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Stability assessment of sulphur (II) compounds in medicinal water from B-8b Michał intake in Busko-Zdrój

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Iwona Lipiec [1,a], **Piotr Rusiniak** [2,b]

[1] Polish Geological Institute-National Research Institute, Kielce, Poland
[2] AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Krakow, Poland

Correspondence: AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Department of Hydrogeology and Engineering Geology, Krakow, Poland. E-mail: piotr.rusiniak@agh.edu.pl

[a] https://orcid.org/0000-0002-2429-0386, [b] https://orcid.org/0000-0001-6699-2282

Abstract. In this paper, the stability of sulphur (II) compounds determined as the sum of hydrogen sul-phide, hydrosulphides and sulphides was evaluated in groundwater sourced from the B-8b Michał intake. Sulphide waters are a valuable raw material used as a basis for spa treatment in Busko-Zdrój. Based on the chemical composition analyses conducted in the years 1946–2018, a general analysis of random variability and statistical analysis of data was performed using PS IMAGO 5.0.1 software. Stability assessment was carried out on the data set for the 2009–2018 period on the basis of individual measurement control charts. Trend analysis was also performed using the GWSDAT software.

Key words:
sulphide waters,
B-8b Michał,
stability assessment,
analysis of trends

Introduction

Pursuant to the Geological and Mining Law of 9 June 2011 (PGG 2017), which is a Polish legal act currently in force, sulphide waters are groundwaters that are neither chemically nor microbiologically contaminated, that exhibit a natural variability of physicochemical properties and that contain at least 1 mg/dm^3 of sulphur (II) compounds – these are the ingredients that endow the water with therapeutic properties. Sulphide waters are used for balneotherapeutic purposes, both as baths and drinking cures (Legwant 1995; Kucharski and Śliwińska 2006; Jędrzejczak et al. 2010; Legwant et al. 2013). It is therefore very important that their chemical composition be stable, including, but not limited to, a stable content of the sulphur (II) compounds that are their therapeutic ingredient. This paper presents an analysis of the stability of concentrations of sulphur (II) compounds in the medicinal water sourced from the B-8b Michał well owned by Uzdrowisko Busko-Zdrój S.A. (health resort).

Characteristics of the study area and water intake

Morphologically, the study area is situated in the Nida Basin, which lies in the southern part of the Szczecin-Miechów Synclinorium (Kondracki 2009; Żelaźniewicz 2011). The basin is an extensive brachysyncline (brachyfold) filled with incomplete Mesozoic formations: from the Cretaceous – sands, sandstones with conglomerate and marl inserts in places; from the Jurassic – limestones; and from the Triassic – claystones, mudstones and limestones with sandstone and conglomerate inserts (Łyczewska 1972). The substrate is made up of dislocated and strongly tectonically disturbed Palaeozoic formations, while the overburden consists of unconformable Neogene formations, mostly consisting of clayey, muddy and sandy factions with evaporate (gypsum) interbeddings (Łyczewska 1972; Pożaryski 1974). The study area is characterised by a block-fold structure with faults running in the NW–SE direction and subordinate faults in the NE–SW direction. This complex geological structure is reflected by the presence of varied hydrogeological conditions. Several aquifers (Quaternary, Neogene, Upper Cretaceous, Jurassic and Triassic – Fig. 1) have been identified in the study area (Paczyński and Sadurski [eds] 2007; Chowaniec et al. 2014). It is one of the most promising regions in Poland in terms of the presence of sulphide waters (Paczyński and Sadurski [eds] 2007). The B-8b Michał intake in question is situated within the boundaries of the Busko II mining area with an area of 49.85 km^2, which lies within the town and municipality of Busko-Zdrój (Busko District) (Midas 2019). As at January 2019, a concession granted by the Minister of the Environment for the extraction of medicinal waters in this area was held by Uzdrowisko Busko-Zdrój S.A.

The 60.0-metre-deep well of the B-8b Michał intake was drilled in 1989. The approved extraction rate is 3.6 m^3/h. The aquifer is situated in Upper Cretaceous sandy marl (Turon-Cognac) at depths ranging from 26.0 to 56.0 m (Krawczyk et al. 1999; Porwisz et al. 2002). According to the Szczukariew-Prikłoński classification, it holds sodium-chloride, sulphide and iodide water. On the basis of the results of the authors' own physicochemical analysis carried out in 2018, the total mineralisation of this water was determined, which amounted to 13.8 g/L. The basic chemical composition of water from the B-8b intake is presented in Table 1.

