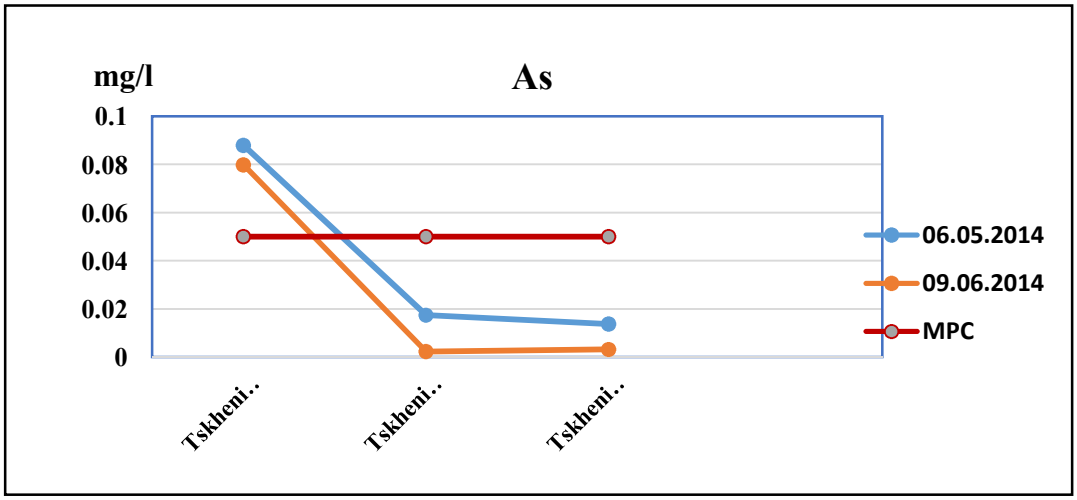

Figure 4. Arsenic concentration in the river Tskhenistkali in In May-June 2014

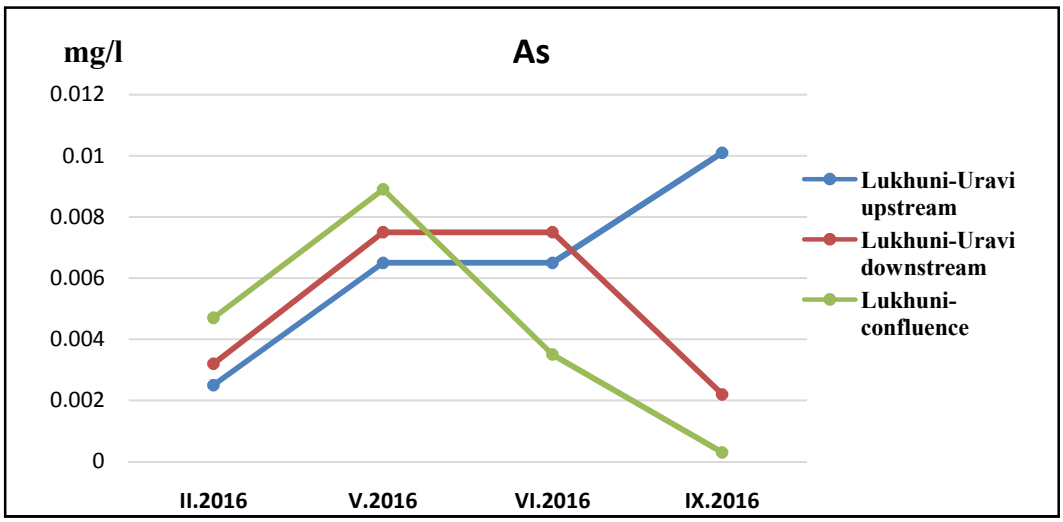

Figure 5. Arsenic concentration in the river Lukhuni in May-September 2016

The soil samples were taken from Tsana upper and lower territories in each location 5 samples depending the envelope principle and analyses were made by a mixed pattern. The obtained results shows that concentrations of arsenic here ranges from 21.52 - 48.55 mg/kg. At the same time, the higher concentration was observed in lower Tsana - 48.55 mg/kg, while at the upper Tsana was observed - 21.52 mg/kg. The river Tskenistkali is the main source of drinking water for the many of the regions of Western part of Georgia, also river is used for agricultural irrigation and for industrial purposes. Since the river Tskhenistskali and Lukhuni are Rioni River tributaries, so it in terms of eco-chemistry river water quality protection and determination of the content of arsenic in their waters is very important. Major source of arsenic is slightly mineralized spring and summer flows, which flows through the arsenic contaminated soils and other facilities (waste ore, concentrates). Ecologically most polluted rivers are: Tskhenistskali (Qoruldashi, Tsana, Mele, etc.) and Lukhuni (Uravi, Likheti, etc.). Figure 3. shows the concentration of arsenic in the riv. Tskhenistskali in 2014-2016. As can be seen from the drawing, in November 2015 was observed a high concentration of arsenic. Which in our opinion was caused by damaged tomb of arsenic waste storage. Due to above mentioned Arsenic levels exceeded the MPC in November 2015 in this point, but does not exceed the maximum permissible concentrations in other points. After construction of the sarcophagus arsenic concentrations in 2016 have been reduced compared with the results in 2015.

