


International Journal of Medicine and Public Health

An Official Publication of SciBiolMed.Org

Vol 4, Issue 3, Jul-Sep 2014

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Editor : Dr. Subhankar Chakraborty (USA)



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Lithium content in potable water, surface water, ground water, and mineral water on the territory of Republic of Macedonia

Abstract

The aim of this study was to determine lithium concentration in potable water, surface water, ground, and mineral water on the territory of the Republic of Macedonia. Water samples were collected from water bodies such as multiple public water supply systems located in 13 cities, wells boreholes located in 12 areas, lakes and rivers located in three different areas. Determination of lithium concentration in potable water, surface water was performed by the technique of inductively coupled plasma-mass spectrometry, while in ground water samples from wells boreholes and mineral waters with the technique of ion chromatography. The research shows that lithium concentration in potable water ranging from 0.1 to 5.2 µg/L; in surface water from 0.5 to 15.0 µg/L; ground water from wells boreholes from 16.0 to 49.1 µg/L and mineral water from 125.2 to 484.9 µg/L. Obtained values are in accordance with the relevant international values for the lithium content in water.

Key words: Ground water, inductively coupled plasma-mass spectrometry, ion chromatography, lithium, mineral water, potable water, surface water

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Access this article online

Website: www.ijmedph.org

DOI: 10.4103/2230-8598.137700

Quick response code:



INTRODUCTION

Lithium is one of the most important trace elements for the functioning of the human organism. Mainly in the human body is inserted through the food of plant origin (cereals, nuts, vegetables) and water. Surveys conducted by Weiner^[1] for the lithium intake in our organism, show that the main part of the lithium intake is inserted through cereals and vegetables 430 and 2900 µg/day, while through food from animal origin in our body are inserted insignificant concentration (2.5 µg/day).

As a result, of the importance that lithium has on the functioning of the human body, scientists^[2] found that recommended daily dietary intake of lithium (recommended dietary allowance) for adults with an average body mass of 70 kg is 1 mg/day, which is equivalent to 14.3 µg/kg body mass. The US Environmental Protection Agency established standards for daily intake of lithium which for an adult, weight of 70 kg ranging from 650 to 3100 µg.^[3] This concentration of lithium could be provided with food and water intake which contain adequate concentrations of lithium.

Lithium from food or water in the form of soluble salts in the body is being completely absorbed in the gastrointestinal tract (small intestine) through Na⁺ channels. Absorbed lithium almost equally is being distributed in the body fluids with little difference between the extra cellular and intracellular fluid. Lithium excretion of the body is carried out through kidneys. According to Hager *et al.*,^[4] after the autopsy in men and women who do not have any hetero anamnesis data of prior therapy with lithium preparations, the presence of lithium was found in the following organs: Cerebellum, cerebrum, kidney, thyroid, pancreas, lungs, and bones. From the obtained results can be concluded that the distribution of lithium is greater in women's organs than in men, except in the pancreas. During embryogenesis, the concentration of lithium in the internal organs reaches a maximum concentration in the first trimester of gestation, with a gradual decline to the end of the pregnancy.^[5]

Biochemical mechanism of action of lithium in the body is very complex and is correlated with the present enzymes, hormones, vitamins and some drugs/medications. Influence of the lithium taken as a remedy on people's mental behavior is due to increasing activity of monoamine oxidase,

as well as increased transport of folic acid and vitamin B12 in L1210 cells.^[6] Biological activity of lithium is due to the powerful polarization feature which is a result of its small ionic radius. Lithium can replace sodium, potassium, magnesium and calcium ions from the enzymes cofactors.^[5] According to Ohgami *et al.*^[7] the lack of lithium in the body leads to a change in people's behavior and increased aggression.

Lithium as an element which in nature is found in soil, primary in the clay fraction,^[8] potable water, surface water, mineral water, ground water and marine waters as well.

Because the primary source of lithium in humans are water and food, the objective of our research was determination of lithium content in potable water, surface water, ground water from wells boreholes and mineral water on the territory of the Republic of Macedonia, since such data have not been available so far.

MATERIALS AND METHODS

Water sampling

The samples of potable water from public water supply systems were investigated, as well as surface water, ground water from wells boreholes and mineral water taken from the territory of the Republic of Macedonia [Figure 1].