Chemical composition characteristics according to Kurlov's formula are as follows:

$$\mathbf{I^{2.1}S^{36.7}M_{13.8}\frac{Cl^{79}SO_4^{17}}{Na^{78}Ca^{10}}T^{11.1}}$$

Methodology and data analysis

The database consists of the results of archival analyses carried out from 1946 to 2017 and the results

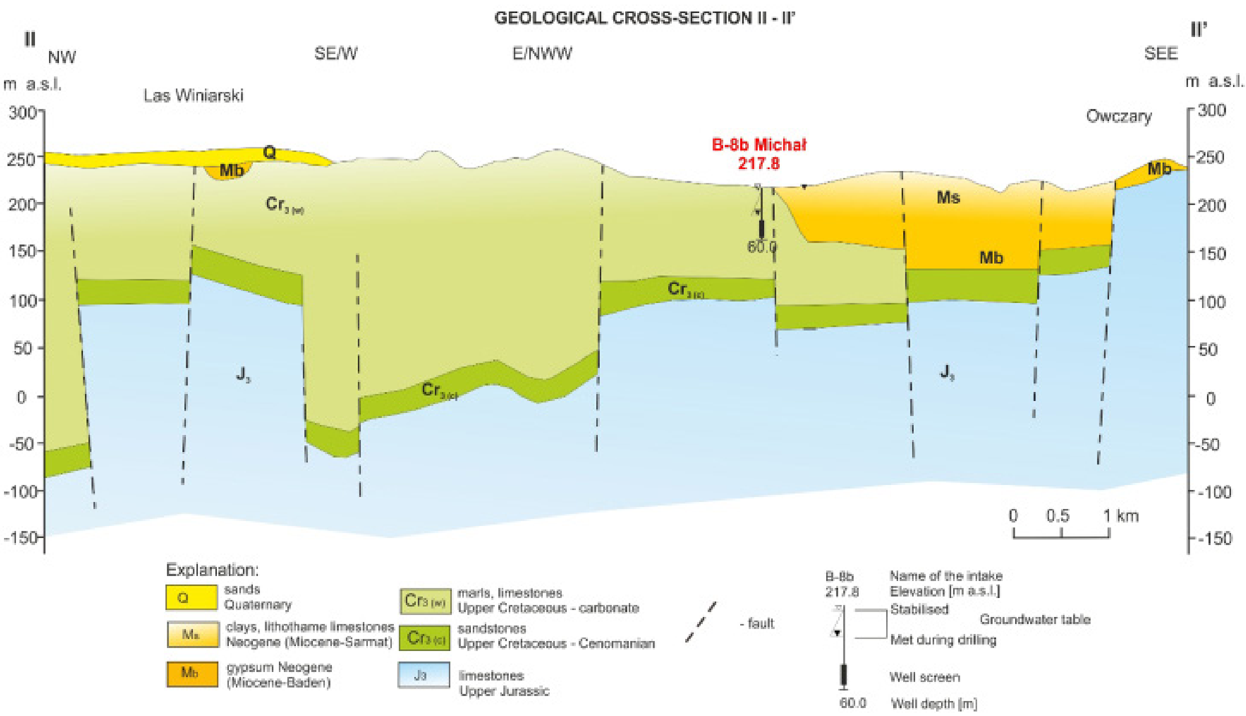

Fig. 1. Geological cross-section of the Busko-Zdrój region with marked location of the B-8b Michał intake (according to Porwisz et al. 2002; Gorczyca and Tott 2010)

of the authors' own 2018 tests. In total, 57 determinations of sulphur (II) compounds were gathered (S[II] was not always measured). The analyses were performed once a year by various laboratories. The database was verified by means of box-and-whisker plot analysis (Fig. 2). No outliers or extreme observations were found, and therefore the entire database was used for further analysis (Wątor et al. 2016).

