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Distribution of the total arsenic content in drinking water obtained from different water sources in the Republic of Macedonia

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Abstract: The present study investigates the total arsenic (As) content in the samples of drinking water in the Republic of Macedonia, which is obtained from different water sources, such as: springs, surface accumulations, underground accumulations and drilled wells. From January 2013 to December 2013, a total of 780 samples obtained from the public water supply systems at 35 measurement points distributed throughout the whole territory of the Republic of Macedonia were analyzed on the total As content. A flow injection atomic absorption spectrometry (FIAS) was employed for the determination of the total As content after wet digestion of the samples with nitric acid (67%, W/V) and hydrogen peroxide (30%, V/V). The results of the study revealed that in 96.7% of the tested samples, As content was below established maximum allowable concentration (MAC) of 10 µg/L. As concentrations up to 26.4 µg/L were found in the samples of drinking water that comes from the water sources located in the vicinity of Kozhuf Mountain, which is due to the mineral composition of the mountain body rich with As containing minerals: lorandite, orpiment, realgar, arsenopyrite etc. Higher As concentrations (5.47 µg/L – 26.6 µg/L) were also found in the samples of drinking water obtained from the water supply system of the towns from the Dojran Municipality which are located in the vicinity of thermal-mineral area of Mala Boshka – Toplec. It can be concluded that the presence of total As in the potable water in the Republic of Macedonia comes only from natural sources.

Keywords: Arsenic (As), Drinking Water, Flow Injection Atomic Absorption Spectrometry (FIAS), Maximum Allowable Concentration (MAC)

1. Introduction

Arsenic (As) is a naturally occurring toxicant of global concern. As is a an element found in the atmosphere, soils and rocks, natural waters and organisms. It is mobilised in the environment through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions, as well as, through a range of anthropogenic activities. Most environmental arsenic problems are result of mobilisation under natural conditions, but man has had an important impact through mining activity, combustion of fossil fuels, the use of arsenical pesticides, herbicides and crop desiccants etc [1].

Many epidemiological studies have demonstrated that chronic exposure to As is associated with increased cardiovascular disease, hypertension, respiratory problems, diabetes mellitus, gastrointestinal effect, and nervous system disorders [2, 3]. It includes several kinds of skin lesions and cancers, such as hyper-pigmentation, hyperkeratosis, gangrene, skin cancer, lung cancer and bladder cancer. From the various sources of As in the environment, drinking water probably possesses the greatest threat to human health. Long-term consumption of drinking water with elevated As concentrations can cause development of arsenicosis, the commonly used term for diseases caused by chronic exposure to As. It includes several kinds of skin lesions and cancers, like hyper-pigmentation, hyperkeratosis, gangrene, skin cancer, lung cancer and bladder cancer [2]. Drinking water is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rain water. These sources are very variable in terms of As risk. Besides the obvious point sources of As contamination, high concentrations are mainly found in ground waters.

As contamination of groundwater has been found to occur due to geothermal influenced groundwater, mineral dissolution (e.g., pyrite oxidation), desorption in the oxidising environment, and reductive desorption and dissolution [4,5].

Over the past two or three decades, occurrence of high concentrations of As in the drinking-water has been recognized as a major public-health concern in several parts of the world. The World Health Organization estimated in 2001 that about 130 million people worldwide are exposed to As concentrations over 50 µg/L. According to the United Nations Synthesis report, As poisoning is the second most important health hazard related to drinking water [6.]. Therefore, assurance of safe drinking water is one of the Millennium Development Goals for public health It is suggested by the World Health Organization (WHO) that the As level in drinking water should not be over 10 µg/L [7].

The Republic of Macedonia is considered as a Country which is rich with waters, both underground and surface. The underground waters include: artesian, sub-artesian, well waters and springs. The surface waters cover 1.88 % of the territory (188 m^2/ha). There are about 35 rivers, and 53 natural and artificial lakes. After undergoing the suitable technological treatment, the most of the underground and surface waters are used for production of drinking water, which is distributed through the water supply systems.

The aim of this study is determination of the total As content in drinking water in the Republic of Macedonia that comes from different water sources (lakes, rivers, springs, drilled wells, underground accumulations, etc.).

2. Materials and Methods

2.1. Study Area

The Republic of Macedonia is a country situated in southeastern Europe with geographic coordinates 41°50′N 22°00′E, Kosovo and Serbia border countries on the north, Bulgaria on the east, Greece on the south and Albania on the west. Macedonian basement consists of five major tectonic units from west to east: The Chukali-Krasta zone, the Western Macedonian zone, the Pelagonian massif, the Vardar zone, and the Serbian and Macedonian massif (Fig. 1) [8].

