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Investigation of the Concentration of Heavy Metals in the Drinking Fountains of the Mountain Massif Shale and Bajgore in Kosovo

Sadija Kadriu, Milaim Sadiku*, Mensur Kelmendi, Hana Mehmetaj

Faculty of Food Technology, Department of Technology, UMIB, Mitrovica, Kosovo

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Abstract

Taking in consideration that drinking water is a vital element without which the normal existence of humans and other living things in our planet cannot be thought of, we are motivated to research the wells and springs used for drinking in the villages of Bajgora, Kovacica and Kaqandoll. The suspicion that the waters of this mountain massif contain heavy metals due to the presence of mineral ores also prompted us to investigate the degree of presence or not of heavy metals in these waters. To assess the water quality of these wells, in the monitoring network that includes these three villages, we have pinpointed five monitoring points, determining the organoleptic, physic-chemical, and microbiological and heavy metal parameters. During the research process, in order to evaluate the water quality as accurately as possible, classical and instrumental methods of chemical analysis were applied. We have compared the results of the analysis with the standard values of AI16 / 2012- Administrative Instruction of Kosovo that has to do with the quality of water for human consumption and that is in full compliance with EU Directive 98/83 EC. The obtained results denote the presence with heavy metals of Pb, Zn, Cd and Ni, in four of the five samples taken for research. Therefore, we have come to the conclusion that the presence of these metals results as a consequence of the geological composition and ore-rich underground layers of this mountain massif.

Keywords: Drinking water, Water quality, Mountain massif, Bajgora and Shale, Heavy metals

1 Introduction

The mountain massif Shale and Bajgore, our object of study, has an area of 433 km^2, at an altitude of 600-1789 m, and lies in the north-eastern part of Kosovo, whose territory is divided into five municipalities: Mitrovica, Vushtrri, Besiana, Zvecan and Kastriot. The massif of Shale and Bajgora lies in geographical coordinates, at latitude $42^0$53'13 "north latitude and east latitude from $20^0$52'21". The territory of this mountain massif includes several villages and is characterized by great agricultural and natural resources located around the Stantërg mine. This mountain massif, in addition to being rich in mineral ores, although at an altitude of up to 1789 m, is also rich in sufficient surface and groundwater that was used for drinking. Due to the geological composition of the soil, mineral wealth, in the 30s of the last century was established the well-known Trepça Mine, which in the past and today, is active in the production of non-ferrous metals that are also known on the international stock exchange. The pivotal scope of this study is related to the content of heavy metals in drinking water, not as a result of industrial activity, but because of the geological composition of the soil and its influence on this groundwater (1). Numerous scientific studies, conducted in different parts of the world, have shown that half of the worlds (especially developing countries) suffer from various and dangerous diseases caused as a result of the use of water contaminated with various microbes and minerals (2).

The presence of heavy metals beyond the standard values in the springs and wells of this mountain massif, has been and is known by various local and foreign researchers, but the inhabitants of these villages did not have ample knowledge and information about the negative impact of these metals, although they have consistently faced health consequences (3). It is already evident about the toxic effects of some of the heavy metals in the human body, the impact of which leaves obvious consequences, not only in the brain, heart, kidneys, liver, pancreas and bones, but also in DNA (4). Such consequences are still clearly observed in the health and physique of some of the inhabitants of this mountain massif rich in Pb-Zn ore and other accompanying metals.

