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HEAVY METALS IN DRINKING-WATER SOURCES OF SOME VILLAGES OF ARMENIA

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People who use contaminated drinking water, have a significant number of serious health problems closely related to chemical contaminants, especially to high concentration of heavy metals. These kind of waterborne diseases occur mainly due to the ability of heavy metals to cause adverse health effects after prolonged periods of exposure. In Armenia thousands people of rural areas regularly drink water with unsafe levels of chemical contaminants. For this propose, in the first time heavy metals' content in drinking-water source of Aragac, Ara, Vardenut, Tsakhashen and Nigavan villages at Aragats mountain's south-east foothills in Armenia was determined. The source for drinking water of villages is snow-melt water from the mixing surface runoff, which form catchment system at 2200 m down top of Aragats Mountain. One of the major inflows to drinking-water catchment described as acidic environment with a yellow-brick color. In our studies was shown, that drinking-water of a major source of Aragats village contained extremely high concentration of manganese, zinc and nickel. High concentration of these metals can develop the chronic diseases in population, such as manganese increase urolithiasis, nickel cause various forms of malformations in the offspring and increase the body's sensitivity to allergic pathogens and so on.

Keywords: Drinking water, Heavy metals, Toxic chemicals, Health.

Introduction

According to the World Health Organization (WHO) the 80% of worldwide human diseases are result of low quality and unhygienic-handled drinking and bathing water used by people [1]. In the risk group for waterborne diseases are included infants, children, people with poor immunity or who are living in unsanitary conditions, also older people. The vast majority of obvious health problems, associated with drinking-water, are result of microbiological (bacteriological, viral, protozoan or other biological) contamination. Nevertheless, a significant number of serious health problems closely related to chemical contaminants in drinking-water [1-5].

The diseases related to chemical contaminants in drinking-water are considerably different from diseases caused by microbial contamination. They occur mainly due to the ability of chemical pollutants to cause adverse health effects after prolonged periods of exposure [1-3]. Specific affection the human body linking to chemical contaminants of drinking-water was established for many substances, such as fluoride (caries, fluorosis), nitrates (methemoglobinemia), mercury (Minomata disease), etc [1, 3]. The exceeding amounts of heavy metals in drinking-water are affecting to various organs and systems (especially, the central, peripheral, cardio vascular) [5-8]: nickel and chromium can cause various forms of malformations in the offspring and increase the body's sensitivity to allergic pathogens;

cadmium, arsenic, chromium (also radionuclides) being to appearance of malignant tumors; high concentrations of manganese in drinking-water leads to increase urolithiasis. In most cases, excess or shortage of such chemicals in drinking-water affect as a non-specific factor, which will cause to develop certain diseases [3].

In order to identify health risk by water-related diseases, it is necessary to investigate definitively the hydrochemical (in some cases also microbiological) content of drinking-water source and also find out causes of possible changes its quality.

In Armenia thousands people of rural areas are exposed to unsafe levels of chemical contaminants in their drinking-water. It is more obviously in the area, which population drinks water from surface sources or homemade wells. The statistics shown in that case, the 90% of that areas' population regularly use contaminated water for drinking and bathing [9].

The main aim of our research is to investigate heavy metals content in some water source for drinking of Armenian villages, especially for Aragac, Ara, Vardenut, Tsaxkashen, Nigavan villages at Aragats mountain's south-east foothills.

Description of the location

Our research was implemented for small (about 360-700 people) and relatively large (about 1700-3000 people) villages, which are located at south-east of Aragats mountain's foothills. The population of small villages of this region drinks water from homemade well without any treatment and disinfection. In these villages there are no any water supply systems. Therefore, it was not have water treatment plant. Moreover, water level in wells usually is dropped in summer and people are forced to drink water from irrigation system.

The drinking water source of the relatively large villages of this region (about 1700-3000 person) is the catchment in which collected the runoffs of snow-melt water at 2200 m down top of Aragats Mountain. These runoffs are the parts of Gexarot River's streams system and they flow through the manganin and iron ores [10]. The two of these snow-melt runoffs are the major and they define hydrochemical regime of drinking water source (they are forming the catchment). These villages have the piped distribution systems, but do not have water treatment plant. The drinking water is disinfected with calcium hypochlorite. The sanitary protection zone of catchment, in the best case, is served only ones during a year or two years, because of barely passable mountain location.