In the Republic of Macedonia, there are numerous geological formations of heterogeneous petrographic - mineralogical composition The Mountains are composed of non-calcareous hard rocks, including quartzite, and various silicate rocks: acidic, neutral, basic and ultra basic rocks; as well as calcareous rocks such as pure limestone, marbles and dolomites. Basins are composed of loose and lightly cemented sediments, and a small quantity of young volcanic rocks [9].

Hydrographical conditions show an influence on soil genesis, properties and geography through surface flow (river system and erosion), floods and waterlogged lands, ground waters and irrigation. In hydrological sense the Republic of Macedonia is divided among the three water river basins of Adriatic sea (15% of the territory), with the main mouth, river Crni Drim, Aegean Sea (85% of the territory), with the rivers Vardar and Strumica, as the biggest water courses and Black Sea, its river basin has not a significant territory. Vardar is the biggest river with about 80% of the total water flow out from Macedonia. Larger right side tributaries of the Vardar River are the Crna River and the Treska River, while the longest left side tributaries are the Bregalnica River and the Pchinja River. In the Republic of Macedonia there are three natural lakes: the Ohrid Lake, the Prespa Lake and the Dojran Lake.

For the purpose of a denser network of points of measurement that shall reflect the As distribution in potable water obtained from water supply systems throughout the territory of the Republic of Macedonia more objectively, 35 cities and towns were suitably selected. The selected cities and town were located in the Chukali-Krasta zone (Debar), the Vardar zone (Skopje, Veles, Shtip, Radovish, Probishtip, Sveti Nikole, Gradsko, Kavadarci, Demir Kapija, Valandovo, Gevgelija, Bogdanci, Strumica); the Western Macedonian zone (Tetovo, Gostivar, Mavrovo, Kichevo, Makedonski Brod, Krushevo, Ohrid, Struga, Resen, Bitola); the Pelagonian massif (Prilep,) and Serbian-Macedonian massif (Kochani, Vinica, Pehchevo, Berovo, Delchevo, Kratovo, Makedonska Kamenica and Kriva Palanka (Fig. 2) Two of the selected towns (Star Dojran, Nov Dojran) are located on the border between the Vardar zone and the Serbian-Macedonian massif (Fig. 3).

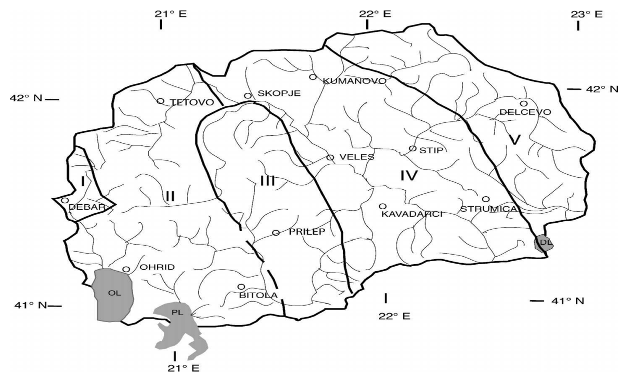

Figure 1. *Major tectonic units of Macedonia. I. Chukali-Krasta unit; II. Western Macedonian unit; III. Pelagonian massif; IV. Vardar zone; and V. Serbian - Macedonian massif. Lakes: DL— Dorjan Lake, OL—Ohrid Lake, and PL—Prespa Lake*

Figure 2. *Map showing sampling points on the whole territory of the Republic of Macedonia*

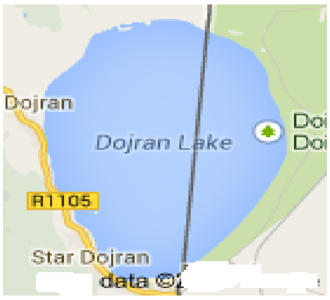

Figure 3. *Map showing sampling points in Dojran municipality*

2.2. Sampling

From January 2013 to December 2013, a total of 780 drinking water samples were taken from the public water supply systems. The samples were collected in polyethylene containers previously cleaned with HNO_3 (1+9) in compliance with ISO 5667-3 [10]. The samples were sealed and labeled with a unique sample code and placed in a potable refrigerator. These samples then were digested and analyzed (within the 24 hours from the time of the collection) for the total presence of As, according to the ISO 15586 [11].

2.3. Reagents

High pure grade reagents were used: nitric acid for trace analysis (67%, W/V) was obtained from Sigma - Aldrich, Germany; hydrogen peroxide (30%, W/V) for ultra trace analysis was obtained from Fluka, Germany; sodium borohydride (NaBH4) was obtained from Fluka, Germany, and NaOH for trace analysis was obtained from Merck, Germany. Water for the trace analysis was obtained from Sigma-Aldrich, Germany. High purity arsenic standard solution 1000 mg/L (prepared from As_2O_3 in 5 M HNO_3) was obtained from Merck, Germany. Palladium nitrate - magnesium nitrate matrix modifier solution containing 0.15% *(W/V)* $Pd(NO_3)_2$ and 0.10% *(W/V)* $Mg(NO_3)_2$ in 2% (W/V) HNO_3 were obtained from Specpure, USA.

