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ORIGINAL PAPERS

CALCIUM AND MAGNESIUM CONTENT IN TREATED WATERS AND THEIR TOTAL HARDNESS

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Abstract

Household water is subject to special protection, as confirmed by the number of evaluated parameters, of which hardness and magnesium content deserve special attention. On the other hand, although calcium is not a limiting constituent although its concentration as well as the calcium compounds affect water hardness. Therefore, calcium is an element which is usually determined in raw water, after treatment as well as at the end-user. For hygienic reasons, particular attention is paid to magnesium concentration in water as well as quantitative relations between Mg and Ca.

The aim of the study was to determine water hardness and the content of calcium and magnesium in treated water intended for consumption by residents of the town of Leszno. The investigations were carried out in 2006-2009 on water samples derived from three water intakes and a water treatment plant. Water samples were collected in accordance with the PN-ISO 5667 standard and the aforementioned parameters were determined with the assistance of the ethylene diamine tetraacetic acid (EDTA) method (PN-ISO 6059).

Total hardness of the examined waters ranged from 192.0 to 410.0 mg $CaCO_3$ dm^{-3}, averaging 334.9±33.16 mg $CaCO_3$ dm^{-3}. The above values, despite apparently high extreme ranges with respect to mean values, were similar between the examined intakes and years, not showing any statistically significant differences.

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Calcium concentrations in the examined waters ranged from 24.7 to 152.4 mg dm^{-3}, on average 73.46±31.15 mg dm^{-3}, while those of magnesium from 1.6 to 107.1, on average 20.45±27.77 mg dm^{-3}. It is evident from the analysis of the experimental data that the overall hardness of the examined waters failed to correlate with calcium and magnesium concentrations. On the other hand, positive correlation was observed between calcium and magnesium concentrations. It was also concluded that, after treatment, household water in Leszno met the qualitative requirements of the examined parameters. The recorded mean water values showed that household waters in Leszno can be described as moderately hard of lowered magnesium concentration.

Key words: household water, hardness, calcium, magnesium.

OKREŚLENIE TWARDOŚCI OGÓLNEJ I ZAWARTOŚCI WAPNIA I MAGNEZU W WODACH UZDATNIONYCH

Abstrakt

Woda do konsumpcji podlega szczególnej ochronie, o czym świadczy liczba parametrów jej oceny. Wśród nich należy wyróżnić twardość oraz zawartość magnezu. Z kolei wapń nie jest składnikiem limitowanym, ale jego koncentracja i związki składają się na twardość wody, dlatego jest on pierwiastkiem na ogół oznaczanym zarówno w wodach surowych, po uzdatnieniu, jak i u odbiorcy. Ze względów zdrowotnych szczególną uwagę zwraca się na koncentrację magnezu w wodach oraz na relacje ilościowe między Mg i Ca.

Celem pracy było określenie twardości oraz zawartości wapnia i magnezu w wodach uzdatnionych przeznaczonych do spożycia dla mieszkańców miasta Leszna. Badania przeprowadzono w latach 2006-2009 na próbkach wód pochodzących z trzech ujęć i stacji uzdatniania wody. Próbki wód pobierano zgodnie z normą PN-ISO 5667, a powyższe parametry oznaczono metodą wersenianową (PN-ISO 6059). W okresie badań zanalizowano ogółem 270 próbek na twardość oraz po 30 próbek na zawartość wapnia i magnezu.

Twardość ogólna wód kształtowała się od 192,0 do 410,0 mg $CaCO_3$ dm^{-3}, średnio 334,9±33,16 mg $CaCO_3$ dm^{-3}. Wartości te mimo pozornie dużych zakresów skrajnych pod względem średnich są zbliżone między ujęciami i latami, co skutkowało brakiem istotnych statystycznie różnic.

Stężenie wapnia w wodach wynosiło od 24,7 do 152,4 mg dm^{-3}, średnio 73,46±31,15 mg dm^{-3} a magnezu od 1,6 do 107,1, średnio 20,45±27,77 mg dm^{-3}. Z analizy danych wynika, że twardość ogólna wód nie korelowała z koncentracją wapnia i magnezu, natomiast stwierdzono dodatnią zależność korelacyjną między koncentracją wapnia i magnezu. Stwierdzono, że po uzdatnieniu, wody do konsumpcji w Lesznie spełniały normy jakościowe badanych parametrów. Według średnich wartości, wody te zaliczono do średnio twardych o zaniżonej koncentracji magnezu.