Determination of the concentration of lithium was performed in 30 samples of potable water from multiple public water supply systems/network in the Republic of Macedonia (Skopje, Tetovo,

Ohrid, Sveti Nikole, Bitola, Prilep, Strumica, Shtip, Radovish, Kriva Palanka, Kavadarci, Gevgelija and Veles). Determination of lithium concentration in surface water was done on 15 samples taken from several measuring points from the Ohrid Lake, river Lepenec and river Vardar (Gevgelija). The ground water samples from wells boreholes, 35 in total were taken from the territory: Skopje, Kavadarci, Radovish, Kumanovo, Bitola, Sveti Nikole, Prilep, Strumica and Negotino.

The proportion of different water samples in which content of lithium was determined is shown in the following Figure 2.

Analytical methods for determination

Determination of the concentration of lithium in potable water and surface water was performed with the technique of inductively coupled plasma-mass spectrometry. The NexION® 350D ICP-MS features a dual-channel Universal Cell as well the ability to use Dynamic Reaction Cell™ technology, giving analysts the flexibility to choose Kinetic Energy Discrimination (KED) and/or the use of a scanning quadrupole in the Dynamic Reaction Cell. These capabilities make it the ideal solution for biomonitoring applications. The limit of detection of lithium with this instrument is 0.05 µg/L.

Concentration of lithium in the ground water from wells boreholes and surface water were performed with the technique of ion chromatography with conductivity detector which covers the concentration areas for this type of waters. The performance of this instrument is given in Table 1.

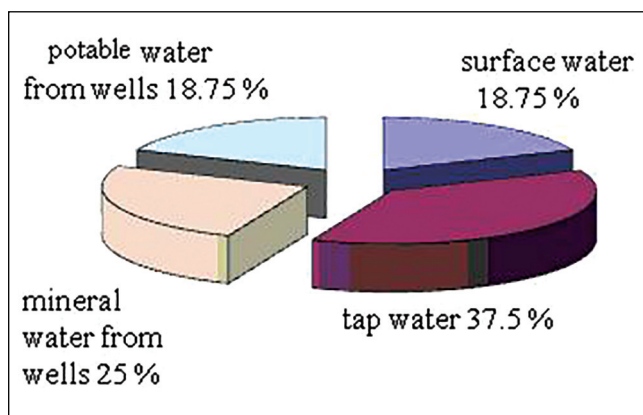


Figure 1: Distribution of sampling sites from the territory of Republic of Macedonia

Table 1: Instrumental condition for determination of lithium with IC

Guard column	Analytical column	Eluent	Regenerant
CG 16 3 mm × 50 mm	CS 16 3 mm × 250 mm	30 mM methanesulfonic acid	100 mM tetrabutyl ammonium hydroxide

IC = Ion chromatography

**Figure 2:** Percentage of the types of water in which is determined the concentration of lithium

RESULTS AND DISCUSSION

Purpose of our investigation is to determine the concentration of lithium in potable water, surface water, ground water from wells boreholes and mineral water on the territory of the Republic of Macedonia. The results of the tests are given in Tables 2-5. Regulations for the water quality in the Republic of Macedonia provide no lithium content data. Therefore, our results were compared with literature data.

Lithium was found in all analyzed water samples from the territory of Republic of Macedonia. Its concentrations depended on the type of water sample, which was analyzed [Table 6]. The heterogeneity of the results in the general research with a high coefficient of variation values implied that differences in the location and period of sampling had a major influence on the lithium content.

Research shows that concentration of lithium in the potable water from public water supply systems in the Republic of Macedonia ranging from 0.11 to 5.20 µg/L [Table 2]. In some regions of the world,^[7,9] in order to increase the daily intake of lithium in human nutrition, lithium is added as a supplement in the potable water (tap water), with the final concentration of lithium in water of 170 µg/L. Low lithium concentration in potable water from multiple public water supply systems from the network in the Republic of Macedonia points to the possibility for a beginning of the enrichment of Macedonian potable water with lithium.

