

ORIGINAL ARTICLE

HEALTH RISK RELATED TO EXPOSURE TO TOXIC COMPOUNDS CONTAINED IN MINERAL AND SPRING WATERS

DOI: 10.36740/WLek202107107

Katarzyna Tomczyk^{1,4}, Grzegorz Dziubanek², Anna Kowalska³, Iwona Szymala³, Beata Łabuz-Roszak⁴¹DOCTORAL STUDIES OF THE FACULTY OF HEALTH SCIENCES IN BYTOM, DEPARTMENT OF ENVIRONMENTAL HEALTH, UNIT OF ENVIRONMENTAL HEALTH RISK FACTORS, MEDICAL UNIVERSITY OF SILESIA IN KATOWICE, BYTOM, POLAND²DEPARTMENT OF ENVIRONMENTAL HEALTH, UNIT OF ENVIRONMENTAL HEALTH RISK FACTORS, FACULTY OF HEALTH SCIENCES IN BYTOM, MEDICAL UNIVERSITY OF SILESIA IN KATOWICE, BYTOM, POLAND³DEPARTMENT OF ENVIRONMENTAL HEALTH, UNIT OF ENVIRONMENTAL HEALTH, FACULTY OF HEALTH SCIENCES IN BYTOM, MEDICAL UNIVERSITY OF SILESIA IN KATOWICE, BYTOM, POLAND⁴DEPARTMENT AND UNIT OF BASIC MEDICAL SCIENCES, FACULTY OF HEALTH SCIENCES IN BYTOM, MEDICAL UNIVERSITY OF SILESIA IN KATOWICE, BYTOM, POLAND

ABSTRACT

The aim: The study aimed to assess the content of selected toxic compounds in mineral and spring waters available on the Polish market regarding potential health risks to consumers.

Materials and methods: Selected mineral and spring waters available on the Polish market were the study's objects. The content of such chemical compounds as arsenic, cadmium, lead, copper, and mercury in selected mineral and spring waters was analyzed. The content of metals in the samples was determined by inductively coupled plasma mass spectrometry (ICP-MS). Additionally, a literature review was performed to determine nitrates contamination of bottled waters available on the Polish market. Based on the collected data, an assessment of exposure and health risk to consumers was performed.

Results: Arsenic had the highest mean concentration in the analyzed water samples. Consumption of such contaminated waters may be a significant health risk factor for consumers. Literature data indicate a relatively low content of nitrates in bottled waters available on the Polish market. Consumption of such mineral waters is not a significant source of exposure and does not translate into a significant health risk for consumers.

Conclusions: To ensure consumers' health safety, there is a need to monitor the content of potentially harmful compounds in mineral and spring waters available on the Polish market.

KEY WORDS: mineral and spring waters, health risk, heavy metals, nitrates

Wiad Lek. 2021;74(7):1587-1594

INTRODUCTION

Water is one of the main components of the human body. It accounts for 60-70% of an adult's body weight and 75% – of a child [1]. It plays an essential role in vital human functions. It participates in biological and physiological processes such as the formation of mouthfuls in the oral cavity, absorption of nutrients, humidification of inhaled air, removal of unnecessary products of metabolism, cushioning of joints, and protection of internal organs [2]. The daily water requirement of an adult ranges from 30 to 50 mL per kilogram of body weight and depends on physical activity, food intake, ambient temperature, air humidity, and health status [3, 4].

In Poland, a steady increase in mineral and spring water consumption has been observed in recent years, which is primarily related to changes in society's dietary habits [5, 6]. According to the Food and Nutrition Safety Act of August 25, 2006 (Polish Journal of Laws, 2006, No. 171, item 1225), natural mineral water is distinguished from water

intended for human consumption by its original biological and chemical purity, stable mineral composition and physiological properties having a beneficial effect on human health [7]. According to the Regulation of the Minister of Health of 31 March 2011 changing the classification of mineral waters based on the provisions of the Directive 2009/54/EC of the European Parliament and the Council of 18 June 2009, the name 'mineral water' is currently applied to all waters extracted from the ground, regardless of their mineralization [8, 9]. Spring water, which is often an alternative to tap water, is defined in the Act as: "underground water extracted through one or more natural or drilled boreholes, originally pure in chemical and microbiological terms, not differing in properties and mineral composition from water intended for human consumption defined in the provisions of the Act of 7 June 2001 on collective water supply and collective sewage disposal" [7, 10].

Water is one of the essential sources of elements necessary for the proper functioning of the human body. Due to

bioelements content, natural mineral waters are often used for prophylactic and therapeutic purposes [11]. They are a valuable source of mineral components, especially when their amount in the diet is insufficient [5, 12]. Therefore, it is justified to determine trace elements such as iron, copper, zinc, manganese, and nickel in mineral and spring waters [13]. Their concentrations are given on the label by bottled water producers. They mainly include information on the content of calcium, magnesium, sodium, potassium, elements whose role in the human body has been well recognized [14, 15].