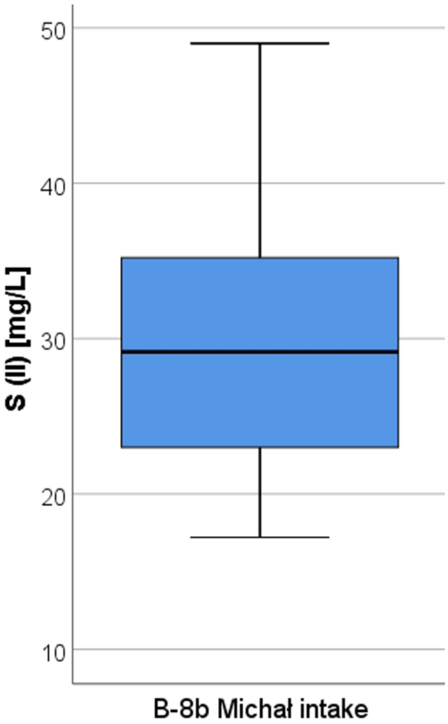

Fig. 2. Box-and-whisker plot for sulphur (II) compounds in groundwater from the B-8b Michał intake

A statistical analysis was performed for the entire database. For this purpose, the PS IMAGO 5.0.1 exploration procedure was used. On the basis of the results obtained (Table 2), it was found that the mean concentration of sulphur compounds (II) amounted to 29.9 mg/L and was close to the value for the average sample (median = 29.1 mg/L). These values significantly exceed the 1 mg/L threshold value stipulated in the Geological and Mining Law (PGG 2017).

Figure 3 shows the range of variation in concentrations of sulphur (II) compounds in the entire observation period together with the name of the laboratory performing the test. The chart shows clear groups of results related mainly to the change of laboratory, and thus also of methods for collecting samples and determining concentrations of sulphur (II) compounds.

Laboratories performing analysis of sulphur (II) compounds used different analytical methods over time (Table 3). Changes in the laboratory performing the analyses, and at the same time changes of analytical method for determining specific components in groundwater samples can lead to apparent changes in concentration of the component being analysed, as presented in a paper by Wątor et al. (2018). While taking into account the uncertainty that affects all the mentioned parameters of the method, the results are similar.

Further assessment of the stability of sulphur (II) compound concentrations over time was based on analytical results from the last ten years (from 2009 to 2018) in order to avoid the impact of an excessively long measurement series on trend assessment results. This made it possible to limit the analysis to results obtained by basically a single laboratory (Fig. 3) and to observe actual changes that could have been distorted in excessively long measurement series (Kmiecik and Korzec 2015; Rusiniak et al. 2017; Kmiecik 2018a, b; Wątor et al. 2018). For this purpose, individual measurement control charts were produced using the PS IMAGO Pro 5.0.1 software (a system based on IBM SPSS Statistics). The stability of the parameter tested is estimated on the basis of the locations of points which correspond to the values of that parameter in relation to the relevant control lines (Wątor et al. 2016). For the concentration of sulphur (II) compounds, basic control limits were set as the mean ±3σ (UCL – upper control limit and LCL – lower control limit) and warning limits were set as the mean ±2σ (UWL – upper warning limit and LWL – lower warning limit), which limits

Table 1. Basic chemical composition of water from the B-8b Michał intake based on authors' studies

Intake name	pH	TDS [g/L]	Na^+ [mg/L]	K^+ [mg/L]	Mg^{2+} [mg/L]	Ca^{2+} [mg/L]	Cl^- [mg/L]	SO_4^{2-} [mg/L]	HCO_3^- [mg/L]	S(II) [mg/L]
B-4b Michał	7.11	13.84	4091	121	261	445	6512	1909	441	36.7