As working standards were prepared from the stock standard solution by dilution with ultra pure water at the time of the analysis. A calibration curve was prepared with a calibration blank and five standards (0.1 µg/L, 1 µg/L, 5 µg/L, 10 µg/L, 50 µg/L). Nitric acid 67% (*W/V*) was added to the standard solutions to result in an acid concentration of 1% *(V/V)*.

2.4. Sample Preparation

100 mL of well-mixed water sample were transferred in a 250-mL Griffin beaker. 2 mL of 30% (*V/V*) hydrogen peroxide was added together with sufficient HNO_3 (67%, *W/V*) to result in an acid concentration of 1% (*V/V*). The solution was heated, until digestion was completed, at 95^0C or until the volume became slightly less than 50 mL. After cooling, the solution was transferred to a volumetric flask, and was supplemented up to 50 mL with ultra pure water. Aliquots of 20 µL of samples and 10 µL of the matrix modifier solution were used for all the determinations.

2.5. Instrumentation

The total arsenic determination was carried out using the FIAS technique (Perkin-Elmer atomic absorption spectrometer AAnalyst 600) equipped with a Zeeman background correction, FIAS-100 hydride generation system; graphite furnace and autosampler (Perkin-Elmer Corp., Norwalk, CT, USA). Hydride generation was performed using a 3% (*W/V*) $NaBH_4$ in 1% (*W/V*) NaOH. In order to overcome the matrix effect, pyrolytically coated tubes with inserted L'vov platform were used. The radiation source was an electrodless discharge lamp of arsenic (Perkin-Elmer) used at a wavelength of 193.7 nm and a spectral slit width of 0.7 nm. Furnace conditions are given in Table 1.

Table 1. *Furnace conditions*

Step	Temperature (^{0}C)	Ramp time (s)	Hold time (s)	Internal flow (mL/min)	Gas type (argon)
1	110	1	20	250	Normal
2	120	5	50	250	Normal
3	130	5	50	250	Normal
3	1300	10	5	250	Normal
4	2500	0	5	0	Normal
6	2600	1	2	250	Normal

2.6. Statistical Analysis

Statistical analysis was performed using Origin software package version 7.0. The statistical significance of the difference between the data pairs As content was evaluated by analysis of variance (ANOVA) followed by the Tukey's honest significance test. Statistical differences were considered significant at $p < 0.05$.

3. Results and Discussion

Sixteen cities and towns in which there are water facilities that draw out water from natural springs were included in the 2013 study. The obtained results for total As content in drinking water (minimum and maximum value), as well as statistical data (median value, standard deviation – SD) are shown in Table 2.

Table 2. *Results for the total arsenic content in drinking water from supply systems that draw out water from the springs*

City/Town (number of samples)	Location in the Republic of Macedonia	Water origin	Type of water supply system	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Median (µg/L)	SD (µg/L)
Tetovo (15)	Northwest	Springs (Sharr Mountain)	Local	<0.1	0.30	0.178	0.220	0.098
Mavrovo (16)	Northwest	Springs (Bistra Mountain)	Local	0.45	2.99	1.064	0.940	0.568
Gostivar (20)	Northwest	Whirlpool "Vrutok"	Local	<0.1	0.82	0.371	0.440	0.240
Debar (20)	Central west	Springs (Rosoki Mountains)	Local	0.18	0.56	0.324	0.315	0.098
Kichevo (30)	Central west	Springs (Bistra Mountain)	Regional "Studenčica"	0.53	2.89	1.585	1.59	0.457
Makedonski Brod (20)	Central west	Springs (Bistra Mountain)	Regional "Studenčica"	0.65	2.69	1.873	1.90	0.390
Krushevo (15)	Southwest	Springs (Bistra Mountain)	Regional "Studenčica"	0.15	0.772	0.281	0.25	0.143
Prilep (20)	Southwest	Springs (Bistra Mountain)	Regional "Studenčica"	0.70	2.46	0.991	0.90	0.365
Resen (15)	Southwest	Springs (Galičica Mountain)	Local	0.18	0.34	0.236	0.230	0.045
Struga (15)	Southwest	Spring "Shum" (Jablanica Mountain)	Local	0.10	0.58	0.308	0.310	0.125
Ohrid (30)	Southwest	Springs: "Biljanini izvori; "Letnica"	Local	0.66	1.62	1.122	1.15	0.211
Makedonska Kamenica (15)	Northeast	Spring in the valley near Kamenichka River	Local	0.55	2.17	1.084	1.05	0.392
Kriva Palanka (20)	Northeast	Springs "Kalin Kamen" (Osogovo Mountain)	Local	0.97	7.98	2.361	2.09	1.384
Pehchevo (15)	Central east	Springs (Bukovik Mountain)	Local	0.84	2.60	1.585	1.55	0.415
Kavadarci (35)	South central	Water intakes from the springs (Kozuf Mountain)	Local	2.54	9.54	7.196	7.15	1.61
Valandovo (15)	Southeast	Springs in the valley near the Anska River	Local	0.34	1.12	0.636	0.57	0.249

