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DETERMINATION OF ALUMINIUM CONTENT IN THE POTABLE WATER IN THE REPUBLIC OF MACEDONIA FROM THE PERIOD 2011- 2014

Vesna Kostik[1*], Biljana Manevska[1], Shaban Memeti[1], Biljana Gjorgeska[2], Sofija Petkovska[2]

[1]Institute of Public Health, '50 Divizija" No. 6, 1000 Skopje, Republic of Macedonia,
[2]Faculty of Medical Science, Department of Pharmacy, University "Goce Delchev", Krste Misirkov bb., 2000 Shtip, Republic of Macedonia

[*]e-mail: vesna2mk@yahoo.com

Abstract

Aluminium is one of the heavy metal contaminants of great concern. Al is the most abundant element and occurs naturally by several mobility factors in the environment as silicates, oxides and hydroxides. Excessive addition of Al salts as coagulants in water treatment process might produce elevated concentrations of Al in final water.

Al salts are used to reduce organic matter, colour, turbidity, and micro-organisms levels.

The present study investigates Al 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 2011 to November 2014, a total of 288 samples obtained from the public water supply systems at 25 measurement points distributed throughout the whole territory of the Republic of Macedonia were analyzed on the Al content. A graphite furnace atomic absorption spectrometry (GFAAS) was employed for the determination of Al content after wet digestion of the samples with nitric acid (67%, *W/V*) and hydrogen peroxide (30%, *V/V*). $Mg(NO_3)_2$ was used as an matrix modifier.

The results of the study revealed that Al content in the potable water originated from different water sources ranged from below limit of quantification set at 0.1 µg/L to 228 µg/L with the average median value of 21.7 µg/L. Al concentration was exceeded above maximum allowable concentration (MAC) of 200 µg/L in one of tested sample. Statistical evaluation of the results (ANOVA test followed by the Tukey's significance test) showed statistical differences between the Al content in potable water that comes from springs and underground accumulations ($p < 0.05$) *vs.* Al content in potable water that comes out from surface accumulations. Namely, the Al content in potable water that comes out from springs and underground accumulations was lower (average value 5.6 µg/L) in comparison with potable water that comes out from surface accumulations (average value 65.7 µg/L). This was due to the usage of Al based coagulant in the process of water treatment.

From the obtained results, it can be concluded that potable water from the water supply systems in the Republic of Macedonia contains Al well below established MAC, which is due to the usage of good sanitation system in the process of water production.

Keywords: *Aluminium (Al), water supply system, graphite furnace atomic absorption spectrometry (GFAAS), maximum allowable concentration (MAC)*

1. Introduction

Safe drinking water is an essential need for human well-being, health, development, and necessity, and therefore, it is internationally recognized as fundamental human right [1].

One of the heavy metal contaminants of great concern is aluminium (Al). Aluminium is the most abundant metal and the third most abundant element, after oxygen and silicon, in the earth's crust. It is widely distributed and constitutes approximately 8% of the earth's surface layer [2]. However, aluminium is a very reactive element and is never found as the free metal in nature. It is found combined with other elements, most commonly with oxygen, silicon, and fluorine. These "chemical compounds" are common. Small amounts of aluminium are found in water in dissolved or ionic form. The concentration of aluminium in natural waters is generally below 0.1 parts of aluminium per million parts of water (0.1 ppm) unless the water is very acidic.

Excessive addition of Al salts as coagulants in water treatment process might produce elevated concentrations of aluminium in processed finished water [3]. Aluminium is also released in the environment due to anthropogenic activities such as mining and industrial uses, as for example production of aluminium metal and other aluminium compounds. The major route of exposure to aluminium for the general population is through food. Drinking water represents another source of exposure Children may be exposed to high levels of aluminium in drinking water.

After absorption, aluminium distributes to all tissues in animals and humans and accumulates in some, and in particular in bones. The main carrier of the aluminium ion in plasma is the iron binding protein, transferrin. Aluminium can enter the brain and reach the placenta and foetus. Aluminium may persist for a very long time in various organs and tissues before it is excreted in the urine [4].

Numerous scientific studies had shown that Al is the risk factor of Alzheimer's disease (AD) [5, 6], dementia, osteomalacia (OM) [7], encephalopathy [8] and total parenteral nutrition (TPN) [9].

Exposure to Al can be determined in human by biological samples such as blood, urine, hair, brain and bones. Both urinary and plasma aluminium levels reflect body burden and current exposure [10]. But according to the newest scientific investigations urine is the most important route of aluminum excretion [11, 12].