Nevertheless, it is also essential to analyze the content of toxic substances that may potentially occur in mineral and spring waters. In particular, heavy metals such as cadmium, mercury, lead, and arsenic have been identified by the World Health Organization (WHO) as chemical substances that pose a significant threat to public health [13, 16]. The maximum permissible content of elements in water intended for drinking was determined by the Ministry of Health. The Regulation of the Minister of Health of March 31, 2011 on Natural Mineral Waters, Spring Waters and Table Waters gives a detailed list of potentially toxic components that may be present in natural mineral waters along with their maximum concentrations, exceeding of which may cause significant health risks [8].

Heavy metals belong to persistent environmental pollutants. The effects of their negative impact on human health are often observed after a long period of exposure. They enter the body by oral, respiratory, and dermal routes of exposure, although the oral route is the most important. Toxic metals accumulate in the human body in the kidneys, liver, lungs, bones, muscles, hair, and skin. Long-term exposure to heavy metals may lead, among others, to damage of individual organs, behavioral disorders, cognitive impairment, development of hypertension, reproductive disorders, increased risk of malignant tumors, and many other disorders [17]. The group of compounds classified as “undesirable and toxic constituents in excessive concentrations” found in natural mineral water also includes nitrates (III, V) [8]. The main effect of exposure to nitrates is methemoglobinemia, a hazardous disorder for children, which can lead to hypoxia of the central nervous system, myocardium, and disorders of consciousness [18, 19]. These compounds are mainly not shown on the labels of bottled waters [14, 20].

The harmfulness of individual constituents of consumed water depends on factors such as the concentration, volume, and frequency of water consumption, its overall mineralization, and the presence of other chemical compounds with which contaminants may interact [6, 21]. Water contaminated with heavy metals, nitrates, and other toxic compounds can pose health risks to its consumers, especially young children who consume a more significant water volume per kg of body weight than adults. For example, infants’ daily water requirements are up to 4 times higher than those of adults. Exposure to harmful compounds found in taken water may be exceptionally high in children who are artificially fed. It results from the

fact that low- and very low-mineralized mineral waters, as well as spring waters, are more and more frequently used for the preparation of meals for infants [20]. An essential criterion for selecting natural mineral water for children and infants is the degree of its mineralization and the presence of nitrate and nitrite, sulfate and chloride anions [22].

The problem of potential harmfulness of mineral and spring waters is usually unknown to the society whose knowledge concerning the consumed waters comes mainly from information contained in labels [16]. The constantly increasing popularity of mineral and spring waters creates the necessity to monitor their composition taking into account the largest possible number of components, especially compounds with proven toxic and carcinogenic properties.

THE AIM

The study aimed to assess the content of some toxic compounds in selected mineral and spring waters available on the Polish market regarding potential health risks to consumers.

MATERIALS AND METHODS

The study material consisted of selected mineral and spring waters available on the Polish market. Data on the content of chemical compounds such as arsenic, cadmium, lead, copper, mercury in mineral and spring waters were obtained from the database of the Provincial Sanitary and Epidemiological Station in Katowice, implementing the monitoring of mineral, spring, and table waters. This study takes into account the results of studies conducted in 2013-2016.

Chemical compounds were determined in 45 samples of mineral water and 57 samples of spring water. Various mineral waters were analyzed, whose intakes are located in: Nałęczów, Grodzisk Wielkopolski, Muszyna, Andrzejówka, Milik, Kęty, Tylicz, Drzewce near Nałęczów, Skalka, as well as various types of spring waters extracted in such places as: Jeleśnia near Żywiec, Nałęczów, Bystra, Aleksandria near Ozorków, and Kalisko.

The samples subjected to analysis were collected within the framework of the “Sampling Plan for food analysis within the framework of official control and monitoring for the State Sanitary Inspectorate”, which is developed annually by the Chief Sanitary Inspectorate in cooperation with research and development units at the central level. In accordance with the State Sanitary Inspectorate’s competence, it covers official control and monitoring of food of non-animal origin produced and marketed and products of animal origin in retail trade. Determination of arsenic, cadmium, lead, copper, and mercury in mineral and spring waters was carried out using inductively coupled plasma-mass spectrometry (ICP-MS). An X Series ICP-MS mass spectrometer from Thermo Elemental was used to determine the elements. Multi-element certified reference materials at 10 ppm (Merck), multi-element