Tetovo and Gostivar are towns located in the northwest on the foothills of one of the most important mountains in the region the Sharr Mountains. The Mountain massif was formed in the Tertiary Period [12]. The water supply system of Tetovo draws water out from the springs situated in the mountain. The upper parts of the mountain have been frozen with large amounts of ice and snow. The analysis of drinking water from the public water supply system showed low concentrations of As ranging from less the limit of quantification (LOQ) of 0.1 µg/L to 0.3 µg/L. The water supply system of Gostivar draws water out from the whirlpool "Vrutok", where the Vardar River springs are located, situated at an altitude of 683 meters from the base of the Sharr Mountains (Fig. 4). The concentrations of As in tested drinking water samples was found to be bellow 1 µg/L.

The regional water supply system "Studenchica" is a capital facility in the country, which occupies springs of the River Studenchica at an altitude of 965 m above the sea level (Fig. 5). The springs of the River Studenchica are located at the eastern side of mountain range Bistra, which is situated in the central part of the Western Macedonia. Bistra Mountain has complex geotectonic structure. In the lower part appears the old Paleozoic shale, and the highest part is covered with limestone, the thickness of it is 400 m. The clear limestone had allowed intensive karstification and appearance of almost all surface and underground karst forms [12]. The drinking water from the regional water supply system "Studenchica" was subject of testing at four intentionally selected sample points (Kichevo, Makedonski Brod, Krushevo, and Prilep). For that purpose a total of 85 samples of drinking water were tested on the presence of total As. The obtained results showed low concentrations of total As in the water, ranging from 0.15 μg/L (Krushevo) to 2.89 μg/L (Kichevo). Mavrovo, which is located in the northwest, in the vicinity of the mountain Bistra is not connected with the regional water supply system "Studenchica". There is a local water supply system that draws water out from the springs located high in the Bistra Mountain. The concentrations of As in the tested samples of drinking water were found to be also low (0.45 μg/L – 2.99 μg/L).

Debar is a city in the western part of the Republic of Macedonia, near the Albanian border. The water supply system of Debar draws water out from the water intakes from the springs situated high in the Rosoki Mountain, which is located within the boundaries of the National Park Mavrovo. The concentrations of As in the tested water samples were found to be low (0.18 μg/L – 0.56 μg/L).

Resen, Struga, Bitola and Ohrid are cities in south-west Macedonia. Resen is approximately equidistant between Bitola and Ohrid. The town is 880 m above sea level and is situated near the Prespa Lake. The water supply system draws water out from the water intakes from the springs in the Galichica Mountain. The basic geological foundation of Galichica Mountain is mainly from the Paleozoic silicates covered with a layer of spongy massif limestone thickness of 500 m - 550 m. This geological structure and the presence of the karst geomorphology, gives the appearance of the of the Dinaric Mountains system. The porosity of the limestone layer makes the Galichica Mountain as one of the driest mountains in the Republic of Macedonia with only few permanent very low yield sources. The concentrations of total As in the drinking water from the water supply system in Resen were found to be very low, ranging from 0.18 μg/L to 0.34 μg/L, which is mainly due to the As poor bedrock litology. Unlike the mountainous part, the costal area is rich with water resources. At the northeast slope of the Galichica Mountain several karst springs "Letnica" are located. They are used for the water supply of Ohrid. At the foothills of the Galichica Mountain, the springs "Biljanini izvori" are also used as an additional source for the water supply of the City. The results of our investigations showed low As concentrations (0.66 μg/L – 1.62 μg/L) in tested samples of drinking water from the water supply system of the city. Low concentrations of As (0.1 μg/L – 0.58 μg/L) were also found in the samples of drinking water from the water supply system of Struga. The origin of the water is from the karst spring Shum situated in the foothills of the Jablanica Mountain. Jablanica is a mountain in south western Macedonia, situated between Ohrid – Struga and Debar Valley. One part of the mountain belongs to Albania.

Makedonska Kamenica and Kriva Palanka are the towns situated in the north east part of the Republic of Macedonia, at the foothills of the Osogovo Mountain. The water supply system draws water out from the springs near the Kamenichka River, which is located near the iron and zinc ore Mine Sasa. Contrary to the initial expectations for the increased As concentrations in the drinking water due to the mining activities and the deposits of the tailings dam near the river [13], the results for the total As concentration in the drinking water were found to be low ranging from 0.55 μg/L to 2.17 μg/L. This is due to the good sanitation system, applied for water purification in 2011.