The aim of this study is determination of the aluminium 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

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, 25 cities and towns were suitably selected. The selected cities and town were located in the north: (Skopje); northeast: (Kumanovo, Kriva Palanka, Sveti Nikole, Kriva Palanka, Kočani); northwest: (Tetovo, Mavrovo, Gostivar); central: (Veles); central east: (Vinica, Berovo, Štip), central west: (Debar, Kičevo, Makedonski Brod), southeast: (Radoviš, Strumica) and southwest part of the country: (Kruševo, Prilep, Resen, Struga, Ohrid, Bitola).

2.2 Sampling

From January 2011 to November 2014, a total of 288 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 [13]. The samples were sealed and labeled with a unique sample code and placed in a portable refrigerator. These samples then were digested and analyzed (within the 24 hours from the time of the collection) for the total presence of Al, according to the ISO 15586 [14].

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. Water for the trace analysis was obtained from Sigma-Aldrich, Germany. High purity aluminium standard solution 1000 mg/L (prepared from $Al(NO_3)_3 \cdot 9H_2O$ in 2% HNO_3) was obtained from Sigma - Aldrich, 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.

Al 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 and 200 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 ^{0}C 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 graphite furnace atomic absorption spectrometry (GFAAS) technique (Perkin-Elmer atomic absorption spectrometer AAnalyst 600) equipped with a Zeeman background correction, graphite furnace and auto sampler (Perkin-Elmer Corp., Norwalk, CT, USA). In order to overcome the matrix effect, pyrolytically coated tubes with inserted L'vov platform were used. The radiation source was an electrodeless discharge lamp of arsenic (Perkin-Elmer) used at a wavelength of 309.3 nm and a spectral slit width of 0.7 nm. Furnace conditions are given in Table 1.

Table 1. Furnace conditions

Step	Temperature (ºC)	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 8.0. 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

Fourteen cities and towns with water facilities that draw out water from natural springs were included in the study. The obtained results for Al content in drinking water (minimum and maximum value), as well as statistical data (median value, standard deviation - *SD*) are shown in Table 2. Assessment of the obtained results was made according to national Regulation for Water Safety [15].

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 (8)	Northwest	Springs (Sharra mountain)	Local	<0.1	7.56	4.52	3.78	1.45
Mavrovo (8)	Northwest	Springs (Bistra mountain)	Local	0.25	8.54	5.15	4.50	1.80
Gostivar (8)	Northwest	Whirlpool "Vrutok"	Local	<0.1	9.55	6.40	6.12	2.05
Debar (8)	Central west	Springs Rosoki mountains	Local	<0.1	10.43	6.93	6.50	2.15
Kichevo (8)	Central west	Springs (Bistra mountain)	Regional "Studenčica"	<0.1	8.70	5.90	6.04	1.95
Makedonski Brod (8)	Central west	Springs (Bistra mountain)	Regional "Studenčica"	<0.1	6.75	4.44	3.90	1.50
Krushevo (8)	Southwest	Springs (Bistra mountain)	Regional "Studenčica"	<0.1	5.60	3.60	3.05	1.20
Prilep (10)	Southwest	Springs (Bistra mountain)	Regional "Studenčica"	0.17	6.56	2.90	2.14	1.70
Resen (12)	Southwest	Springs (Galičica mountain)	Local	0.22	4.5	3.08	3.12	2.30
Struga (12)	Southwest	Spring "Shum" (Jablanica mountain)	Local	<0.1	3.75	2.25	1.90	0.98
Ohrid (16)	Southwest	Springs: "Biljanini izvori; "Letnica"	Local	<0.1	8.54	4.40	3.67	2.57
Kriva Palanka (12)	Northeast	Springs "Kalin Kamen" (Osogovo mountain)	Local	0.18	6.8	5.12	4.60	2.96
Pehchevo (10)	Central east	Springs (Bukovik mountain)	Local	0.34	12.5	8.70	6.95	1.95
Valandovo (8)	Southeast	Springs in the valley near the Anska River	Local	<0.1	8.80	7.05	6.60	1.70

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. 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). The obtained results showed low concentrations of Al in the potable water, ranging from less of Limit of Quantification (LOQ) - 0.1 μg/L (Kichevo, Makedonski Brod and Krushevo) to 8.70 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 Al in the tested samples of drinking water were also low (0.25 μg/L - 8.54 μg/L).

The results of our investigation showed also low Al concentration in the potable water obtained of the water supply systems of Tetovo, Gostivar, Debar, Resen, Struga, Ohrid, Kriva Palanka, Pehchevo and Valandovo, ranging from less of LOQ (Tetovo, Gostivar, Debar, Struga, Ohrid and Valandovo) to 12.5 μg/L (Pehchevo).

The results of the content of Al in the drinking water obtained from water supply systems that draw out water from the drilled wells and underground accumulations are shown in Table 3.

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 2.40 to 14.5 μg/L with a mean value of 6.70 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 [16]. 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 Al concentration ranging from 1.20 to 9.80 μg/L. Similar values was obtained for Al 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.