Such a situation has also affected the demographic movement of the inhabitants of this mountain massif, since the vast majority of this population has abandoned their settlements and settled in villages and other cities of Kosovo. in the geographical area, where humanity wants to build and organize their settlements (5). The problem of providing sufficient drinking water, as in many other countries of the world, as well as in many settlements of Kosovo, has been and is the fundamental problem for the

Corresponding author: Milaim Sadiku, Faculty of Food Technology, Department of Technology, UMIB, Mitrovica, Kosovo. E-mail: milaim.sadiku@umib.net

organization of quality of life Water is a major natural source and basic human need for life. In recent decades, groundwater has become an essential resource due to its purity and availability (6). In order to have a more realistic picture of the water quality, although abundant of this mountain massif, but also given the ore-mining terrain and the possible consequences of heavy metals on the health of the inhabitants of this massif, we have isolated drinking waters of the villages Kovacica, Bajgora and Kaqandoll. The purpose of the study is to investigate the presence of heavy metals in drinking water in some villages that includes the mountain massif Shale e Bajgore (to see Pb-Zn and other social metals), due to geological control of the soil and its impact on groundwater. Regarding the impact of geological strata on groundwater quality, researchers Fawell & Nieuwenhuijsen, have expressed: The physic-chemical quality of drinking water is also based on hydrogeological criteria. These criteria relate to the type of water layer feeding, the composition and structure of the terrain, the level of protection of the water layer etc. (7).

2 Drinking water monitoring

In order to have a comprehensible picture regarding the degree of the concentration of heavy metals in the waters of the mountain massif Shale and Bajgore, for the research area we have selected the villages Kovacica, Bajgora and Kaqandoll and we have marked five monitoring points marked with M_1, M_2, M_3, M_4 and M_5. Within the monitoring network, except for a well in the village of Kovaçica, whose water is used for drinking, all other sampling sites are spring water. The drinking water monitoring network and the coordinates of the five sampling sites of the three villages are presented in Figure 1 and Table 1. Sampling site M_1 - represents the sample taken in a well in the village of Kovaica, whose water is used for drinking by households. According to the representative of the household, the well has a depth of 3 m and a diameter of 80 cm. Sampling site M_2 - represents the source of the Bajgora village, whose water has been used for drinking for years, not only by the inhabitants of this village and other villages around, but also by thousands of inhabitants of the cities like Mitrovica, Vushtrri, Besijana, and so on. There is an opinion that the waters of this spring are of a high quality and have healing properties, for family needs and mainly for drinking, large amounts of water up to 50,000 liters per day are used and transported. Sampling site M_3 - reflects the waters of the spring located between two villages, Bajgora and Kaqandoll. Like the waters of the sampling site M_2, the waters of this sampling site, although in smaller quantities, are considered and used as waters of high quality and healing. Therefore, the waters of this spring, as in M_2, are carried and used by many inhabitants not only of this mountain massif, but also by inhabitants of other parts of Kosovo. Sampling site M_4 - represents the well located in the village of Kaqandoll at a distance of approximately 15 km from the sampling site M_2 and M_3. This natural spring is associated with a gentle topography of the terrain, with meadows and and abundant amounts of water. Sampling site M_5 – part of the Kaqandoll village close to the sampling site M_4. This well, in addition to its water capacity, is also supplied by the waters of three other springs, which occurred at a distance of approximately 1.5 km. Due to the abundant amount, the waters of this spring do not become turbulent even during rain and snow.

3 Materials and methods

During the research work, in order to have the analyzes as accurate and representative as possible, we paid special attention to the sampling process. The method of sampling, the quantity of the sample taken, the transport and the maximum time that the sample can stand before the chemical analysis, is done in accordance with the method ISO 5667: 1,3,11 (8-10). The conservation of aqueous samples is made in full compliance with the conservation rules of the American Public Health Association (11). For the determination of organoleptic parameters, such as: smell, taste and color, we are based on the sensory method, while for the determination of physico-chemical parameters, standard methods applied for the analysis of each parameter, are denoted within the table of results (Table 2).