METHODS

Water Sampling. The drinking water sampling was implemented by ISO 5667-1:2006 and ISO 5667-5:2006 international standards [11].

The water samples were taken in 5 snow-melt runoffs, in the homemade well and in the distribution system. The sampling points are following (Figure 1):

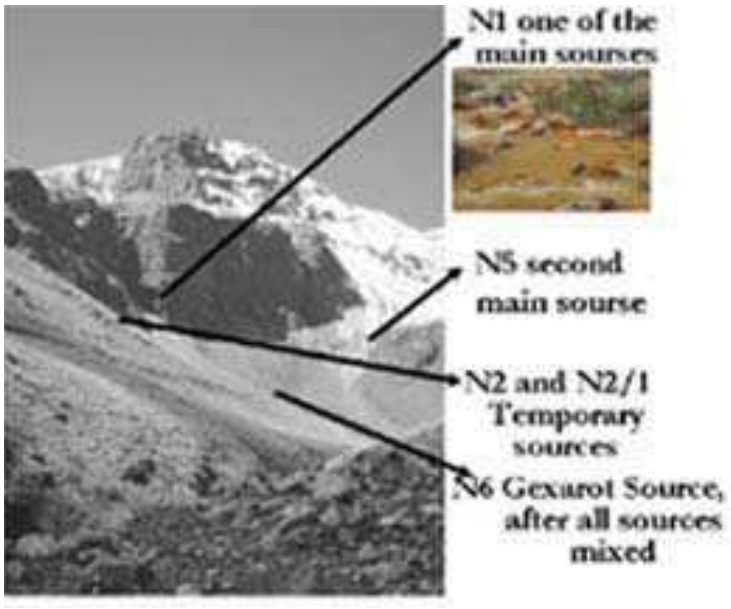

Figure 1. *Location of sampling points of N1, 2, 2-1, 5, 6 drinking-water sources at south-east of Aragats mountain.*

N1- the first snow-melt runoff, which forms at high above 2700m inside mountain's top. Water in this runoff has yellow-brick color and low temperature (+4-0^{O}C) independent of season. This runoff is the one of major inflow to catchment.

N2- located the near of N1 runoff. It has low water flow and disappears in summer. Water in this runoff has a high transparency, and has higher temperature than N1 runoff (water temperature depends of season).

N2-1- located the near of N1 and N2 runoffs. It is a drainage system of low inflows into pipe.

N3- at the beginning of distribution system: water pipe in the nearest house after and Daily Regulated Reservoir.

N4- the homemade well in Nigavan village. The water was sampled from is point only ones in June 2011. The water has a high transparency and middle temperature (+12^{O}C).

N5- the second snow-melt runoff, which forms at high above 2650m inside mountain's north top. Water in this runoff has not any color and the temperature depends on season. This runoff the people called «Qaxcr Jur» («Sweat water»).

N6- Gexarot source, after mixing all runoffs.

The N1, N2, N2-1 and N5 runoffs form the drinking water for Aragac, Ara, Vardenut, Tsaxkashen villages, and N4 froms – for Nigavan.

The expeditions were implemented in June, July, October 2011 and June, July, November 2012.

Water samples conservation and analysis. In water samples were measured temperature, pH and heavy metals.

The heavy metals determination in water samples was done by ISO 17294-1:2004 standard [11]. Before analysis, all water samples were conserved by concentrated 1N nitric acid and 1ml indium solutions in situ. Then, the water samples were transferred to laboratory for analysis [11]. Heavy metals' content in water samples were determined by Perkin Elmer Elan 9000 ICP-mass spectrometer with argon plasma [11]. All standard solutions of metals for instrumental calibration were brand of Fisher ChemAlert, US. A number of blanks was prepared for

minimization of contaminate errors. In water samples were determined Ti, V, Cr, Al, Fe, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Ag, Cd, Sn, Sb, Ba, Pb, Bi, U metals.