certified reference materials at 10 ppb (Merck), and single element certified reference materials at 1000 ppm (Merck) and ultrapure water with an electrical resistance of 18.2 MΩ were used to prepare working standard solutions of metals. Working standard solutions of the tested elements were prepared by diluting the primary certified reference materials with a 2% nitric acid solution or, in the case of working standard solutions of mercury, with a 2% hydrochloric acid solution. The water used was deionized in the laboratory using a Millipore® ultrapure water purification system. Calibration functions of analytical signal dependence on analyte concentration based on weighted linear regression of the first degree ($y = ax + b$) were used for calibration. The method detection limits for the determination of arsenic, cadmium, lead, copper, and mercury were: 0.00024 mg/L, 0.000023 mg/L, 0.000005 mg/L, 0.00005 mg/L, 0.00007 mg/L, respectively, and they were much lower than the required detection limit included in Appendix 2 of the Regulation of the Minister of Health of March 31, 2011 on natural mineral waters, spring waters and table waters [8]. The working range was established, taking into account the maximum permissible level of arsenic, cadmium, copper, lead, and mercury according to the above-mentioned Regulation and the most frequent concentrations of these elements in the examined water samples. The precision of the method under repeatability conditions for the whole working range for arsenic, cadmium, lead, copper, and mercury were: 2.15%, 2.70%, 3.84%, 0.91%, 6.82%, respectively, and they were lower than the required precision included in Appendix 2 to the Regulation of the Minister of Health [8]. The obtained correctness of the method for the quantitative determination of the studied elements also meets the requirements set in the aforementioned Regulation of the Minister of Health [8]. The mean recovery for the range of the method of determination of the elements tested was within 90% to 110% and met the criteria included in the management system procedure implemented in the Regional Sanitary and Epidemiological Station in Katowice laboratory. Confirmation of the validity of the test results was ensured by determining the calibration curves with the use of certified reference materials, checking the purity of the auxiliary materials used, checking the invariability of the environmental conditions and the invariability of the detection and quantification limits, analyzing the sample of ultra-pure water used for the dilutions before and after the determinations, checking the calibration curve by analyzing the control sample with a concentration corresponding to the working range of the calibration curve for a given element and analyzing enriched samples.

The obtained results were statistically analyzed using MS Excel, Microsoft Office 2013 and STATISTICA 12, Stat Soft Poland, and pqStat computer program. The result was considered statistically significant if the obtained significance level p was less than or equal to 0.05. Measurable data were characterized using the mean X and standard deviation SD and the median M and interquartile range IQR . The consistency of the distribution of variables with the nor-

mal distribution was verified using the Shapiro-Wilk test. Depending on the type of distribution, the significance of mean differences was tested using Student's t -test, Mann-Whitney U -test, or Kruskal-Wallis test.

On the basis of the determined concentrations of heavy metals in the studied spring and mineral waters, the multiplicity of exposure and health risk of adult consumers was estimated according to the guidelines of the United States Environmental Protection Agency (US EPA). Daily intakes of arsenic, cadmium, and lead from consumed waters were calculated considering two exposure scenarios. The first scenario (S1) took into account the consumption of water with the mean content of tested metals, and the second scenario (S2) – consumption of water with the highest concentrations of metals. The study assumed that an adult consumed 2 liters of water per day and had a body weight of 70 kg. The daily intake was estimated using the following formula:

$$\text{Intake dose} = C \times K / MC$$

C – metal concentration in water ($\mu\text{g/L}$),

K – daily water consumption (2 L/day),

MC – body weight of an exposed person (70 kg).

The magnitude of consumers' health risk was estimated by calculating the hazard quotient (HQ) according to the formula:

$$\text{HQ} = \text{Intake dose} / \text{RfD}$$

It is assumed that when the hazard quotient is higher than 1, the risk of non-carcinogenic health effects is significant. The calculations performed considered that the reference dose (RfD) for arsenic was 0.3 $\mu\text{g/kg}$ body weight/day [23], the reference dose for cadmium was 1 $\mu\text{g/kg}$ body weight/day [24], and the BMDL10 (benchmark dose or concentration lower-confidence limit) for lead was 0.63 $\mu\text{g/kg}$ body weight/day [25]. Due to the lack of recommendations on reference doses for mercury and copper, no assessment of exposure and health risk of consumers to these two elements was performed.

RESULTS

POLLUTION OF WATERS WITH HEAVY METALS

In the analyzed mineral and spring waters, heavy metals' mean concentrations did not exceed the maximum permissible values. Both in mineral and spring waters, the highest mean content was recorded in the case of arsenic. In one of the mineral waters studied, the concentration of arsenic exceeded the maximum permissible level almost three times (Table 1), which might have been related to significant consumer exposure to that metal. However, in the case of spring waters, no arsenic concentration exceeding the maximum permissible concentration was found in any of the analyzed samples. In one of the samples tested, this metal's content reached over 90% of the normative value (Table 2). Among the analyzed heavy metals determined in mineral and spring waters, the lowest concentration was found for cadmium which was below the limit of detection (LOD) and 0.092 $\mu\text{g/L}$, respectively (Table 1 and Table 2). Additionally, mercury content was

Table 1. Mean concentrations of heavy metals in the analyzed mineral water samples.