The results of the content of Al in the drinking water obtained from water supply systems that draw out water from the surface accumulations are shown in Table 4.

Statistical evaluation of the results for Al content (ANOVA test followed by the Tukey's significance test) showed statistical differences between the Al content in potable water that comes from springs and underground accumulations ($p < 0.05$) *vs.* Al content in potable water that comes out from surface accumulations. Namely, the Al content in potable water that comes out from springs and underground accumulations was lower (average value 5.6 μg/L) in comparison with potable water that comes out from surface accumulations (average value 65.7 μg/L). This is due to the addition of Al salts as coagulants in water treatment process [3]. Namely, the most widely used metal coagulant for water is aluminium sulphate ("alum"). Other Al coagulants are the aluminium chloride ($AlCl_3 \cdot 6H_2O$) and the sodium aluminate ($NaAlO_2$). The application of simple metal coagulants (conventional) is widespread, especially due to the relatively low cost and the simpler application route. But, the excessive addition of Al salts as coagulants in water treatment process might produce elevated concentrations of Al in finished water.

According to the investigations conducted in Germany in 1995, levels of Al in public water supplies averaged at 10 μg/L in the western region, whereas levels in 2.7% of public supplies in the eastern region exceeded

Table 3. Results for Al 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 (36)	North	Underground accumulations Drilled wells	Local	2.40	14.5	6.70	6.05	1.15
Kochani (8)	Northeast	Underground aquifer	Local	1.20	9.80	8.80	7.92	1.05
Shtip (16)	Central east	Underground accumulation beside Bregalnica river	Local	<0.1	10.2	9.05	8.05	2.15

Table 4. Results for Al content in drinking water from supply systems that draw out water from 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 (14)	Norheast	Lipkovo Lake (accumulation)	Local	<0.1	167	58.3	46.5	13.5
Strumica (16)	Southeast	Turija River (accumulation)	Local	0.5	111	48.9	46.7	6.72
Veles (16)	Central	Water intakes from Topolka River	Local	0.25	49.9	19.2	13.9	6.12
Sveti Nikole (8)	Northeast	Zletovica River	Regional "Zletovica"	17.3	164	84.2	76.4	15.5
Vinica (8)	Central east	Water intake from the river	Local	34.2	228	112.4	84.3	18.4
Berovo (8)	Central east	Berovsko Lake (accumulation)	Local	45.5	121	85.6	80.2	12.4
Delchevo (8)	Northeast	Water intakes from Loshana River	Local	55.3	95.6	78.5	70.5	14.5
Bitola (14)	Southwest	Surface accumulation from Shemnica River	Regional "Strezhevo	18.5	56.4	38.3	39.3	10.6

200 μg/L [17]. In a 1993 - 1994 survey of public water supplies in Ontario, Canada, 75% of all average levels were less than 100 μg//L, with a range of 40 - 85 μg/L [18]. In a large monitoring program in 1991 in the United Kingdom, concentrations in 553 samples (0.7%) exceeded 200 μg/L [19]. In a survey of 186 community water supplies in the USA, median Al concentrations for all finished drinking-water samples ranged from 30 to 100 μg/L; for facilities using aluminum sulfate coagulation, the median level was 100 μg/L, with a maximum of 2.7 mg/L [20]. In another US survey, the average aluminum concentration in treated water at facilities using aluminum sulfate coagulation ranged from 0.01 to 1.3 mg/L with an overall average of 0.16 mg/L [21].

4. Conclusions

- From January 2011 to November 2014, a total of 288 samples obtained from the public water supply systems at 25 measurement points distributed throughout the whole territory of the Republic of Macedonia were analyzed on the Al content**.** The results of the study revealed that Al content in the potable water originated from different water sources exceeded MAC of 200 μg/L in one of tested sample.

- Statistical evaluation of the results (ANOVA test followed by the Tukey's significance test) showed statistical differences between the Al content in potable water that comes from springs and underground accumulations ($p < 0.05$) *vs.* Al content in potable water that comes out from surface accumulations.

- The Al content in potable water that comes out from springs and underground accumulations was found to be lower (average value 5.6 μg/L) in comparison with potable water that comes out from surface accumulations (average value 6.7 μg/L), which is due to is due to the addition of Al salts as coagulants in water treatment processes.

- In order to overcome elevated concentrations of aluminium in finished water**,** as a result of addition of Al salts as coagulants, there is a need for the usage of new types of coagulants as the pre-polymerized coagulants (poly-aluminium chlorides, poly-aluminium sulphates or poly-aluminium chlorine-sulphates) or organic poly-electrolytes. These coagulants are found to be to be more efficient in lower dosages, in wider pH, temperature and colloids concentration ranges, than the conventional simpler ones, leading to cost and operative more effective treatment [22, 23].

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