The water supply system of Kriva Palanka draws water out from the springs situated in the Osogovo Mountain. The mountain consists of volcanic and volcano – intrusive rocks and represents a metallogenic zone. Quartz graphite schist is the most important host rocks for the lead – zinc mineralization. The concentrations of total As in the samples of drinking water obtained from the city water supply system were within the range 0.97 μg/L – 7.98 μg/L. The obtained values were below MAC, but higher then those found in the drinking water from the previously described water supply systems. This is due to the metallogenic composition of the mountain body which includes the presence of arsenic impurities in the ores [14].

Pehchevo is a town situated at the eastern part of the Republic of Macedonia at the altitude of 1000 m. The water supply system draws water out from the springs of the Bukovik Mountain, rich with iron ore. The total arsenic content in the samples of drinking water are within the range from 0.84 μg/L to 2.6 μg/L.

Kavadarci is situated in the south - central part of the Republic of Macedonia. The local water supply system draws water out from the water intakes from the Kozhuf Mountain. As concentrations in the samples of drinking water ranged from 2.54 μg/L to 9.54 μg/L. The higher concentrations of As in the samples of drinking water are in connection with the mineral composition of the Kozhuf Mountain. Namely, the ore bodies of the mountain consist of a large number of As containing minerals as: lorandite ($TlAsS_2$), orpiment (As_2S_3), realgar (As_4S_4); arsenopyrite (FeAsS), etc. [15,16].

Valandovo is a town located in the southeast part of the country. The local water supply system draws water out from the springs situated in the valley near the Anska River which is a left side tributary of the Vardar River. The concentrations of As in all the tested samples of drinking water were below the MAC, ranging from 0.34 μg/L to 1.12 μg/L.

At the 0.05 level of significance, the analysis of variance revealed that the population means for total As content showed a significant difference between the analyzed samples of drinking water obtained from the water supply system of Kavadarci and of all the other cities and towns that draw out water from the springs ($p<0.05$). This is due to the composition of the body of the Kozhuf Mountain, which consists of a large number of As containing minerals. Maximum concentration of total As that was determined in the potable water was close to MAC. This implies that an additional purification step of the potable water should be included.

The results of the determination of total As in the potable water of the cities and towns that draw out water from the springs except those ones in the town of Kavadarci, showed low level of As ranging from less than LOQ for Tetovo and Gostivar to 7.98 µg/L for Kriva Palanka. The presence of low level of total As in drinking water in the most of the cities and towns is a result of a As-poor karstic limestone composition of the water springs terrain. These findings are in line with those of Seyler and Martin [17]. Namely, they found As concentrations of 0.13 µg/L in the water in the Krka region of Yugoslavia obtained from springs where the bedrock is As-poor karstic limestone.

The results of the content of total As in the drinking water obtained from water supply systems that draw out water from the surface accumulations are shown in Table 3.

Table 3. *Results for the total arsenic content in drinking water from supply systems that draw out water from the surface accumulations*

City/Town (number of samples)	Location in the Republic of Macedonia	Water origin	Type of water supply system	Minimum (µg/L)	Maximum (µg/L)	Mean (µg/L)	Median (µg/L)	SD (µg/L)
Kumanovo (45)	Northeast	Lipkovo Lake (accumulation)	Local	0.95	8.35	1.855	1.75	1.059
Kratovo (22)	Northeast	Zletovica River	Regional “Zletovica”	0.55	1.95	0.852	0.765	0.294
Sveti Nikole (20)	Northeast	Zletovica River	Regional “Zletovica”	0.95	2.05	1.579	1.58	0.263
Probištip (15)	Northeast	Zletovica River	Regional “Zletovica”	0.22	0.57	0.393	0.38	0.101
Delčevo (15)	Northeast	Water intakes from Loshana River	Local	0.25	0.75	0.399	0.350	0.152
Veles (36)	Central	Water intakes from Topolka River	Local	0.78	4.37	1.299	1.175	0.599
Berovo (15)	Central east	Berovsko Lake (accumulation)	Local	0.27	1.3	0.71	0.68	0.227
Radovish (20)	Southeast	Radovishka River	Local	1.25	2.61	2.174	2.195	0.305
Strumica (21)	Southeast	Turija River (accumulation)	Local	0.25	13.62	3.048	2.65	2.512
Demir Hisar (20)	Southwest	Water intakes from Crna River	Local	0.86	8.15	3.39	3.22	2.98
Bitola (35)	Southwest	Surface accumulation from Shemnica River	Regional “Strezhevo”	0.45	2.08	0.754	0.67	0.298

Kumanovo is a city situated at the northeast part of the Republic of Macedonia. The water supply system draws water out from the Lipkovo accumulation, which is an artificial lake situated at an altitude of 478 m in the catchment area of the Lipkovska River, the right side tributary of the Pchinja River. After the treatment, the water from the reservoir is distributed into the water supply system of the City. The concentrations of the total As in the drinking water obtained from the water supply system were within the range from 0.95 µg/L to 8.35 µg/L. The higher concentrations of As in the drinking water (8.35 µg/L) were obtained in the summer period, when the additional water supply sources as drilled boreholes located in the Proevce district rich with thermal- mineral water were included.