Heavy metal concentration [$\mu\text{g/L}$]	N	$X \pm S$	M (IQR)	Level of detection (LOD)	Min.	Max.	Maximum permissible concentration [$\mu\text{g/L}$]
Arsenic	15	2.39 ± 7.07	0.30 (1.10)	0.24	< LOD	27.80	10
Cadmium	10	< LOD	0.00 (0.00)	0.038	< LOD	< LOD	3
Lead	10	0.04 ± 0.126	0.00 (0.00)	0.008	< LOD	0.40	10
Copper	10	0.31 ± 0.744	0.00 (0.18)	0.08	< LOD	2.40	1000
Mercury	no data	no data	no data	no data	no data	no data	1

Legend:

$X \pm S$ – mean \pm standard deviation

M (IQR) – median (interquartile range)

Min.- minimum value

Max.- maximum value

Table 2. Mean concentrations of heavy metals in the analyzed spring water samples.

Heavy metal concentration [$\mu\text{g/L}$]	N	$X \pm S$	M (IQR)	Level of detection (LOD)	Min.	Max.	Maximum permissible concentration [$\mu\text{g/L}$]
Arsenic	14	2.40 ± 3.381	0.85 (3.70)	0.24	< LOD	9.20	10
Cadmium	13	0.092 ± 0.175	0.00 (0.00)	0.038	< LOD	0.40	3
Lead	11	0.73 ± 2.412	0.00 (0.00)	0.008	< LOD	8.00	10
Copper	13	0.92 ± 2.759	0.00 (0.13)	0.08	< LOD	10.00	1000
Mercury	6	0.046 ± 0.081	0.00 (0.073)	0.07	< LOD	0.20	1

Legend:

$X \pm S$ – mean \pm standard deviation

M (IQR) – median (interquartile range)

Min.- minimum value

Max.- maximum value

determined in spring water samples, and its concentrations were within normal limits, reaching a maximum of 20% of the maximum allowable concentration (Table 2).

The analysis did not show statistically significant differences between mean metal concentrations in the analyzed mineral and spring waters ($p > 0.05$) (Table 3). Slightly higher contents of lead, copper, and cadmium were found in spring waters available on the Polish market compared to mineral waters (Table 3).

EXPOSURE AND HEALTH RISK ASSESSMENT

For the first exposure scenario assuming consumption of mineral and spring waters with a mean content of the tested heavy metals, it was shown that ingested metal doses did not pose a significant health risk to consumers. The hazard quotient values were less than unity ($HQ < 1$). It is noteworthy that exposure to arsenic results in one to two orders of magnitude higher HQ values than HQ resulting from exposure to lead or cadmium.

In the second scenario, which included consumption of the most heavily contaminated waters, significant health

risks were found for mineral waters consumers with the highest arsenic content. It was estimated that the ingested arsenic dose was more than twice the reference dose. A relatively high hazard quotient value ($HQ = 0.88$) was also calculated for consumers of spring waters most heavily contaminated with arsenic. Exposure representing more than one-third of the threshold dose was calculated for spring water consumers with the highest lead concentration (Table 4).

DISCUSSION

The conducted research showed the highest content of arsenic in the analyzed mineral and spring waters. The results are alarming due to this metal's strong toxic and carcinogenic properties [26, 27]. Frequent consumption of the analyzed waters containing such high concentrations of arsenic should be considered a significant health risk factor for consumers. The problem of strong contamination of waters with arsenic and, consequently, exposure of the public to this metal occurs in many countries, such as Australia, New Zealand, Thailand, India, Argentina, or Mexico [26, 28]. The highest concentrations of this metal

Table 3. Comparison of the content of selected heavy metals in the analyzed mineral and spring waters available on the Polish market in 2013-2016.

Mineral waters vs spring waters		N	X ± S [µg/L]	p-value (p < 0.05)
Arsenic	Mineral waters	15	2.39 ± 7.07	0.504539
	Spring waters	14	2.40 ± 3.381	
Cadmium	Mineral waters	10	< LOD	
	Spring waters	13	0.092 ± 0.175	
Copper	Mineral waters	10	0.31 ± 0.744	0.780185
	Spring waters	13	0.92 ± 2.759	
Lead	Mineral waters	10	0.04 ± 0.126	1.000000

Legend:

X ± S – mean ± standard deviation

Table 4. Exposure to heavy metals and health risks of consumers of analyzed mineral and spring waters.

Type of analyzed bottled waters	Metal	Exposure scenario			
		Scenario No 1		Scenario No 2	
		Dose µg/kg/day	HQ	Dose µg/kg/day	HQ
mineral waters	As	0.0683	0.228	0.7943	2.648
	Pb	0.0011	0.002	0.0114	0.018
spring waters	As	0.0686	0.229	0.2629	0.876
	Cd	0.0026	0.003	0.0114	0.011
	Pb	0.0209	0.033	0.2286	0.363

Table 5. The mean concentration of nitrates (V) in mineral waters available on the Polish market based on literature data [49, 50].

