Metasilicic acid in thermal water from Banska PGP-1 well, Podhale

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ABSTRACT

This paper presents a characteristics and analysis of concentration stability of metasilicic acid in thermal waters exploited by Bańska PGP-1 well, using the results of the chemical composition conducted in the years 2014–2015. Statistical analysis was performed using IBM SPSS Statistics and assessment of trends by GWSDAT software (Jones, Spence, 2013). This assessment shows that the concentration of metasilicic acid in thermal water from Bańska PGP-1 can be classified as stable.

1. INTRODUCTION

The use of thermal waters in Poland grows in popularity for several years. Subsequent sectors interested in their properties, looking for new possibilities of using these waters. Areas where more and more valued are thermal waters are recreation, balneotherapy and cosmetology.

In European Union law, there are no regulations directly applicable to medicinal waters. These waters are subject to the general requirements contained in Directive 2001/83/EC of the European Parliament and of the Council of 6 November 2001 on the Community code relating to medicinal products for human use (Directive 2001) as amended by Directive 2004/27/EC of 31 March 2004 (Directive 2004). The Directives neither provide any definition of curative waters nor specify any parameters that determine their medicinal qualities (Wątor et al., 2016).

However, in Poland, to apply the thermal waters in different kinds of therapies, it is necessary to carry out tests which allow determining the chemical composition and its variability over time. According to Polish law, it is necessary to check the stability of the chemical composition, particularly specific components, to qualify waters as a curative water. Stability of the chemical composition should base on at least 3 years studies. Discussion of legislation on this issue and an example of the assessment of the medicinal character of waters, using probabilistic method, can be found in the publication Wątor et al. (2016).

According to Polish Geological and Mining law ([Dz.U] No. 163/2011, item 987), medicinal water is groundwater, which is not contaminated in terms of chemical and microbiological. It is also characterized by the natural variability of physical and chemical characteristics, and also it has a sufficiently high concentration of the specific component. The concentration of metasilicic acid in silica waters should be not less than 70 mg/L (GML, 2011).

Daily human demand for silicon is 20–30 mg. Silicon is involved in many metabolic processes. Silica is used in the treatment of tuberculosis, cancer and ulcer disease. It helps in treating the elderly people, among others effect on slowing down the process of aging, sclerosis, atrophy of the thymus (Skrzypczak, 2012). Silicon compounds also play an important role in the proper functioning of the skin — are involved in intercellular communication, influencing regulate the metabolism, accelerate the healing process (Exley et al., 2006; Jugdaohsingh et al., 2002; Jugdaohsingh 2007; Klempous et al., 1998 ; Maehira et al., 2008; Sripanyakorn et al., 2005, 2009; Schwarz et al., 1997). What is also important for the cosmetics industry, silicon compounds soften the collagen fibers (Goldman et al., 2007; Sapińska-Śliwa et al., 2009). It is believed that the silicon improves bone mineralization, slowing their decalcification and accelerates regeneration after injuries (Dobrzyński, Exley, 2010).

So many medicinal properties of silicon determined the growing interest in the silica waters in industry balneological and cosmetic (Goldman et. al., 2007).

2. CHARACTERISTIC OF THE RESEARCH AREA

Bańska PGP-1 well is located in Bańska Niżna village in Małopolska province (fig. 1).