Słowa kluczowe: woda do spożycia, twardość, wapń, magnez.

INTRODUCTION

Owing to its role in sustaining life on Earth, water is subject to special protection, necessary because of reduced water resources and growing human pressure. Changes in the chemical composition of water are among the consequences of man-made pressure (JIANG et al. 2009). Therefore, appropriate legal regulations for protection of water, nature and man are implemented in many countries. In such context, potable water gains in significance – specific bacteriological, physicochemical and sensory requirements as well as directives related to monitoring, water supply network construction etc., have been formulated in Poland (*Regulation* … 2007). Among numerous parameters of water quality assessment, magnesium content and hardness are crucial. The Polish legal acts do not contain any regulations referring to calcium limits although the element is determined during water hardness tests.

Hard water sometimes causes considerable technical and exploitation problems in public water supply mains or industrial installations, for example due to limescale formation. Magnesium present in waters mainly affects human, animal and plant health. The element can activate about 300 enzymes and takes part in many metabolic processes (MARX, NEUTRTA 1997). Magnesium can influence smooth muscles, thrombocytes and cardiac muscle cells (RAYSSIGUIER GUEUX 1986, WASTON et al. 1986, HATTORI et al. 1988, CHRYSANT et al. 1988). A survey conducted in many countries has indicated some dependence between magnesium concentration in drinking water and diet versus ischemic heart disease (MARX, NEUTRTA 1997). Thus, it is necessary to provide people with appropriate amounts of magnesium to ensure good balance of elements in our bodies (ELIN 1988). Calcium present in waters should be taken into account in terms of its role in physiological processes as well as the formation of the Ca:Mg ratio (KOUSA et al. 2006), which is important during metabolic magnesium transformations. Thus, presence of both elements in drinking water brings health considerations although no content limits have been set for calcium. Numerous reports also reveal dependence between hard waters and some diseases and disorders which can be associated with both magnesium and calcium concentrations. Therefore, continuous monitoring and quality assessment of treated waters that includes the three above indicators seems justifiable and reasonable.

The present study aimed at an assessment of the quality of potable water in Leszno based on three parameters: hardness, calcium content and magnesium content.

MATERIAL AND METHODS

Residents of Leszno (51°51´N and 16°34´E) are provided with drinking water at three water intake points connected to a water treatment plant, which are localized in Zaborowo, Karczma Borowa, and Strzyżewice, all within the borders of the town. Each of these intake points has its own wells 20 to 150 m^3 h^{-1} in capacity. The water intake point in Zaborowo consists of

5 drilled wells (21.2 to 28 m), which collect underground water from the Quaternary layer; the point in Karczma Borowa has 3 wells, which also exploit Quaternary waters; the water intake point in Strzyżewice has 4 wells collecting water from the Tertiary layer (down to 120 m), 4 wells (down to 30 m) from the Quaternary, and a single well (down to 60 m) from deep levels of the Quaternary layer. Fresh underground waters are characterized by elevated iron, manganese, and ammonia concentration, hence they are treated by means of open aeration in Strzyżewice (hydrosulfide presence) as well as closed aeration, filtration (rapid pressure filters), and emergency disinfection at other water intake points.

Treated water samples were collected for analyses in accordance with the norm PN-ISO 5667 (2003). Water hardness (n=270), calcium (n=30), and magnesium content (n=30) were determined according to the PN-ISO 6059 (1999) norm.

RESULTS AND DISCUSSION

In general, underground waters cannot occur in a chemically pure form because they contain dissolved gases and minerals in various concentrations and therefore they should be treated before reaching the water supply system.

Due to its unquestionable importance in man's life, water is subject to rigorous control, which the WHO's guidelines (2004) as well as latest Polish legal acts included in the Decree of the Minister for Health (2007) can prove. These acts consider the microbial, sensory, physicochemical, and radiological survey of drinking water as necessary. Besides, Appendix No 4 sets additional chemical requirements that drinking water should meet: hardness and magnesium content. Calcium has not been limited in drinking water.