Mineral waters	N	X	S	Min.	Max.	Maximum permissible concentration	Source
Nitrates (V) concentration (NO ₃ mg/L)	10	2.31	0.406	0.62	6.66	10.0 ¹	Pasternakiewicz et al. (2014) [50]
	12	2.38	no data	0.05	12.37		Michalski et al. (1998) [49]

Legend:

X – mean

S – standard deviation

Min – minimum value

max – maximum value

¹The level of 10.0 (mg/L) refers to natural mineral waters extracted within the territory of the Republic of Poland**Table 6.** Nitrate (V) exposure and health risk to consumers of mineral waters available on the Polish market.

Nitrate (V) concentration (mg/L)	Intake (L)	body weight (kg)	dose mg/kg/d	RfD mg/kg/d	HQ	Source
Min.	2	70	0.018	1.60	0.01	Pasternakiewicz et al. (2014) [50]
Mean			0.066		0.04	
Max.			0.190		0.12	
Min.	2	70	0.001	1.60	0.00	Michalski et al. (1998) [49]
Mean			0.068		0.04	
Max.			0.353		0.22	

are found in Bangladesh, which are 0.5 – 2500 µg As/L. It has been estimated that 10% of this country's population consumes water containing more than 500 µg As/L. The

reason for such substantial arsenic contamination of water is the ingress of industrial and municipal wastewater and plant protection products [29].

In Poland, tap water intended for consumption is subject to continuous monitoring by Sanitary and Epidemiological Stations and is within the maximum permissible concentrations. Bottled waters, the consumption of which has significantly increased in recent years, can be a potential source of public exposure in Poland. According to its definition, mineral water should be characterized by absolute quality and purity [6]. In the present study, the above-normative concentration of arsenic was demonstrated in mineral waters. The content of this element exceeded the standard almost three times (10 µg/L) [8]. Moreover, elevated concentrations of arsenic were also noted in samples of spring waters commonly consumed by the public. As indicated in the literature data, other authors also showed high arsenic contents in Polish mineral waters [11].

The study carried out by Drobik et al. (2008) demonstrated that the maximum permissible concentration of arsenic was exceeded in 4 out of 10 intakes in Polish thermal stations [21]. Excessive exposure to arsenic may result in such symptoms as nausea, headache and abdominal pain, vomiting, diarrhea, dry mouth, weight loss, and anemia [30]. On the other hand, high doses of arsenic ingested in the long-term with consumed water can cause cardiovascular, reproductive, and nervous system disorders, skin lesions, and cancer. The International Agency for Research on Cancer (IARC) has classified arsenic in a Group I cancer risk in humans [4, 31]. As indicated by the health risk assessment results in this study, consumption of the most contaminated mineral waters is associated with a high health risk. The estimated dose more than two and a half times exceeded the reference dose's threshold value. It is worth mentioning that arsenic enters the human body mainly with food. Exposure to this metal can result from eating contaminated rice, fish, and seafood. Therefore, the total dose of arsenic entering the body of consumers consuming such highly contaminated waters may be much higher and translate into even more significant health risks.

Mercury also belongs to the group of the most toxic heavy metals [32]. The human body accumulates it in kidneys, liver, and the nervous system [17]. The studies did not show above-normal mercury content in the analyzed spring waters. The absence of even trace mercury content was also found in mineral waters studied by Chorotyński et al. (2018) [33]. On the other hand, almost one hundred times higher concentration of this metal (19 µg/L) in comparison with the most heavily contaminated sample studied in the present work (0.2 µg/L) was found in mineral waters analyzed in the paper by Wojciechowska-Mazurek et al. (2010) [34]. Based on the results obtained by the Provincial Sanitary and Epidemiological Station in Katowice, mercury concentrations revealed in bottled waters available on the Polish market do not pose a health risk to consumers.

Lead was another toxic metal included in the study. Lead shows harmful effects on nervous system functions, especially in children. Moreover, it has a detrimental impact on bone tissue, hematopoietic system, fertility, and embryotoxicity [17, 35, 36]. The conducted studies showed higher

mean lead concentrations in spring waters than mineral waters, which were 0.73 µg/L and 0.004 µg/L, respectively. On the other hand, Długaszek et al. (2006) reported higher lead content in mineral waters than in spring waters [14]. In the cited study, the highest concentrations of lead were found in such mineral waters as "Kazimierz" and "Muszynianka" [37]. According to the results of the study, the most contaminated spring water sample contained as much as 8 µg lead/L, whereas the maximum permissible lead content in bottled waters is 10 µg/L. The health risk assessment showed that the exposure of consumers of such waters is more than one-third of the BMDL10, which defines a safe exposure sample. Because lead enters the human body in the greatest amounts with edible plants, exposure associated with spring water consumption may significantly contribute to health risks.

Cadmium was found to have the lowest concentration. In mineral waters, this metal's content did not exceed the level of quantification, and in spring waters, the mean concentration reached 0.09 µg/L. Also, low cadmium content in the range of 0.01-0.13 µg/L was shown in other studies carried out in bottled waters available on the Polish market [14]. Due to trace amounts of cadmium found in analyzed waters, the health risk for consumers of such products is negligible. The obtained results should be considered favorable as cadmium is a highly toxic metal, causing many disorders in a human organism, such as bone system damage, harmful effect on pregnancy, and carcinogenicity [38, 39].