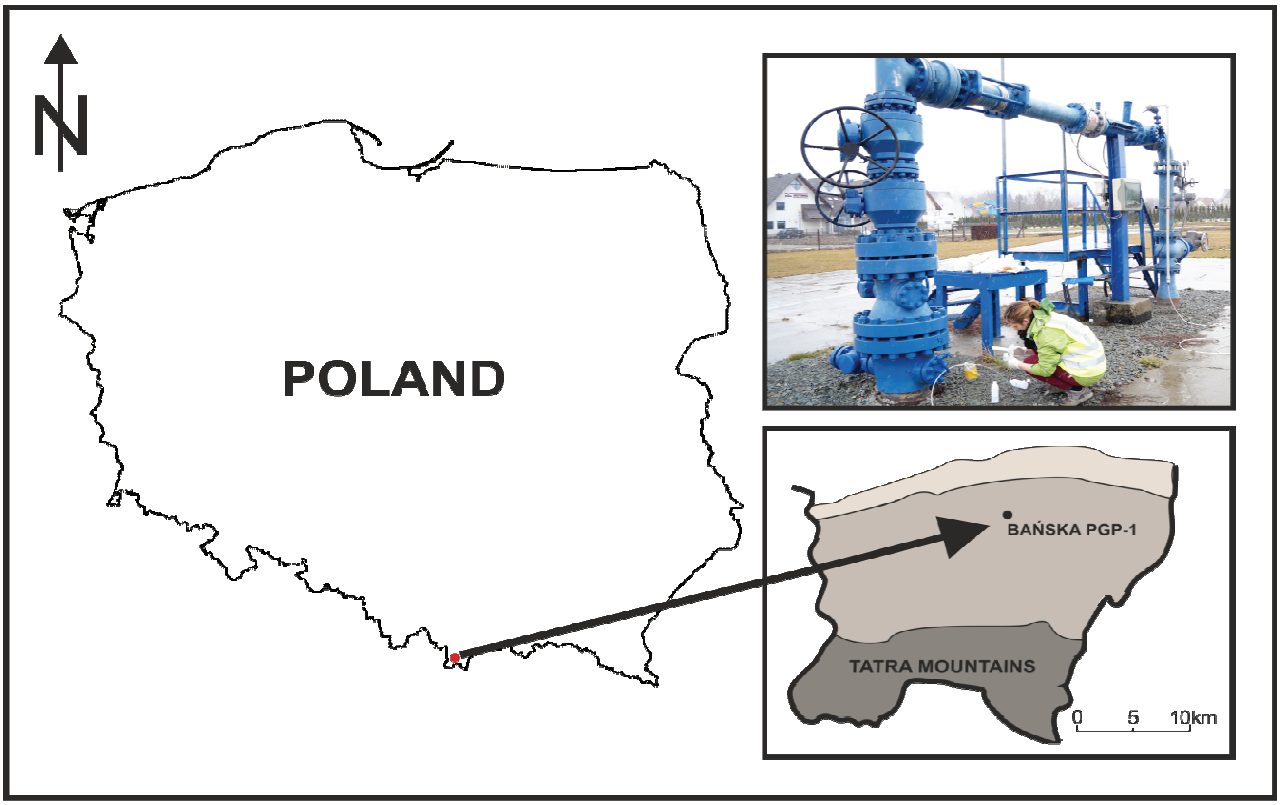

Figure 1: Location of Bańska PGP-1 well (photo by K. Korzec)

Bańska PGP-1 well with the Bańska PGP-2 well forms a geothermal doublet and they are part of geothermal heating system of PEC Geotermia Podhalańska S.A. company (Kleszcz, Tomaszewska, 2013).

Reservoir rocks for thermal waters constitute marly limestones of middle Eocene, mainly limestones and dolomites of middle Triassic and sandstones with carbonate rocks of Jurassic (Kępińska, Ciągło, 2008).

The conditions of circulation of these waters, lithology of reservoir rocks, oxidation-reduction conditions, pressure, temperature and microorganism activity affect on chemical composition of these waters (Kępińska, Ciągło, 2008).

Based on carried out research, thermal water exploited by Bańska PGP-1 well is sulfate-chlorine-sodium-calcium water (according to Szczukariew-Prikłoński classification). Mineralization of these waters is about 2,5 g/L, including specific components as a metasilicic acid.

3. METHODOLOGY OF RESEARCH

Samples of thermal waters were taken every two weeks by one operator accordance with the procedure specified in standard ISO 5667-11: 2004. During field research there were also measured non-stable parameters on the flow — pH, conductivity, Eh and temperature. Other physical and chemical indicators were determined in certified hydrogeochemical laboratory of Hydrogeology and Engineering Geology Department at the AGH University of Science and Technology in Krakow (Certificate of Polish Centre for Accreditation No. AB 1050).

Concentration of specific component, metasilicic acid H_2SiO_3 was calculated from the concentration of silica determined by ICP-OES method (inductively coupled plasma optical emission spectrometry) using a spectrometer OPTIMA 7300DV made by PerkinElmer (according to PN-EN ISO 11885:2009). Declared laboratory detection limit of silica for this method is 0,2 mg/L and the extended measurement uncertainty is approx. 12% (k=2, 95%).

The correctness of chemical composition analysis were verified by calculate analytical error based on the ion balance. According to Polish technical standard PN-89/C-04638/02, analytical error for highly-mineralized waters should not exceed 2%. Average error of the analyzes do not exceed this value.

4. THE ANALYSIS OF THE DATA

In order to assess the stability of the concentration of metasilicic acid in waters exploited by Bańska PGP-1 well, there has been performed analysis of the results of determinations in samples taken between January 2014 to December 2015. Sampling period was characterized relatively stable yield of Bańska PGP-1 well, without any interruption.

In Table 1, there have been collated the basic descriptive statistics of metasilicic acid concentration. Statistics were obtained with the exploration procedure using PS IMAGO Software based on IBM SPSS Statistics v. 23 — http://psimago.pl/. Both the average concentration of metasilicic acid (79,7 mg/L) with the confidence level, and the median (79,8 mg/L) significantly exceed the minimum concentration value for the curative waters specified in the law (GML, 2011).

Table 1: Concentration of metasilicic acid in thermal water samples from Bańska PGP-1 well. Descriptive statistics

H_2SiO_3 [mg/L]	Statistic
Mean	**79,7**
95% Confidence interval for mean	
Lower bound	**77,7**
Upper bound	**81,8**
Median	**79,8**
Variance	33,3
Standard deviation	5,8
Minimum	67,1
Maximum	92,0
Range	24,9
Skewness	-0,172
Kurtosis	0,157

Based on Kołmogorow-Smirnov and Shapiro-Wilk tests, there found that there is no reason to reject the hypothesis of normal distribution of the analyzed results (Table, 2).