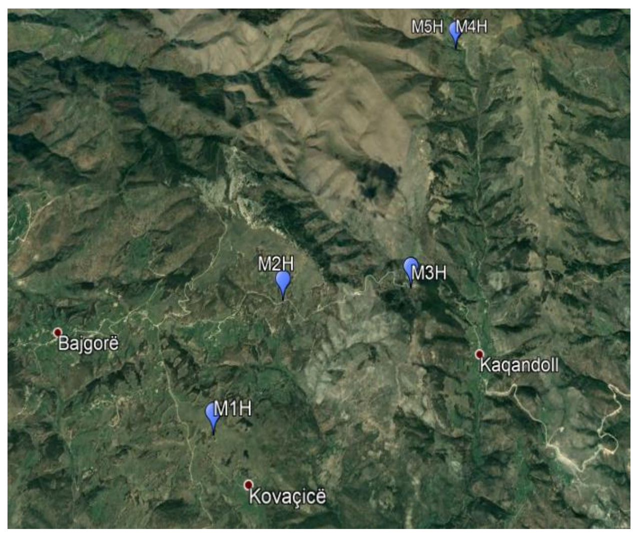

Figure 1: Monitoring network

Table 1: Coordinates of monitoring points

Sample number	Sampling point	Latitude	Longitude	Altitude (m)
M_1	Kovaçicë Village	42°57'4.66"N	21° 1'45.53"E	1339.9
M_2	Bajgorë Village	42°58'13.27"N	21° 1'48.96"E	1342.0
M_3	Kaqandoll- Bajgorë Village	42°58'43.81"N	21° 3'3.42"E	1240.8
M_4	Kaqandoll Village	43° 0'57.07"N	21° 2'25.69"E	1265.8
M_5	Kaqandoll Village	43° 0'57.19"N	21° 2'25.73"E	1264.6

Table 2: Results of organoleptic and physico-chemical parameters according to sampling sites

Organoleptic and physico-chemical parameters								
Parameters	Standard Method	Unit	Reference values	M_1	M_2	M_3	M_4	M_5
Color	Sensing method	-	None	None	None	None	None	None
Wind/Odor	Sensing method	-	None	None	None	None	None	None
Taste	Sensing method	-	None	None	None	None	None	None
Temperature	ISO 10523:2012	^0C	8-12	11.3	10.5	10.0	6.5	13.0
Turbidity	ISO 7027:1999	NTU	1.2-2.4	0.29	0.10	<0.01	<0.01	2.16
Conductivity	ISO 7888:1985	µS/cm	2500	182	120	481	307	229
Soluble substances	ISO 7888:1985	mg/L	1500	91	60	245	153	115
pH	ISO 10523:2008	-	6.5-9.5	6.88	6.90	7.75	7.43	8.31
Dissolved oxygen	ISO 5814:2012	mg/L	>5	5.1	8.4	9.3	10.0	10.2
COD	ISO 15705:2002	mg/L	5.0	5.6	12.4	3.5	6.6	18.6
Phosphates	EN ISO 6878:2004	mg/L	0.3	0.16	0.20	0.10	0.20	0.25
Ammonia	ISO 7150-1:1984	mg/L	0.5	< 0.01	<0.01	<001	<0.01	<0.01
Nitrates	DIN 38405-9: 2011	mg/L	50	1.8	0.8	2.0	<0.1	<0.1
Nitrites	ISO 677 7:1984	mg/L	0.5	0.094	0.118	0.113	0.126	0.114
Sulfate	APHA 4500-SO_4^{2-}	mg/L	250	5	3	7	4	5
Chloride	ISO 9297:1989	mg/L	250	2.84	2.98	3.91	3.12	2.38
Overall strength	ISO 6059:1984	d^0H	30	5.1	3.4	16.2	9.5	7.2

* UA 16/2012; Directiva 98/83/EC

For microbiological parameters, such as the determination of the total number of coliform bacteria and Escheria Coli we are based on the standard method EPA 1604 (12), while the number of colonies at 37 ˚C (CFU/mL) was worked in correlation with the standard method EN ISO 6222 (13). Regarding the concentration of heavy metals in the aqueous samples taken, we have previously mineralized the samples, applying the EPA method 3015A (14). Whereas, for determining the concentration of heavy metals in aqueous samples, the standard method EPA 6020A has been applied (15). We performed the experimental part in the environmental analysis laboratory of the Kosovo Hydrometeoro-logical Institute (KHMI) in Prishtina.