Hardness is an insignificant parameter for hygienic and sanitary properties of water; however, it is important in industry and economy and that is why determination of its level is part of water quality assessment. According to the Polish Norms (*Regulation*… 2007), its permissible range is from 60 to 500 mg dm^{-3} recalculated as calcium carbonate. Treated waters in Leszno were characterized by a relatively high stability of the parameters in question over the studied period (Table 1).

For all the data (n=270), the parameter values oscillated within the range from 192 to 412 mg $CaCO_3$ dm^{-3}, with slightly higher differences between water treatment stations (SUW) than between the years: in Zaborowo 330.4 mg $CaCO_3$ dm^{-3}, in Karczma Borowa 321.5±32.89 mg $CaCO_3$ dm^{-3}, and in Strzyżewice 352.7±28.94 mg $CaCO_3$ dm^{-3}, on average. The mean water hardness value for the years and SUW's reached 334.9±33.16 mg $CaCO_3$ dm^{-3}.

Table 1

Hardness of treated water (mg $CaCO_3$ dm^{-3})

Site of water collection and processing	Years				Mean n=270	SD*
	2006	2007	2008	2009		
Zborowo	240-370	270-380	296-372	304-372	330.4±29.71	29.71
Karczma Borowa	240-390	192-370	286-382	293-412	321.5±32.89	22.89
Strzyżewice	290-410	300-410	292-394	307-380	352.7±28.94	28.94
Mean	332.0±46.39	348.4±36.83	338.0±24.75	335.9±22.84	334.9±33.16	33.16
SD	46.39	36.83	24.75	22.84	-	-

*Standard deviation

The extreme values (192 and 412 mg $CaCO_3$ dm^{-3}) occurred only once, which did not affect the total result of the parameter. The data listed in the above table classify the treated water from Leszno from 10.7°dH to 23.0°dH, with the mean level of 18.7^0dH. However, a problem of choosing the most appropriate hardness scale can arise, because literature contain different scales. i.e. some cite a 5-grade scale, while others rely on a 6-grade scale but in other ranges of $CaCO_3$ dm^{-3} mg content or hardness degrees (°dH). Referring the parameters of the above assessment to BISZOF'S norms (2010), the analyzed waters can be considered as moderately hard.

Considering water hardness, reports on less sudden deaths due to acute cardiac infarction at women from populations drinking harder waters are appearing more frequently (RUBENOWITZ et al. 1999). On the other hand, MIYAKE and IKI (2003) did not report significant dependence between hard water and mortality resulting from cardiovascular and cerebrovascular diseases. Earlier studies presented high mortality due to coronary heart disease in Australia, where large amounts of soft water are drunk, in contrast to the smallest number of deaths in western Texas, where drinking water is very hard (SHARMA 2010, cit. after ASHMEAD 1981).

Statistical analysis of our data reveals that the hardness of treated water did not correlate with the calcium and magnesium content, which means that the former was probably determined by other substances present in water and not analyzed in the study. Instead, positive dependence between calcium and magnesium concentrations in the analyzed water samples was found (Figure 1). Interactions between both elements are common, although scientists cannot agree about an optimum ratio between these elements in waters. Conventionally, it is assumed as a 2:1 ratio (DURLACH 1989), but recent studies indicate it should be modified due to higher magnesium requirements for an organism (SHARMA 2010). KISS et al. (2004) claim that the

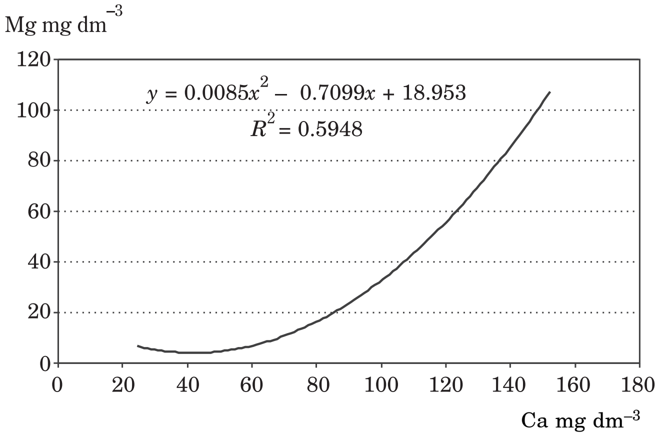

Fig. 1. Relationship between of total concentrations of calcium and of magnesium in water

ionic calcium to magnesium ratio is better for dietetic and sanitary evaluation of water than the ratio of their concentrations. It is obvious that the question of a ratio between calcium and magnesium in potable water is important because of its effect on human health.