The water supply of the Kratovo, Probishtip and Sveti Nikole is carried out through the hydro system “Zletovica”, which is situated in the northeast part of the Country. The hydro system “Zletovica” consists of the accumulation of the rivers in the catchment area of the Zletovska River, which is the right side tributary of the Bregalnica River. The Zletovska River springs from the Osogovo Mountain at an altitude of 1700 m. The concentration of total As in the samples of drinking water was found to be low, ranging from 0.22 µg/L (Probištip) to 2.05 µg/L (Sveti Nikole).

Delchevo is situated in the tectonic valley in the upper course of the Bregalnica River near the border with Bulgaria. The local water supply system draws water out from the water intakes of the Loshana River, the left side tributary of the Bregalnica River. The concentrations of total As in the tested samples of drinking water were found to be very low, ranging from 0.25 µg/L to 0.75 µg/L.

Veles is a city in the central part of the Republic of Macedonia. The local water supply system draws water out from the water accumulation intake of the Topolka River, the right side tributary of the Vardar River. The Topolka River is a river that springs from the Jakupica Mountain, which belongs to the Sharr Mountainous Massif. The concentrations of the As in the samples of drinking water from the water supply system were found to be below MAC, ranging from 0.78 µg/L – 4.37 µg/L.

Berovo is situated in the eastern part of the Republic of Macedonia. The water supply system draws out water from the Berovo Lake artificial accumulation. The lake is situated in the Maleshevo Mountain at the altitude of approximately 1000 m. Maleshevo Mountain is a part of the Osogovo – Belasica Mountain range. The results of our investigations showed low As concentrations in tested samples of drinking water ranging from 0.27 μg/L to 1.3 μg/L.

Radovish is a town situated in the southeast of the country in the upper catchment area of the Radovishka River at the altitude of 380 m. The Buchim-Damjan-Borov Dol ore district is situated 15 km on the north-west from the City. This district has been defined as an individual metallogenic unit which is directly related to the Tertiary intermediary calc-alkaline magmatism. The endogen mineralization of iron, copper, gold, lead – zinc is related to the volcanogenic intrusive formations. In the most time of the year, the water supply system draws water out from the water intake of the Radovishka River, a tributary of the Strumica River. In the summer period an additional water sources as drilled boreholes are included in the water supply of the City. The concentration of As in the samples of drinking water ranged from 1.25 μg/L to 2.61 μg/L.

Demir Hisar is situated in the southwest part of the Country in the region of the Bigla Mountain, which is rich with iron ore. The local water supply system draws water out from the water intake of the Crna River, major right side tributary of the Vardar River. The Crna River springs from the mountain at the altitude of 760 m. The concentration of As in drinking water was found to be between 0.86 μg/L to 8.15 μg/L.

Bitola is a city situated in the southwestern part of the Republic of Macedonia in the southern part of the Pellagonia valley, surrounded by Baba and Nidze mountains. The water supply system draws water out from the artificial accumulation “Strezhevo”, located in the middle part of the Shemnica River, a right side tributary of the Crna River. The Shemnica River springs from the Baba Mountain. The mountain consists of granite rocks and is the northward continuation of the Pelagonian basement [18]. The concentration of As in the drinking water of the water supply system in the City ranged from 0.45 μg/L to 2.08 μg/L.

The analysis of variance at the 0.05 level of significance revealed that the population means for total As content didn’t show significant difference in the samples of potable water obtained from the water supply systems of Strumica and Radovish (p=0,116). This is due to the fact that these cities belong to the same geo- tectonic valley in the vicinity of the Belasica Mountain. The mean value, as well as, the median value for total As concentration in the drinking water of Strumica and Radovish were found to be higher in comparison with those determined in the other cities except for Demir Hisar. The highest mean and median values (3.39 μg/L and 3.22 μg/L, respectively) for total As content were obtained in the drinking water of Demir Hisar. This mainly is due to the mineral composition of Bigla Mountain, which is rich with iron ores which contain As impurities. But, despite this fact, in all tested samples of drinking water, the As content was found to be bellow MAC. The lowest mean and median values for total As were found in the drinking water of Probishtip (0.393 μg/L and 0.38 μg/L, respectively) and Delchevo (0.399 μg/L and 0.35 μg/L, respectively). Although the water supply systems of the two towns draw out water from the different sources, the analysis of variance at the 0.05 level didn’t show significant difference for the population means for the total As content.