4 Results and discussion

The results of analyses performed for organoleptic, physico-chemical, microbiological and heavy metal parameters, presented in Tables 2, 3 and 4 reflect the real situation of drinking water quality in the monitored sampling sites M_1, M_2, M_3, M_4 and M_5. We took the representative samples and analysed them in August 2020, at a time when there was a lack of atmospheric precipitation in Kosovo. The obtained results, based on the organoleptic and physico-chemical parameters, we have compared with the reference values of UA 16/2012-Administrative Instruction of Kosovo that has to do with the quality of water for human consumption (16) and Directive 98/83/EC for the quality of drinking water (17). All obtained results, except the chemical consumption of oxygen are in full correlation with the reference (standard) values. Chemical oxygen consumption (COD) is a measure of the content of organic substances in water and provides data on the total water load with organic matter (18).

In addition to the M_3 sampling site, where the analysis results in accordance with the reference values, exceedances of the allowed limits (Figure 2) with COD were encountered in the M_1 (5.6 mg/L), M_2 (12.4 mg/L), M_4 (6.6 mg/L) sampling sites) and M_5 (18.6 mg/L). The results of the samples taken, reflected in Table 3 for microbiological parameters, in all sampling sites are in full compliance with the reference values based on UA 16/2012 and Directive 98/83/EC.

The tabular data reflect the concentration beyond the reference values with these heavy metals: With Cd at the M3 sampling site, at a value of 0.238mg/L (Figure 3). When cadmium enters the body it is accumulated in the kidneys and can cause problems such as kidney dysfunction. Brittle bones, lung cancer and acute pneumonia are other health effects that arise from cadmium exposure (19). With Ni exceeding the reference values (Figure 4) we encountered the sampling site M2 (0.027 mg/L) and M3 (0.076 mg/L). Nickel is relatively non-toxic if consumed in normal quantities through water and food. At higher concentrations, Ni can cause changes in the respiratory tract - with the appearance of tumors, as well as changes in the skin. It also causes mutations in the p53e gene in cooperation with the oncogene V-Ha-Ras acting as a carcinogen (20). Zn results in exceeding the reference value at the M4 sampling site, in the amount of 1,084 mg/L (Figure 5). Zinc is a component of many enzymes important for immune function and with catalytic and structural roles. It is necessary for wound healing, regeneration of new cells, and acid-base balance as a component of carbonic anhydrase. Consumption of excess zinc can cause ataxia, lethargy, copper deficiency and neurological dysfunction (21).

With Pb exceeding the standard limits we encountered in the sampling sites M1, in the amount of 0.015mg / L and in M3, in the amount of 0.017 mg/L (figure 6). Lead is toxic to the central and peripheral nervous system causing neurological and behaviour effects. The consumption of lead in higher quantity may cause hearing loss, blood pressure and hypertension and eventually it may be prove to be fatal (22).

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Table 3. Results of microbiological parameters according to sampling sites

Microbiologic Parameters								
Parameters	Standard Method	Unit	Reference values*	M_1	M_2	M_3	M_4	M_5
Escheria Coli	EPA 1604:2002	Number/100ml	0	0	0	0	0	0
Total number of coliform bacteria	EPA 1604:2002	Number/100ml	0	0	0	0	0	0
Number of colonies at 37˚C (CFU / mL)	ISO 6222:1999	Number/1ml	20	0	0	0	0	0