Calcium and magnesium concentrations in the analyzed treated water samples varied, as demonstrated by their absolute content and values of standard errors (Table 2). The quantitative range for calcium oscillated around 24.7 to 152.4 mg Ca dm^{-3} (mean 73.46±31.15 mg Ca dm^{-3}) at the variability of V=42.4%. In the case of magnesium, the range was even wider: from 1.6 to 107.1 mg Mg dm^{-3}, at the average level of 20.45 mg Mg dm^{-3} and the variability coefficient V=135.8%. The quantitative variability of calcium and magnesium in waters results from numerous factors, including geological ones. It is particularly evident during the water intake and while mixing waters originating from different water-bearing layers, which usually differ in their hydrochemical properties (BUCZYŃSKI, MODELSKA 2005). Furthermore, some authors point to the fact that the Quaternary layers can be separated from the ground level in different ways, which may increase the risk of contamination of those water layers.

Presence of many elements and substances in underground waters is a natural feature, which largely depends on the geological subsoil. Depending on the structure and elution intensity, both calcium and magnesium are transferred to waters in different amounts. However, changes in the physical and chemical composition of waters, which can occur during particular stages of its distribution, cannot be excluded (WONS 2007). It is therefore necessary to monitor water quality at each stage, not only to prevent some undesirable phenomena can arise (e.g. during industrial processes), but also to protect human health, e.g. by controlling the amounts of calcium and

Table 2

Concentrations of calcium and magnesium in water (mg dm^{-3})

<table>
<tr><th rowspan="2">Element</th><th colspan="3">Site of water collection and processing</th><th rowspan="2">Mean
n=30</th><th rowspan="2">SD</th></tr>
<tr><th>Zborowo</th><th>Karczma Borowa</th><th>Strzyżewice</th></tr>
<tr><td>Calcium (Ca)</td><td>24.7-108.1</td><td>24.9-116.8</td><td>26.4-152.4</td><td rowspan="3">73.46</td><td rowspan="3">31.15</td></tr>
<tr><td>Mean</td><td>71.61</td><td>69.89</td><td>78.88</td></tr>
<tr><td>SD</td><td>29.43</td><td>28.81</td><td>37.14</td></tr>
<tr><td>Magnesium (Mg)</td><td>1.6-97.4</td><td>1.6-98.3</td><td>1.6-107.1</td><td rowspan="3">20.45</td><td rowspan="3">27.77</td></tr>
<tr><td>Mean</td><td>20.32</td><td>19.09</td><td>21.94</td></tr>
<tr><td>SD</td><td>27.67</td><td>28.12</td><td>30.41</td></tr>
</table>

magnesium, which have direct impact on water hardness. For many years, medical sciences have devoted much efforts to the above issues, for example studying the correlation between hard water and various diseases, including prostate cancer (Yang et al. 2000). Besides, water quality is important in agriculture, both for animal and plant nutrition, e.g. irrigation and spraying. It is possible to hydrolyze some active substances in water in order to repress their action. On the other hand, antagonistic effects of water-soluble salts towards chemically active substances contained for example in herbicides can appear. Thus, the problem of drinking water quality gains in importance although the health aspects seem to be a priority. In such a view, the abundance and forms of magnesium in waters are doubtless one of the more important scientific issues to study in the nearest future.

CONCLUSIONS

1. The analyzed waters, after treatment, were characterized by stable hardness, regardless of the year, sample collection locality or the treatment site.

2. The treated underground waters in Leszno can be classified as moderately hard and the hardness scale did not significantly depend on the calcium and magnesium content.

3. The calcium and magnesium concentrations in the waters were characterized by high quantitative variability, first of all over time and then depending on a sampling site, indicating possible influence of geological factors on the content of both elements.

4. In most of the samples, the water contained less magnesium than recommended.

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