The results of the content of total As in the drinking water obtained from water supply systems that draw out water from the drilled wells and underground accumulations are shown in Table 4.

Table 4. *Results for the total arsenic content in drinking water from supply systems that draw out water from the drilled wells and underground accumulations*

City/Town (number of samples)	Location in the Republic of Macedonia	Water origin	Type of water supply system	Minimum (μg/L)	Maximum (μg/L)	Mean (μg/L)	Median (μg/L)	SD (μg/L)
Skopje (55)	North	Underground accumulations Drilled wells	Local	<0.1	5.91	1.82	1.93	0.944
Kočani (15)	Northeast	Underground aquifer	Local	0.48	3.14	1.505	1.40	0.561
Štip (35)	Central east	Underground accumulation beside Bregalnica River	Local	<0.1	3.46	2.204	2.34	0.761
Gradsko (15)	Central	Drilled wells beside Vardar River	Local	0.18	1.13	0.522	0.50	0.206
Demir Kapija (20)	South	Drilled wells beside Boshava River	Local	1.88	5.28	4.184	4.215	0.704
Bogdanci (15)	Southeast	Drilled wells “Gjavato” between Bogdanci and Dojran	Local	2.45	8.35	3.94	3.80	1.347
Gevgelija “Moin” (45)	Southeast	Drilled wells “Moin” in the walleye near the Greek border	Local	5.65	26.4	11.946	10.90	5.53
Gevgelija “Vardar” (25)	Southeast	Drilled wells beside Vardar River	Local	0.18	2.18	1.438	1.55	0.544
Star Dojran (25)	Southeast	Drilled wells	Local	6.15	16.17	10.556	10.330	2.371
Nov Dojran (28)	Southeast	Drilled wells	Local	5.47	26.6	13.061	11.35	5.243

Skopje, the capital of the Republic of Macedonia is located in the upper course of the Vardar River. The water supply system draws water out from the underground accumulation in the vicinity of the village Rashche, and the drilled wells of Lepenec – Nerezi area. Rashche village is located on the right bank of the Vardar River, in the western regions of the Skopje Valley. Nerezi – Lepenec area covers the wider area of the estuary of the Vardar River into the Lepenec River. The content of total As in drinking water ranged from below LOQ to 5.91 μg/L with a mean value of 1.82 μg/L.

The water supply system of Kochani draws water out from the underground aquifer "Grdovski Orman", which is formed in alluvial sediments of the River Terrace Bregalnica. The aquifer belongs to open to semi-closed hydro geological structures easily susceptible to anthropogenic pollution. Contrary to the expectations, the obtained results showed low level of total As concentration ranging from 0.48 μg/L to 3.14 μg/L. Similar values were obtained for total As content in the drinking water obtained from the water supply system of Shtip. This probably is due to the similar soil composition of the water basins. Namely, the water supply system of Shtip draws water out from the underground accumulations besides the Bregalnica River.

Low levels of total As content ranging from 0.18 μg/L to 1.13 μg/L, were also found in the drinking water samples obtained from the water supply system of Gradsko which is located on the both sides of the Vardar River in front of the Tikvesh Valley in the central part of the Republic of Macedonia. The water supply system draws water out from the drilled wells beside the Vardar River.

Demir Kapija is a town situated in the south of the Republic of Macedonia in the valley of the Vardar River. The water supply system draws water out from the drilled boreholes besides the Boshava River, right side tributary of the Vardar River. The concentrations of As in the drinking water of the town ranged between 1.88 μg/L to 5.28 μg/L with a mean value of 4.184 μg/L.

Higher values for total As concentrations were obtained in the samples of drinking water of the water supply system of Bogdanci within the range from 2.45 μg/L to 8.35 μg/L, but they were below the MAC. Bogdanci is a small town located downstream of the Vardar River. The water supply system of the town draws water out from the drilled wells which are located between Bogdanci and Dojran.

Gevgelija is a town located in the very southeast of the Republic of Macedonia along the banks of the Vardar River in the Gevgelija – Valandovo Valley. The town is situated at the country's main border with Greece, between Kozhuf Mountain and Pajak Mountain. The water supply system draws out water from two sources: drilled wells "Moin" located 4 km on the west of the town in a valley, near the Greeek border, and drilled wells located near the Vardar River. The concentrations of As in the drinking water that comes from the water facilities that draw out water from the drilled wells "Moin" ranged from 5.65 μg/L to 26.4 μg/L with a mean value of 11.95 μg/L, which is slightly above the established MAC. The higher concentration of As in drinking water is due to the vicinity of the Moin area to the foothills of Kozhuf Mountain. The metallogenic area of Kozhuf Mountain volcanic complex consists of a large number of minerals containing As [15, 16]. In this case, As is introduced into the water through the dissolution of minerals and ores. On the contrary, the concentration of As in the tested samples of drinking water obtained from the drilled wells located near the Vardar River was found to be low, ranging from 0.18 μg/L to 2.18 μg/L.