Determination of the concentration of lithium was performed in 30 samples of potable water from multiple public water supply systems/network in the Republic of Macedonia. By calculating the average values of the lithium concentration according to the location the follow hierarchical lithium concentration gradient is obtained Skopje 2.84 µg/L, Kavadarci 1.81 µg/L, Sveti Nikole 1.56 µg/L, Gevgelija 1.33 µg/L, Shtip 1.00 µg/L, Strumica 0.67 µg/L, Tetovo 0.49 µg/L,

Table 2: Results of determination of lithium in public water supply systems in the republic of macedonia (µg/L)

Location	Period	Lithium concentration
Ohrid/Gradishte	May 2010	0.25
Ohrid/Hotel Metropol	May 2010	0.11
Tetovo/City tap	April 2010	0.30
Skopje/Hotel Continental	April 2009	5.20
Tetovo/Periphery	May 2010	0.40
Tetovo/Center	May 2010	0.78
Sveti Nikole/City tap	April 2009	1.56
Skopje/Butel	April 2011	2.40
Skopje/Karposh	April 2011	2.89
Bitola/Center restaurant	April 2009	0.23
Strumica/Hotel Sirius	April 2010	0.90
Skopje/Center	September 2011	1.20
Skopje/Chair	November 2011	1.98
Prilep/Center	May 2010	0.23
Strumica/Hotel Sirius	April 2009	0.54
Strumica/Barracks	April 2010	0.67
Strumica/Market-place	May 2011	0.56
Radovish/Restaurant	April 2009	0.43
Radovish/Household	April 2010	0.48
Shtip/Restaurant at cultural home Aco Shopov	April 2010	0.89
Shtip/Periphery (entry)	April 2010	1.12
Kriva Palanka/Center	April 2009	0.35
Veles/Intercity bus station	April 2009	0.15
Kriva Palanka/Center	May 2010	0.22
Skopje/Center	April 2010	2.56
Skopje/Gjorche Petrov	April 2010	3.65
Kavadarci/Center Restaurant	April 2010	1.78
Gevgelija/Center Restaurant	April 2009	1.12
Kavadarci/Center	April 2010	1.85
Gevgelija/Center	May 2010	1.55

Radovish 0.45 µg/L, Kriva Palanka 0.28 µg/L, Bitola 0.23 µg/L, Prilep 0.23 µg/L, Ohrid 0.18 µg/L and Veles 0.15 µg/L. If the territory of Republic of Macedonia is separated with river Vardar on the west and east part the estimated lithium concentrations of potable water are little bit higher in the east part (1.69 µg/L > 1.34 µg/L).

Lithium concentration in surface water of 15 samples taken from several measuring points from the Ohrid Lake, river Lepenec and river Vardar (Gevgelija) are presented in Table 3. Lithium concentrations in surface water varied from 0.53 to 15.03 µg/L. Highest average lithium concentration was obtained on the measuring points at river Vardar near Gevgelija of 13.09 µg/L and the lowest average lithium concentration of 1.07 µg/L was obtained in the measuring points at Ohrid Lake.

Table 3: Results of determination of lithium in surface water in the republic of macedonia ($\mu\text{g/L}$)

Location	Time	Lithium concentration
Ohrid Sveti Naum	September 2009	0.53
Ohrid Gradishte	September 2009	0.78
Ohrid Gradaska Plaza	September 2009	2.30
Ohrid, Peshtani	September 2009	0.78
River Lepenec, Zlokukani	April 2009	5.53
River Lepenc, Gjorche Petrov, before entry into Vardar	April 2009	7.77
River Lepenc, Gjorche Petrov, entry into Vardar	April 2009	8.45
River Lepenc, Gjorche Petrov, after entry into Vardar	April 2009	9.56
River Lepenec, Zlokukani	May 2010	6.43
River Lepenc, Gjorche Petrov, entry into Vardar	May 2010	9.24
River Vardar Gevgelija measuring point 1 before the entrance to the bridge toward Bogorodica	April 2009	12.34
Ohrid Lagadin	September 2009	0.95
River Vardar Gevgelija measuring point 2 exit to the bridge toward Bogorodica	April 2009	10.12
River Vardar Gevgelija measuring point 1	May 2010	15.03
River Vardar Gevgelija measuring point 2	May 2010	14.89

Table 4: Results of determination of lithium in ground mineral water from wells in the Republic of Macedonia, categorized as mineral water ($\mu\text{g/L}$)