RESULTS AND DISCUSSION

The data are listed in Tables 1, 2, 3 that contain pH values and concentration of heavy metals in ppm, samples locations, different patients and WHO and Armenian national recommended concentration limits for drinking water [1, 12].

The chemical analysis of water samples of drinking-water sources was shown that heavy metals concentrations had different changes. According our results we defined the heavy metals into 3 groups. In first group were involved Se, Mo, Ag, Cd, Sn, Sb, Pb, Bi, U, which concentrations during study did not change significantly, and were under 0,1 ppb. The heavy metals content was low in all sources during whole study.

In the second group were involved Ti, V, Cr, Sr, Ba. These metals concentrations were relatively increased during study period, especially in N1, N2, N2-1 and N6 (after all runoffs mixing point). The highest concentrations of these metals was observed in October 2011, when their were increased comparing with June 2011 for Ti about 2,5 times, for V – about 1,9 times, for Cr – 10,1 about times (Table 2). The most increasing of metals content was observed in N1 source, which water pH was acidic environment (< 4 pH) (Table 1). The high content of these metals till be high on Gexarot Source, after all drinking-water sources mixed together, as shown the N6 sampling points data.

The 3rd group was include the metals, which concentration were much more stable and has little increase in the drinking-water sources at south-east of Aragats mountain, except on first spring (N1) and on the all springs mixing point – Gexarot Source (N6). These heavy metals are Fe, Mn, Co, Ni, Cu, Zn, As (Table 3). The analysis data of water samples compared with each other, shows that huge amount of toxic elements was observed in N1 drinking water source in October 2011. In that period the content of heavy metals rised by several decades comparing with data in June 2011, and by several hundreds - with data in July 2011. The concentration of Fe, Ni and Mn were rised on 159,8-264,0 times, Zn and Co – on 304,4 -307,0 times, Cu and As – on 43,7 – 47,0 times. The higher concentration of toxic metals also observed on Gexarot Source in November 2011. The concentration of these metals in water samples of Gexarot Source was rised 16,1-28,9 times in November 2012 comparing with June 2011.

Table 1. pH values of water samples of drinking-water sources.

Parameter	Date/ Sampling points	Jun 2011	Jul 2011	Oct 2011	Jun 2012	Jul 2012	Nov 2012
pH (standard limit 6-9)	N1	-	4,10	3,10	-	-	-
	N2	-	6,80	5,90	-	-	-
	N2-1	-	6,80	6,30	-	-	-
	N5	-	-	6,40	-	-	-
	N6	7,40	7,60	3,76	5,26	8,15	4,32

Table 2. 2nd group heavy metals' concentration (ppm) in drinking-water sources.

Parameter	Date/ Sampling points	Jun 2011	Jul 2011	Oct 2011	Jun 2012	Jul 2012	Nov 2012
Ti (standard limit not defined)	N1	0,0013	0,0124	0,0077	-	-	-
	N2	0,0052	0,0121	0,0082	-	-	-
	N2-1	-	0,0155	0,0181	-	-	-
	N3	0,0026	-	-	-	-	-
	N4	0,0023	-	-	-	-	-
	N5	-	-	0,0064	-	-	-
	N6	0,0047	0,0031	0,0058	0,0034	0,0007	0,0033
V (standard limit 0,1 ppm)	N1	0,0001	0,0062	0,0030	-	-	-
	N2	0,0035	0,0063	0,0061	-	-	-
	N2-1	-	0,0064	0,0062	-	-	-
	N3	0,0017	-	-	-	-	-
	N4	0,0015	-	-	-	-	-
	N5	-	-	0,0039	-	-	-
	N6	0,0006	0,0004	0,0018	0,0009	0,0000	0,0011
Cr (standard limit 0,5ppm)	N1	0,0005	0,0010	0,0090	-	-	-
	N2	0,0003	0,0008	0,0014	-	-	-
	N2-1	-	0,0007	0,0013	-	-	-
	N3	0,0005	-	-	-	-	-
	N4	0,0004	-	-	-	-	-
	N5	-	-	0,0005	-	-	-
	N6	0,0004	0,0009	0,0064	0,0018	0,0003	0,0054
Sr (standard limit 7ppm)	N1	0,0598	0,0247	0,0247	-	-	-
	N2	0,0154	0,0245	0,0245	-	-	-
	N2-1	-	0,0249	0,0249	-	-	-