Higher concentrations of As were also found in the samples of drinking water taken from the water supply system of the towns in Dojran Municipality. Dojran Municipality is located on the western shore of the Dojran Lake in the south-eastern part of the Republic of Macedonia. The tectonic structure of the area represents a border between the Vardar zone and the Serbian-Macedonian massif. There are two small towns in the Dojran Municipality: Nov Dojran and Star Dojran at the distance of 5 km. The water supply system of the towns draws water out from the drilled wells, each of them deep 100 m. The As concentrations in the samples of drinking water obtained from the water supply system of Nov Dojran ranged from 5.47 μg/L to 26.6 μg/L. The As concentration in the samples of drinking water obtained from the water supply system of Star Dojran ranged from 6.15 μg/L to 16.17 μg/L. The obtained mean values were also above the established MAC value: 10.56 μg/L for Star Dojran and 11.35 μg/L for Nov Dojran.

The analysis of variance at the 0.05 level of significance revealed that the population means for total As content didn't show significant difference only in the samples of potable water obtained from the water supply systems of Star Dojran and Gevgelija "Moin" ($p=0.691$); Nov Dojran and Gevgelija "Moin" ($p=0.871$); Star Dojran and Nov Dojran ($p=0.0695$). This is due to the vicinity of drilled wells "Moin" to the foothills of Kozhuf Mountain, as well as, to the vicinity of the drilled wells in Dojran Municipality to the thermal- mineral area of Mala Boshka – Toplec. The analysis of variance at the 0.05 level of significance, also revealed significant difference in the populations means for the total As content in the samples of potable water obtained from the water supply system of Demir Kapija and Gradsko ($p=0.012$). This is due to the fact that the Boshava River springs from the Kozhuf Mountain.

Figure 4. *Apperance of wirlpook "Vrutok"*

Figure 5. *Apperance of Studenchica River at an altidude of 965 m*

4. Conclusions

The results obtained in this study showed that the lowest mean values for the total As content ranged from 0.178 μg/L to 0.371 μg/L and were obtained for the water supply systems that draw out water from the springs which flow out from the Sharr Mountain, the Bistra Mountain, the Rosoki Mountain and the Jablanica Mountain. This is due to the geological composition of the mountain's body made of arsenic poor karst forms [19]. Low content for total As was found in the samples of drinking water obtained from the regional water supply system "Zletovica" (mean value 0.393 μg/L – 1.579 μg/L), which is located in the northeast part of the Republic of Macedonia. This is due to the volcanic composition of the body of the Osogovo Mountain where the Zletovica River flows out [14]. Higher concentrations for total As content were obtained in the samples of drinking water of the water supply system of Kavadarci. Namely, the mean value for total As content was found to be 7.196 μg/L, but is still below the established MAC of 10 μg/L [7]. Higher As content is in line with the mineral composition of the Kozhuf Mountain. The ore bodies of the mountain consist of a large number of As containing minerals [15, 16]. This is also the reason for higher As concentrations in the drinking water obtained from the water supply system that draws water out from the drilled wells "Moin" which are located in a vicinity to the foothills of the Kozhuf Mountain. The concentrations of As in the drinking water that comes from the drilled wells "Moin" ranged from 5.65 μg/L to 26.4 μg/L with a mean value of 11.95 μg/L, which is slightly above the established MAC. In these cases, As is introduced into the water through the dissolution of minerals and ores. Higher concentrations of As were also found in the samples of drinking water taken from the water supply system of the towns in Dojran Municipality which is located on the western shore of the Dojran Lake in the south-eastern part of the Republic of Macedonia. The obtained mean values were above MAC (10.56 μg/L for Star Dojran and 11.35 μg/L for Nov Dojran), which is due to the vicinity of the drilled wells to the thermal - mineral area of Mala Boshka – Toplec. This implies that an additional purification step of the drinking water should be included.

The obtained results revealed that the total As content in the drinking water that comes from different sources (springs, underground accumulations and surface accumulations) in the Republic of Macedonia is below MAC in the 96.7% of the 780 tested samples. Higher concentration of total As in drinking water is due exclusively to the mineral composition of the mountain's body where the water flows out, as well as, to the vicinity of the thermal – mineral springs to the underground water sources. Therefore, it can be concluded that the presence of total As in the potable water in the Republic of Macedonia comes only from natural sources [20].

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