The copper content in bottled waters available on the Polish market was also investigated within this research. Copper is a biogenic element essential for the proper functioning of the human organism. However, excessive supply of this element may have toxic effects. Exposure to high doses of copper may decrease hemoglobin concentration in blood, liver, kidney damage, immune system dysfunction, diarrhea, or intestinal cramps [40, 41, 42]. The analyses conducted in this study indicated low copper content in the assessed mineral waters (0.31 µg/L) and spring waters (0.92 µg/L). Literature data confirms the occurrence of trace amounts of copper in bottled waters. This element's significantly higher content was demonstrated in mineral waters from Rymanów, Kudowa, and Szczawno [6]. Higher concentrations of copper are also noted in water coming from the water supply system, resulting from more and more frequent use of copper pipes. Studies confirm that in households equipped with such systems, there may occur cases of excessive concentrations of copper in water intended for consumption [43]. Therefore, it is recommended that the inhabitants of households where copper was used in water installation should use bottled water as an alternative to tap water.

Inorganic anions such as nitrates (III, V) are another group of compounds that can occur in drinking water. Nitrate contamination of water is most commonly reported in domestic wells located in rural areas [44-46]. Exposure to nitrates can result in the development of methemoglobinemia, the main symptoms of which are red coloration

of the skin, a drop in blood pressure, and cyanosis, occurring as a result of tissue hypoxia [19, 47]. Nitrates are also precursors of carcinogenic nitrosamines, which may cause, among others, esophageal, gastric, pancreatic, colorectal, ovarian, breast, and hematopoietic cancers [48]. According to the literature data, nitrates may also occur in bottled waters available on the Polish market. Studies carried out at the end of the 20th century showed that the highest permissible level was exceeded in one of the mineral waters studied (12.37 mg/L) [49]. The results of the cited studies are summarized in Table 5.

Based on the above results, the exposure and health risk assessment of consumers did not reveal a significant health risk, regardless of whether the minimum, mean, or highest nitrate (V) concentrations shown in the referenced papers were included in the estimates (Table 6). Thus, it can be concluded that adults' exposure to nitrate consuming bottled waters, unlike some metals, is not a significant health risk factor.

CONCLUSIONS

1. The content of analyzed metals in the studied mineral and spring waters did not exceed the maximum allowable concentrations. The exception is one of the analyzed mineral waters, in which an above-normal concentration of arsenic was found.
2. Consumption of the most heavily contaminated mineral waters may be associated with high consumer exposure to arsenic resulting in a significant health risk.
3. Literature data indicate relatively low content of nitrates (V) in bottled waters available on the Polish market. Consumption of such mineral waters is not a significant source of exposure and does not translate into a significant health risk for consumers.
4. To ensure consumers' health safety, there is a need to monitor the content of potentially harmful compounds in mineral and spring waters available on the Polish market.