The analyzed data was also presented on a box-and-whisker plot (Fig. 2).

The box presents the quartile range. There are values falling within the range between the first and the third quartile, median (the center line), whiskers (situated about 1,5 the length of the box), outliers and extremes values. The outliers values lies within 1,5–3 the length of the box from lower and top the edge of the box. The extremes values are located over three lengths (Kmiecik, 2011).

Table 2: Tests of normality

Indicator	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Stati-stic	df	Sig.	Stati-stic	df	Sig.
H_2SiO_3	0,08	33	0,20	0,985	33	0,916

*. This is a lower bound of the true significance.
a. Lilliefors Significance Correction

As the following graph shows, the vast majority value exceeds the limit of 70 mg/L, excluding the value of 67.1 mg/L in a sample from 13th November 2014.

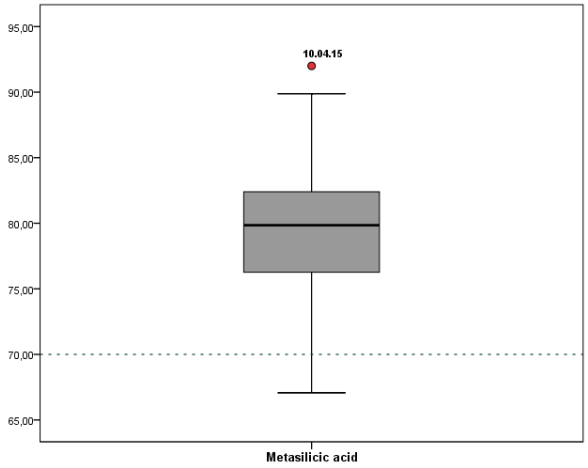

Figure 2: The box-and-whisker plot of metasilicic acid concentration in thermal water samples from Bańska PGP-1 well. Horizontal dotted line means threshold value for curative water determined in GML (2011).

In order to assess the stability of the concentrations of component as a function of time, it was performed an analysis of trends using GWSDAT Software. Methodology of use of the program in the evaluation of trends in water quality changes is described in the work Wątor & Kmiecik (2015).

The analysis of trends is performed using a nonparametric method – local linear regression. In this example, no statistically significant monotonic trend (p-value> 0.05) indicates the stability of concentrations of the analyzed component over time (fig. 3).

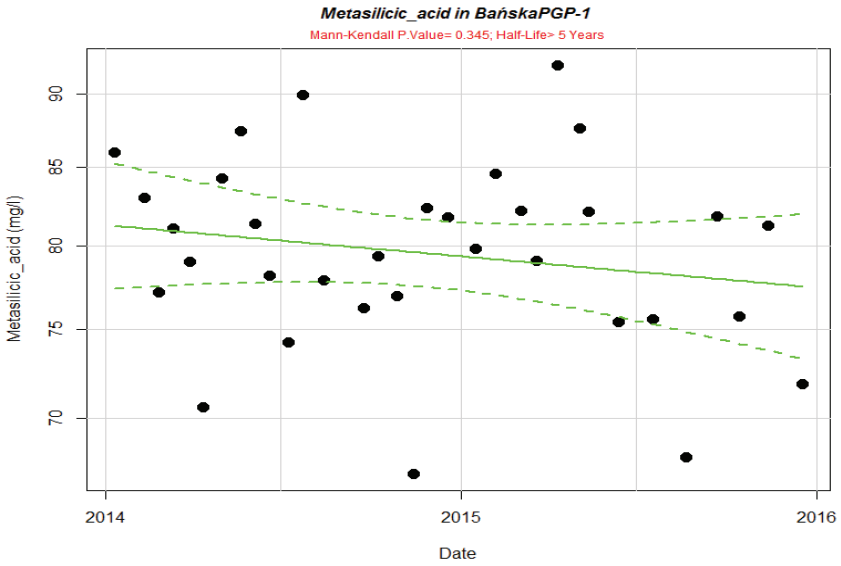

Figure 3: Trend analysis results for metasilicic acid concentration changes in thermal water samples from Bańska PGP-1 well.

5. SUMMARY

This paper presents an assessment of the stability of metasilicic acid concentration in thermal waters exploited by Bańska PGP-1 well based on data from 2014-2015. To this end, there was carried out a statistical data analysis (using PS IMAGO based on IBM SPSS Statistics v. 23) and a trend analysis (using GWSDAT software). Analysis showed no occurrence of a statistically significant monotonic trend, and thus it can be concluded that the concentration of metasilicic acid in the waters from Bańska PGP-1 well is stable and has a value exceeding the threshold value of the specific component for curative waters specified in the law (GML, 2011).

This conclusion opens new avenues for using thermal waters from Bańska PGP-1 well in balneologic and cosmetic industry.

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