Figure 4. shows arsenic content Tskhenistskali (Tsana-down enterprise, the enterprise, the lower-realized) in May-June 2014. Maximum concentration of arse-nic was observed near the enterprise in May - 0.09 mg/l and in June - 0.08 mg/l and in the both cases were higher than the MPC.

As Figure 5. shows the arsenic concentration in the river Lukhuni in 2016 does not exceed the maximum permissible concentration and in most cases it has been a declining trend.

As the obtained results shows there is a need for urgent measures, because there is real danger to the environment, as well as in the regions to the health of the population. The various donors and local organizations are involved in solving of this problems. In 2014-2016 years the project "Arsenic Containing Mining Waste Management in Georgia", was ongoing between the Ministry of the Environment and Natural Resources Protection of Georgia and the Ministry of Economic Affairs of the Netherlands. The project was carried out in bilateral financing, which aims first urgent works to be carried out near the territory of the former arsenic hazardous plants. Within the project in Ambrolauri and Lentekhi areas was carried situation analyses and the safe disposal action plan has been developed. In the frames of the project in the municipalities is planned construction of the new tomb (Uravi 1, Uravi 3), where will be located the arsenic-containing waste, contaminated soil and inert material (Uravi 1, 3, 4). The works were carried out in allocated areas: fencing, repaired one grave (Uravi 2). Also, for the purpose of safe allocation of arsenic waste Lentekhi Tsana 2 and 3 is realized fence.

Research methods

The sampling of the soil and water, conservation, labeling, storage and transportation were produced in the accordance with the International Standard Organization (ISO) standard methodology. The study was conducted in laboratory by the ISO standards and USEPA methods. Analyzes were carried out by the Atmospheric Air, water and Soil analyses Laboratory of the National Environmental Agency of the Ministry of Environment and Natural Resources Protection of Georgia by the following technical and instrumental support: soil arsenic was determined by plasma–emission spectrometer (ICP-OES) by the ISO 11885:2007 – samples treatment was made by microwave pressure digestion. Method EPA-200.2 “Berghof” speed wave MWS-3+ (37). Arsenic in water samples was determined by the ICP-OES –the ISO 11885:2007 in the laboratory and on-site by testing method through Merkoquant-'s testers.

Conclusion

- In 2014-2016 we studied contaminated with arsenic industrial wastes soil (village Uravi-Ambrolauri municipality, village Tsana-Lentekhi Municipality) and surface water (riv. Tskhenistsqali and Lukhuni) eco-chemical conditions;
- According to the survey conducted in 2014 maximum content of arsenic were indicated in Uravi near white arsenic treatment plant and its adjacent area the where the maximum arsenic concentration was 61814.9 mg/kg and in the settling of the surrounding area - 36373.7 mg/kg;
- In 2015 year in the village Tsana arsenic concentration decreases, a high value is observed only in the soil samples taken from 3rd site and sediment - 59025.0 and 55795.0 mg/kg;
- In soil samples taken in 2015 in the village Tsana on the territory near the former Arsenic processing industry arsenic concentrations varies from 21.52 to 48.55 mg/kg. At the same time, in the lower Tsana is observed the arsenic higher concentration 48.55 mg/kg (24 MPC), while the concentration in upper Tsana is 21.52 mg/kg (11 MPC).
- Ecologically highly polluted rivers are Tskhenistskali and Lukhuni. In Tskhenistkali (upper Tsana) the concentration of arsenic in 2014 exceeds the maximum permissible concentration.
- Arsenic concentration in the river Lukhuni in 2016 did not exceed the MPC and in most cases it has been a declining trend.
- 2014-2016 years the project "Arsenic Containing Mining Waste Management in Georgia," was ongoing between the Ministry of the Environment and Natural Resources Protection of Georgia and the Ministry of Economic Affairs of the Netherlands. The project is carried out in bilateral financing, which aims first urgent works to be carried out near the territory of the former arsenic hazardous plants.

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