REFERENCES

1. Łubkowska B. Rola wody w życiu człowieka i środowisku. In: Podgórska W (ed.). *Żywność i środowisko*. Gdańsk: Wydawnictwo Wyższej Szkoły Zarządzania, 2016, pp. 20-37.
2. Petracchia L, Liberati G, Masciullo SG et al. Water, mineral waters and health. *Clin Nutr*. 2006;(25):377-85.
3. Skotnicka M, Rohde D, Kłobukowski F. Zapotrzebowanie na wodę i ocena jej pobrania wśród osób starszych. In: Podgórska W (ed.). *Żywność i środowisko*. Gdańsk: Wydawnictwo Wyższej Szkoły Zarządzania; 2016, pp. 38-50.
4. Jarosz M. Normy żywienia dla populacji polskiej – nowelizacja. Warszawa: Instytut Żywności i Żywienia; 2017.
5. Kłos L. Spożycie wody butelkowanej w Polsce i jej wpływ na środowisko przyrodnicze. *Barometr Regionalny*. 2016;14(1):111-117.
6. Salomon A, Regulska-Iłow I. Polskie butelkowane wody mineralne i lecznicze – charakterystyka i zastosowanie. *Bromatol Chem Toksykol*. 2013;46(3):53-65.
7. Ustawa z dnia 25 sierpnia 2006 roku o bezpieczeństwie żywności i żywienia, Dz. U. 2006 nr 171 poz. 1225.
8. Rozporządzenie ministra zdrowia z dnia 31 marca 2011 r. w sprawie naturalnych wód mineralnych, wód źródlanych i wód stołowych, Dz. U. 2011 nr 85 poz. 466.
9. Dyrektywa Parlamentu Europejskiego i Rady nr 2009/54/WE z dnia 18 czerwca 2009 roku w sprawie wydobywania i wprowadzania do obrotu naturalnych wód mineralnych.
10. Ustawa z dnia 7 czerwca 2001 roku o zbiorowym zaopatrzeniu w wodę i zbiorowym odprowadzaniu ścieków, Dz. U. 2001 nr 72 poz. 747.
11. Ponikowska I, Latour T. Rekomendacje Polskiego Towarzystwa Balneologii i Medycyny Fizykalnej w zakresie zmian w klasyfikacji wód leczniczych. *Acta Balneol*. 2017;1(147):77-78.
12. Wojtaszek T. Woda mineralna jako czynnik ekologicznej profilaktyki zdrowotnej. *J Elementol*. 2006;11:399-403.
13. Piech AP, Baszak A. Pierwiastki śladowe w wybranych wodach mineralnych dostępnych w handlu. *JCEEA*. 2016;63(4):419-432.
14. Długaszek M, Szopa M, Graczyk A. Zawartość metali ciężkich w polskich wodach mineralnych i źródlanych. *J Elementol*. 2006;11(3):243-248.
15. Astel A, Michalski M, Bigus K et al. Fakty i mity o wodzie do spożycia. *LAB*. 2019;19(2):6-14.
16. Hozyasz KK, Ruszczyńska A, Bulska E. Zanieczyszczające pierwiastki w butelkowanych niegazowanych wodach. *Nowa Pediatr*. 2005;(4):128-130.
17. Ociepa-Kubicka A, Ociepa E. Toksyczne oddziaływanie metali ciężkich na rośliny, zwierzęta i ludzi. *Inż Och Środ*. 2012;15(2):169-180.
18. Dżugan M, Pasternakiewicz A. Ryzyko zdrowotne związane z występowaniem azotanów w wodach pitnych. *Zdr Publ*. 2007;117(3):364-368.
19. Bilek M, Rybakowa M. Azotany (III) i (V) w wodzie pitnej studni kopanych i wierconych z terenu Podkarpacia, jako czynniki ryzyka methemoglobinemii. *Przeg Lek*. 2014;71(10):520-522.
20. Rudnicka A, Hozyasz KK. Praktyczne aspekty wyboru wody w żywieniu zdrowych niemowląt i młodszych dzieci. *Pediatr Med Rodz*. 2018;14(1):33-46.
21. Drobik M, Latour T, Sziwa D. Ocena ryzyka zdrowotnego związanego z narażeniem na potencjalnie toksyczne składniki wód leczniczych. *Balneol Pol* 2008;1:60-67.
22. Weker H, Więch M. Woda w żywieniu dziecka. Podstawowe kryteria oceny. *Bromatol Chem Toksykol*. 2004;1(37):321-324.
23. Integrated Risk Information System (IRIS). U.S. Environmental Protection Agency. Chemical Assessment Summary. National Center for Environmental Assessment. Arsenic, inorganic; CASRN 7440-38-2. Washington (DC): US EPA; 1991.
24. Integrated Risk Information System (IRIS). U.S. Environmental Protection Agency. Chemical Assessment Summary. National Center for Environmental Assessment. Cadmium; CASRN 7440-43-9. Washington (DC): US EPA; 1989.
25. European Food Safety Authority (EFSA). EFSA Panel on Contaminants in the Food Chain (CONTAM); Scientific Opinion on Lead in Food. *EFSA Journal* 2010;8(4):1570. [151 pp.]. doi:10.2903/j.efsa.2010.1570.
26. Jaymie R, Meliker, Franzblau A, Slotnick MJ et al. Major contributors to inorganic arsenic intake in southeastern Michigan. *Int J Hyg Environ Health*. 2006;209:399-411.
27. Piotrowski J. Podstawy toksykologii. Warszawa: Wydawnictwo Naukowo-Techniczne, 2006.
28. Skoczyńska A. Arsen w środowisku człowieka. *Med Środow*. 2018;21(1):7-19.
29. Łoźna K, Biernat J. Występowanie arsenu w środowisku i w żywności. *Rocz PZH*. 2008;59(1):19-31.