Location	Time	Lithium concentration
Vizbegovo well 1	April 2009	176.1
Vizbegovo well 2	April 2010	145.8
Vizbegovo well 3	May 2010	135.7
Kumanovo well 1	April 2009	155.8
Bansko, Strumica well 1	April 2009	210.9
Bansko, Strumica well 2	April 2009	256.5
Kumanovo well 1	May 2010	125.2
Medzitlija, Bitola well 1	April 2009	440.3
Medzitlija, Bitola well 2	April 2009	390.3
Kozuf well 1	April 2009	167.5
Medzitlija, Bitola well 1	May 2011	430.4
Medzitlija, Bitola well 2	May 2011	484.9
Bansko, Strumica well 1	May 2011	228.6
Kumanovo well 1	May 2011	150.6
Katlanovo well 1	April 2009	155.3
Katlanovo well 1	April 2010	148.9
Katlanovo well 1	April 2011	138.7
Kozuf well 1	May 2011	160.8
Vizbegovo well 1	September 2011	172.0
Vizbegovo well 4	September 2011	221.3

Lithium composition of 35 in total ground water samples from wells boreholes, are presented in Tables 4 and 5. Twenty samples of ground water are categorized as mineral water, the rest 15 as potable

Table 5: Results of determination of the li in ground water from wells in the republic of macedonia, categorized as potable water ($\mu\text{g/L}$)

Location	Time	Lithium concentration
Sveti Nikole well 1	April 2009	17.56
Sveti Nikole well 2	April 2009	17.28
Prilep well 1	April 2009	23.50
Prilep well 2	April 2009	28.98
Radovish well 1	Maj 2009	19.40
Radovish well 2	Maj 2009	21.20
Radovish well 1	September 2010	16.05
Petrovec well 1	April 2009	34.40
Petrovec well 2	April 2010	24.80
Petrovec well 2	September 2011	22.56
Rosoman, Kavadarci well 1	April 2011	27.98
Rosoman, Kavadarci well 2	April 2011	38.90
Kumanovo well 1	April 2009	41.60
Negotino well 1	April 2009	17.65
Bitola well 1	September 2009	49.10

Table 6: Statistical processing of the results of determination of lithium in potable water, surface water, ground water and mineral water on the territory of republic of macedonia

Type of sample	Lithium concentration
Public water supply systems	
Average	1.21
CV	97.63
Surface water	
Average	6.98
CV	72.61
Ground mineral water from wells	
Average	224.78
CV	51.02
Ground water from wells	
Average	26.73
CV	37.69

CV = Coefficient of variation

water according to our regulation limit.^[10] Lithium levels were very consistent at about 125.20-484.90 $\mu\text{g/L}$ in mineral ground water. By calculating the average values of the lithium concentration according to the location of mineral ground water the follow hierarchical lithium concentration gradient is obtained Bitola 436.47 $\mu\text{g/L}$, Strumica 232.0 $\mu\text{g/L}$, Vizbegovo 170.18 $\mu\text{g/L}$, Kozuf 164.15 $\mu\text{g/L}$, Katlanovo 147.63 $\mu\text{g/L}$ and Kumanovo 143.87 $\mu\text{g/L}$. The estimated lithium concentrations of mineral ground water are higher in the west part of the territory of Republic of Macedonia (300.31 $\mu\text{g/L}$ >173.59 $\mu\text{g/L}$).

The obtained results [Table 5] for potable ground water were somewhat lower from 16.05 to 49.10 $\mu\text{g/L}$. According to the location of mineral ground water the follow hierarchical lithium concentration gradient is obtained Bitola 49.10 $\mu\text{g/L}$, Kumanovo 41.96 $\mu\text{g/L}$, Kavadarci, 33.44 $\mu\text{g/L}$, Petrovec 27.25 $\mu\text{g/L}$, Prilep

26.24 µg/L, Radovish 18.88 µg/L, Negotino 17.65 µg/L and Sveti Nikole 143.87 µg/L. The estimated lithium concentrations of potable ground water are higher in the west part of the territory of Republic of Macedonia (31.61 µg/L > 26.38 µg/L).

Research shows that concentration of lithium in the potable water, surface water, water from wells boreholes and mineral water from the territory of Republic of Macedonia is in accordance with the relevant international values for the content of lithium in water.^[7,11]

CONCLUSION

If the estimated lithium concentrations values from the east and west part from the territory of Republic of Macedonia were compared could be noticed that more lithium was found in the west part.

Macedonian potable water can serve as bad source of lithium able to supplement recommended daily dietary intake of lithium in the diet.

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How to cite this article: Kostik V, Bauer B, Kavrovski Z. Lithium content in potable water, surface water, ground water, and mineral water on the territory of Republic of Macedonia. *Int J Med Public Health* 2014;4:189-93.

Source of Support: Nil, **Conflict of Interest:** None declared.