	N3	0,0318	-	-	-	-	-
	N4	0,0687	-	-	-	-	-
	N5	-	-	-	-	-	-
	N6	0,0335	0,0494	0,1516	0,0449	0,0589	*
Ba (standard limit 0,7ppm)	N1	0,0056	0,0032	0,0144	-	-	-
	N2	0,0031	0,0032	0,0144	-	-	-
	N2-1	-	0,0036	0,0077	-	-	-
	N3	0,0054	-	-	-	-	-
	N4	0,0075	-	-	-	-	-
	N5	-	-	0,0187	-	-	-
	N6	0,0046	0,0032	0,0109	0,0056	0,0074	0,0117

Table 3. 3th group heavy metals' concentration (ppm) in drinking-water sources.

Parameter	Date/ Sampling points	Jun 2011	Jul 2011	Oct 2011	Jun 2012	Jul 2012	Nov 2012
Fe (standard limit 0,3ppm)	N1	1,6568	0,0775	19,7902	-	-	-
	N2	0,0332	0,0487	0,0802	-	-	-
	N2-1	-	0,1043	0,1749	-	-	-
	N3	0,0148	-	-	-	-	-
	N4	0,0589	-	-	-	-	-
	N5	-	-	0,0026	-	-	-
	N6	0,1033	0,0034	1,6233	0,8571	0,0547	2,6599
Mn (standard limit 0,1ppm)	N1	0,3563	0,0103	2,7225	-	-	-
	N2	0,0019	0,0026	0,0024	-	-	-
	N2-1	-	0,0050	0,0076	-	-	-
	N3	0,0007	-	-	-	-	-
	N4	0,0004	-	-	-	-	-
	N5	-	-	0,0010	-	-	-

	N6	0,1262	0,0454	1,4020	0,2190	0,0260	3,6421
Co (standard limit 0,1ppm)	N1	0,0074	0,0002	0,0614	-	-	-
	N2	0,0001	0,0001	0,0001	-	-	-
	N2-1	-	0,0001	0,0001	-	-	-
	N3	0,0000	-	-	-	-	-
	N4	0,0001	-	-	-	-	-
	N5	-	-	0,0001	-	-	-
	N6	0,0017	0,0003	0,0245	0,0033	0,0001	0,0319
Ni (standard limit 0,1ppm)	N1	0,0182	0,0009	0,1438	-	-	-
	N2	0,0004	0,0006	0,0001	-	-	-
	N2-1	-	0,0006	0,0001	-	-	-
	N3	0,0005	-	-	-	-	-
	N4	0,0004	-	-	-	-	-
	N5	-	-	0,0000	-	-	-
	N6	0,0045	0,0020	0,0678	0,0095	0,0022	0,0794
Cu (standard limit 1,0ppm)	N1	0,0046	0,0006	0,0262	-	-	-
	N2	0,0003	0,0005	0,0008	-	-	-
	N2-1	-	0,0005	0,0005	-	-	-
	N3	0,0002	-	-	-	-	-
	N4	0,0009	-	-	-	-	-
	N5	-	-	0,0002	-	-	-
	N6	0,0008	0,0004	0,0117	0,0022	0,0004	0,0129
Zn (standard limit 3,0ppm)	N1	0,1373	0,0027	0,8219	-	-	-
	N2	0,0001	0,0004	0,0012	-	-	-
	N2-1	-	0,0006	0,0008	-	-	-
	N3	0,0038	-	-	-	-	-
	N4	0,0069	-	-	-	-	-
	N5	-	-	0,0001	-	-	-
	N6	0,0279	0,0202	0,5017	0,0796	0,0195	0,6448