30. Hall AH. Chronic arsenic poisoning. *Toxicol Letters*. 2002;128:69-72.
31. Vahidnia A, Romijn F, Tiller M. Arsenic-induced toxicity: effect on protein composition in sciatic nerve. *Hum Exp Toxicol*. 2006;(25):667-674.
32. Cyran M. Wpływ środowiskowego narażenia na rtęć na funkcjonowanie organizmu człowieka. *Med Środow*. 2013;16(3):55-58.
33. Chorostyński A, Łach A, Pasztyła G. Parametry fizykochemiczne i bakteriologia odkrytych wód mineralnych i siarczkowych w okolicach. *Acta Sci Pol Formatio Circumiectus*. 2018;17(1):113-126.
34. Wojciechowska-Mazurek M, Starska K, Mania M et al. Monitoring zanieczyszczenia żywności pierwiastkami szkodliwymi dla zdrowia. Część II. Wody mineralne, napoje bezalkoholowe, owoce, orzechy, ryż, soja, ryby i owoce morza. *Roczn PZH*. 2010; 61(1):27-35.
35. Szymański K. Związki ołowiu i chromu w środowisku naturalnym i odpadach. *Rocz Ochr Sr*. 2009;11:173-181.
36. Dobrakowski M, Kiełtucki J, Wyparto-Wszelaki M et al. Wpływ przewlekłego zatrucia ołowiem na zmiany patofizjologiczne w układzie pokarmowym oraz interakcje ołowiu z wybranymi mikroelementami. *Med Środow*. 2013;16(3):42-46.
37. Łęska J, Bajek D, Nowicki D et al. Oznaczanie ołowiu i kadmu w wodzie pitnej, metodą atomowej absorpcyjnej spektrometrii z wzbudzeniem elektrotermicznym (gfaas). *Chem Environ Biotechnol*. 2018;(21):26-29.
38. Czeczot H, Majewska M. Kadm – zagrożenie i skutki zdrowotne. *Toksykologia*. 2010;(66)4:243-250.
39. International Agency for Research on Cancer (IARC): Beryllium, cadmium, mercury, and exposure in the glass manufacturing industry. *Monographs on the Evaluation of the Carcinogenic Risks to Humans*. IARC Scientific Publications Lyon. 1993;58:119-239.
40. Piontek M, Fedyczak Z, Łuszczynska K et al. Toksyczność miedzi, cynku oraz kadmu, rtęci i ołowiu dla człowieka, kregowców i organizmów wodnych. *Zeszyty Naukowe. Inżynieria Środowiska*. 2014;155(135):70-83.
41. Aoyagi S, Baker D. Copper-amino acid complexes are partially protected against inhibitory effects of L-cysteine and L-ascorbic acid on copper absorption in chicks. *J Nutrit*. 1993;124(3):388-395.
42. Seńczuk W. *Toksykologia współczesna*. Warszawa: Wydawnictwo PZWL; 2006, pp. 360-442.
43. Doscocz M, Konstanciu J, Skrzymowski J et al. Miedź w wodzie pitnej. Zagrożenia związane z zanieczyszczeniem wtórnym wody. *Badania wstępne. Otwarta Innowacja*. 2018;1(2).
44. Tomczyk K, Dziubanek G. Azotany (III, V) jako istotne czynniki ryzyka zdrowia. In: Kujawski J, Doscocz J (eds). *Innowacje w Polskiej Nauce: przegląd aktualnej tematyki badawczej branży chemicznej*. Katowice: Wydawnictwo Naukowe Sophia, 2016, pp. 109-116.
45. Szczurbiński R, Karczewski J, Fiłon J. Azotany (V) w wodzie do picia, jako czynnik ryzyka zdrowotnego ludności województwa podlaskiego. *Rocz PZH* 2006;57(1):39-48.
46. Wójcik-Jackowski S, Bilek M. Woda z „prywatnych” ujęć wody pitnej jako czynnik ryzyka zdrowia człowieka w świetle badań jej jakości na tle obowiązujących uregulowań prawnych. *Bromat Chem Toksykol*. 2015;48:216-222.
47. Wierniowski A, Pach J. Kliniczna problematyka methemoglobinemii toksycznych. *Arch Med Sąd Krym*. 1998;117-125.
48. Kościańska B, Rodecka-Gustaw E. Nawozy sztuczne, azotyny, a nowotwory złośliwe. *Med Og Nauk Zdr*. 2017;(1):033-038.
49. Michalski R. Wybrane jony nieorganiczne w wodach mineralnych. *Przegł Geol*. 1998;46(9/2):698-971.
50. Pasternakiewicz A, Bilek M, Stawarczyk K. Badania zawartości wybranych anionów nieorganicznych w wodach mineralnych i źródłanych – pod kątem bezpieczeństwa zdrowotnego wody. *Probl Hig Epidemiol*. 2014;95(3):788-793.

ORCID and contributionship:

Katarzyna Tomczyk – 0000-0002-1978-4920 ^{A, C, D}
 Grzegorz Dziubanek – 0000-0002-1972-7221 ^{A, E, F}
 Anna Kowalska – 0000-0003-3722-6102 ^B
 Iwona Szymala – 0000-0001-5683-0335 ^B
 Beata Łabuz-Roszak – 0000-0002-9835-8240 ^{E, F}

Conflict of interest:

The Authors declare no conflict of interest.

CORRESPONDING AUTHOR

Katarzyna Tomczyk

Doctoral Studies of the Department of Environmental Health,
 Unit of Environmental Health Risk Factors,
 Medical University of Silesia in Katowice, Bytom, Poland
 e-mail: ktomczyk@sum.edu.pl

Received: 31.12.2021

Accepted: 05.05.2021

A – Work concept and design, **B** – Data collection and analysis, **C** – Responsibility for statistical analysis,
D – Writing the article, **E** – Critical review, **F** – Final approval of the article