* UA 16/2012; Directive 98/83/EC

Table 4: Results of heavy metal concentration by sampling site

Heavy Metals								
Parameters	Standard Methods	Unit	Refernce values*	M_1	M_2	M_3	M_4	M_5
Copper Cu^{2+}	EPA 6020A	mg/L	2.0	0.007	0.004	0.004	0.001	0.002
Chrome Cr^{3+}	EPA 6020A	mg/L	0.05	< 0.001	< 0.001	<0.001	<0.001	< 0.001
Cadmium Cd^{2+}	EPA 6020A	mg/L	0.005	< 0.001	< 0.001	0.238	< 0.001	< 0.001
Nickel Ni^{2+}	EPA 6020A	mg/L	0.02	0.006	0.027	0.076	< 0.006	< 0.006
Zinc Zn^{2+}	EPA 6020A	mg/L	0.5	< 0.001	0.038	0.087	1.084	0.015
Manganese Mn^{2+}	EPA 6020A	mg/L	0.05	< 0.002	< 0.002	0.023	< 0.002	< 0.002
Iron Fe^{2+}	EPA 6020A	mg/L	0.2	0.015	0.005	0.020	0.007	0.019
Lead Pb^{2+}	EPA 6020A	mg/L	0.01	0.015	< 0.002	0.017	< 0.002	< 0.002