As (standard limit 0,05ppm)	N1	0,0159	0,0024	0,1128	-	-	-
	N2	0,0003	0,0005	0,0005	-	-	-
	N2-1	-	0,0008	0,0008	-	-	-
	N3	0,0005	-	-	-	-	-
	N4	0,0005	-	-	-	-	-
	N5	-	-	0,0002	-	-	-
	N6	0,0040	0,0020	0,0049	0,0107	0,0020	0,0032

These metals in the drinking water sources may occur naturally or may be the result of contamination. Naturally occurring metals are dissolved in water when it comes into contact with rock or soil material. The drinking-water source (melting-waters) of large and small villages at Aragats mountain's south-east foothills are flowing through the manganin ores, also in this region there are many acidic mineral water, which can mixing with drinking-water sources and decreasing the water pH. The low pH of water promote to dissolve metals into water, and to increase their content.

Trace amounts of metals are common in water, and these are normally not harmful to our health. In fact, some metals are essential to sustain life. Cobalt, copper, iron, manganese, molybdenum, selenium and zinc are needed at low levels as catalysis for enzyme activities. Drinking water containing high levels of these essential metals, or toxic metals such as arsenic, barium, cadmium, chromium, lead, selenium and silver, may be hazardous to our health.

Almost all the metals concentration fell within their standards limit (according by WHO [1]), which varied from 0,06 ppm to 0,0001 ppm from all areas except water samples from N1 source with very high concentration of iron and manganese. In the water samples of this source the concentrations of iron and manganese were 3-4 times (in autumn 70 times for iron and 27 times for manganese) more than their standards limit. These metals concentration still were high also in Gexarot Source water, after all runoffs mixing. After dilution by water of other sources, the metals content in autumn season still were more than their standards limit in 5-9 times for iron and 14 times for manganese.

One of the major symptoms of chemical toxicity seems to be a breakdown of the immune system, which opens the gateway for all kinds of diseases in the body. Also, another major symptom seems to be damage to the nervous system and increased nervousness.

Toxic doses of chemicals cause either acute or chronic health effects. The levels of chemicals in drinking water, however, are seldom high enough to cause acute health effects. They are more likely to cause chronic health effects that occur after long exposure to small amounts of a chemical. Examples of chronic health effects include cancer, birth defects, organ damage, disorders of the nervous system, and damage to the immune system. Pb, Zn, Cu, Mn, Co, Ni, Cd, Cr and Mo are toxigenic and carcinogenic agents consistently found as contaminants in human drinking water supplies in many areas around the world.

This study shows that people of large and small villages at Aragats mountain's south-east have to use for drinking the water with high concentrations of heavy metals, such as manganese, iron, arsenic, zinc, nickel and so on. Because of poor state of water distribution system and the lack of water treatment plants of drinking water source of these villages, it was not able to protect population from toxicity impact on these metals into population’s health. High

concentration of these metals can develop the chronic diseases, such as manganese increase urolithiasis and increase the body's sensitivity to allergic pathogens, nickel cause various forms of malformations in the offspring, very high concentrations of iron caused the accumulation of stones in different organs of human organism.

CONCLUSION

In our studies were shown, that drinking-water of a major source of Aragats, Ara, Vardenut, Tsakhashen villages contained high concentration of iron, manganese, zinc and nickel. The drinking-water source (melting-waters) of those villages are flowing through the manganin ores and neighborhoods with several acidic mineral water, which mixing within each other caused decreasing drinking water source pH value and rising the heavy metals dilution. Taking into account the lack of water treatment system, therefore people of this region have to drink water with high concentrations of heavy metals, such as manganese, iron, nickel and etc. High concentration of these metals breakdown of the immune system of human and opens the gateway for all kinds of diseases in the body. The high content of these toxic metals cause chronic health effects that occur after long exposure to small amounts of a chemical.

We suggest to completely abandoning to distribute water from N1 spring or reconstruct exist water distribution system with using special water filters for decreasing heavy metals concentrations from N1 source. This is very important for preventing health risk in population.

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