*UA 16/2012; Directive 98/83/EC

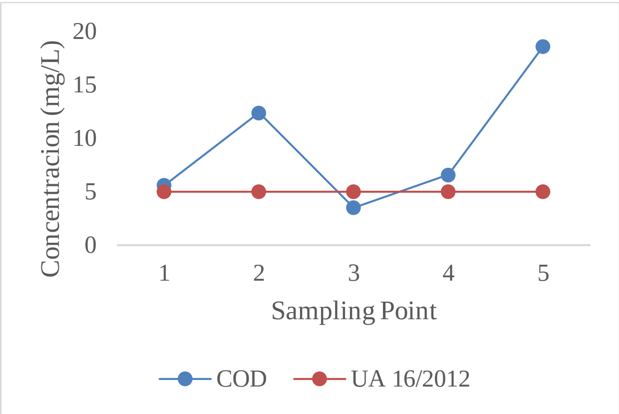

Figure 2: COD concentration according to sampling points

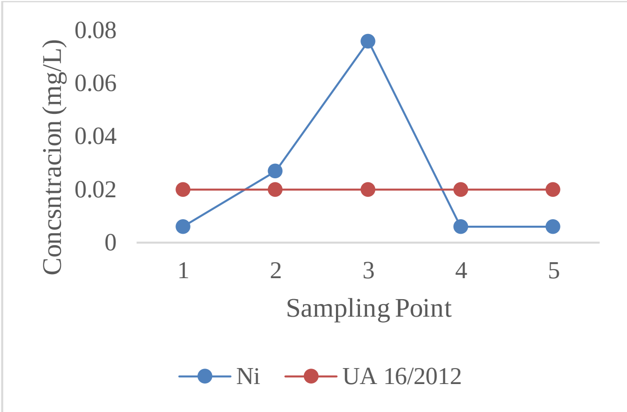

Figure 4: Ni concentration according to sampling points

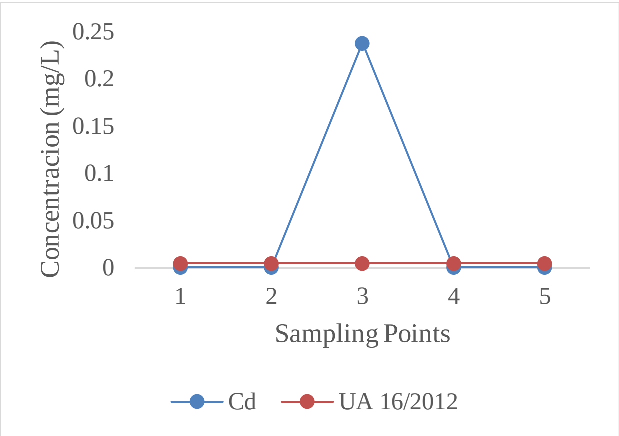

Figure 3: Cd concentration according to sampling points

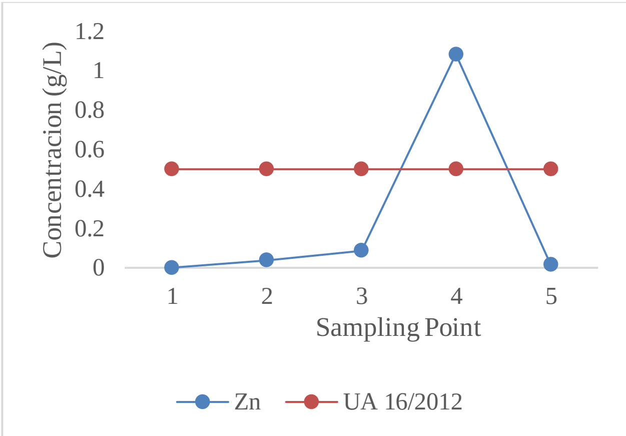

Figure 5: Zn concentration according to sampling points

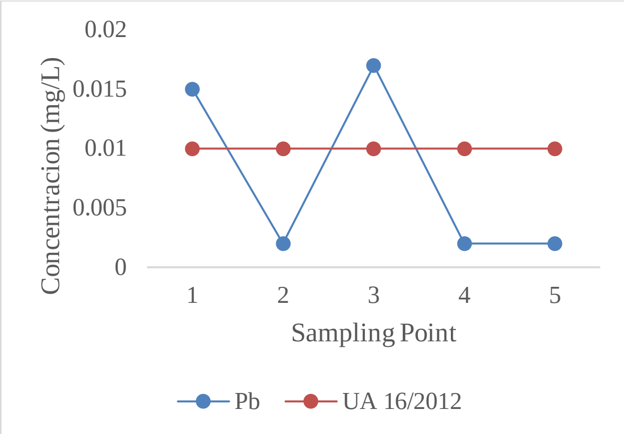

Figure 6: Pb concentration according to sampling points

5 Conclusion

It is vivid that the mountain massif Shale e Bajgore is a territory known for the geological structure of the earth, rich in Pb-Zn ore and other accompanying metals. In addition to mineral wealth, this massif is also rich in abundant groundwater and surface water. However, the water wealth for the inhabitants of this massif, in addition to meeting and satisfying the needs of households, due to the concentration beyond the mass of Heavy metals, has caused various diseases with serious consequences for the health of the inhabitants of this mountain massif. and are located in other rural and urban areas of Kosovo. In order to have a lucid idea about the degree of concentration of heavy metals in the drinking water of these villages and the consequences caused by the excessive presence of some heavy metals, we have designed a monitoring network with five sampling sites. We have compared the results of the analyzes with the reference values of UA 16/2012 and Directive 98/83 / EC. On this basis we have managed to conclude that the concentration of heavy metals beyond the reference values is present in four of the five monitoring points. Obvious excesses were encountered with Pb, Zn, Cd, and Ni. In addition to heavy metals, exceeding the reference values has also resulted in the chemical consumption of oxygen. Enormous use of spring waters M2 and M3, not only by the inhabitants of the villages of the mountain massif Shale e Bajgore, but also by thousands of other citizens of Kosovo, who were constantly supplied with these waters, thinking that they are of high quality and with healing properties, without knowing the degree of contamination with heavy metals and the consequences they may have on their health, obliges us to forward the results to the responsible bodies of the relevant institutions at the local and central level. In the domain of our field of research has been the evidence of the presence or not of heavy metals in the waters of these springs that are used for human consumption, but with the contamination of heavy metals, before the relevant health researchers there is a need to research the consequences that the presence of these metals can cause on human health.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, and manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

All authors of this study have a complete contribution for data collection, data analyses and manuscript writing.

References

1. Thomas MA.The effect of residential development on groundwater quality near Detroit, Michigan. JAWRA Journal of the American Water Resources Association. 2000; 36(5):1023 – 1038.
2. Kadriu S., Sadiku M., Kelmendi M., Ibishi D. Determining the drinking water quality in several rural settlements in Ferizaj municipality, Kosova. Bilimsel Madencilik Dergisi. 2020; 59(3): 207-217.
3. Çullaj A.Kimia e mjedisit.Tiranë. 2010.
4. Odobašič A. Specijacia teških metala polarografskim tehanikama u prirodnim vodama. Doktorska disertacija. Tuzla. 2005.
5. Kadriu S., Sadiku M., Kelmendi M,Tahiraj B., Aliu M., Hyseni A., Shala A. Research of the Drinking Water Quality in Wells and Fountains of Villages in Gjakova Municipality in Kosovo. Journal of Environmental Treatment Techniques. 2020; 8 (3): 1151-1156.
6. Verma A, Thakur B, Katiyar S, Singh D, Rai M. Evaluation of ground water quality in Lucknow, Uttar Pradesh using remote sensing and geographic information systems (GIS). International Journal of Water Resources and Environmental Engineering. 2013;5(2):67-76.
7 Fawell J, Nieuwenhuijsen J.M. Contaminants in drinking water: Environmental pollution and health. British Medical Bulletin.2003 Dec;68(1):199-208.
8 ISO 5667-1:2006. Water quality -Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques. Edition:2. 2006 Dec. 1.
9 ISO 5667-3:2012. Water quality -- Sampling -- Part 3: Preservation and handling of water samples. Edition:4. 2012 Nov. 3.
10 ISO 5667-11:2009. Water quality -- Sampling -- Part 11: Guidance on sampling of groundwaters. Edition:2. 2009 Apr. 11.
11 APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater. 21st Edition. American Public Health Association/American Water Works Association/Water Environment Federation. Washington DC. 2005.
12 EPA Method 1604:2002. Total Coliforms and Escherichia coli in Water by Membrane Filtration Using a Simultaneous Detection Technique (MI Medium). United States Environmental Protection Agency. 2002 Sep.
13 ISO 6222:1999. Water quality - Enumeration of culturable microorganisms - Colony count by inoculation in a nutrient agar culture medium. Edition:2. 1999 May.
14 EPA Method 3015A: 2007. Microwave Assisted Acid Digestion of Aqueous Samples and Extracts. Revision 1. United States Environmental Protection Agency. Washington, DC. 2007 Feb.
15 EPA Method 6020A (SW-846): Inductively Coupled Plasma-Mass Spectrometry. Revision 1. 2007 Feb.

16 Udhëzimi Administrativ Nr.16/2012 për cilësinë e ujit për konsum nga njeriu të Kosovës. Qeveria e Republikës së Kosovës. 2012 Dec 24.
17 EU's drinking water standards, Council Directive 98/83/EC on the quality of water intended for human consumption, Adopted by the Council. 1998 Nov.
18 Kostić I., Perović J., Anđelković T. Korelacija HPK i BPK5 parametara organskih supstanci poznate strukture u vodi. Zbornik radova Tehnološkog fakulteta u Leskovcu. 2009; 215-219.
19 Robards M. Worsfold P. Cadmium Toxicology And Analysis - A review: Analyst. 1991 Jun;116(6):549-568.
20 Rajković M. B. Neke neorganske supstance koje se mogu naći u vodi za piće i posledice po zdravlje ljudi. Hemijska industrija. 2003; 57(1): 24-34.
21 Underwood EJ. Trace elements in human and animal nutrition. 4th ed. Academic Press. New York.1977; 56-108.
22 Terrence T, John F, Shoichi K, Darryl J, Stephen A, Philip C. Chemical safety of drinking water: Assessing priorities for risk management. World Health Organ. Geneva. 2007.