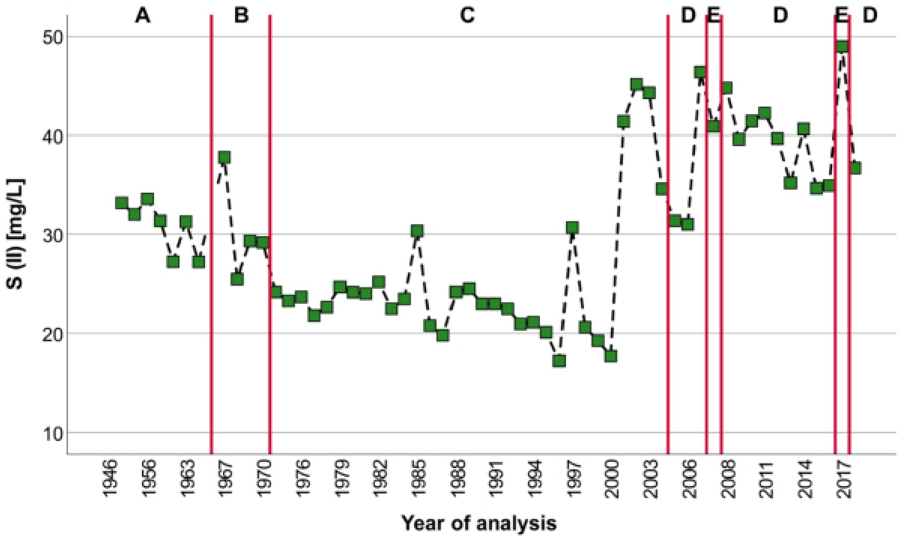

Fig. 3. Changes in the concentration of sulphur (II) compounds in groundwater from the B-8b Michał intake (red lines denote changes of laboratory performing the analysis): A – PPTOU, Laboratory in Szczawno; B – PPTOU, Laboratory in Warsaw; C – "Balneoprojekt" Laboratory, Warsaw; D – AGH University of Science and Technology; E – National Institute of Hygiene, Poznań

Table 2. Descriptive statistics for sulphur (II) compounds in groundwater from the B-8b Michał intake for the analysed period (1946–2018)

Parameter	Statistics			Standard error
Sulphur (II) compounds [mg/L]	Number of analysed data		57	
	Mean		29.9	1.12
	95% confidence interval for the mean	Lower limit	27.7	
		Upper limit	32.2	
	Median		29.1	
	Standard deviation		8.48	
	Minimum		17.2	
	Maximum		49.0	
	Range		31.8	

Table 3. Analytical methods used by laboratories performing analysis of sulphur (II) compounds over entire period (1946–2018)

Laboratory	Analytical method for S (II) determination
PPTOU, Laboratory in Szczawno	n.a.
PPTOU, Laboratory in Warsaw	n.a.
"Balneoprojekt" Laboratory, Warsaw	Ion-selective electrode (PN 1981)
AGH University of Science and Technology	Thiomercurimetric method (PN 1982)
National Institute of Hygiene, Poznań	Ion-selective electrode (PN 1981)

n.a. – not available

at the same time constitute the permissible fluctuation range for medicinal waters (Ciężkowski 2007). The chart control analysis conducted demonstrated that none of the points exceeded the basic control limits, and only one point was situated between the upper warning limit and the upper control limit (Fig. 4). This points to a stable concentration of sulphur (II) compounds in the water tested.

As the last stage, trends in concentrations of the therapeutic ingredient in question were analysed.

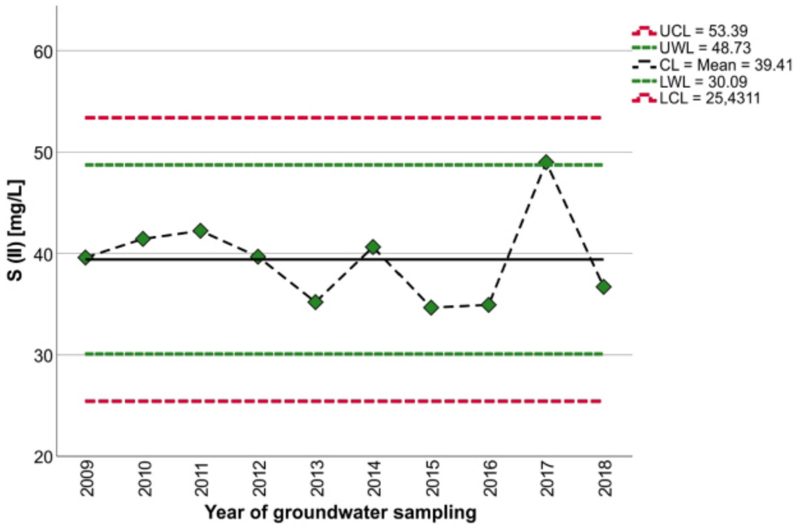

Fig. 4. Control chart for individual measurements of sulphur (II) compounds in groundwater from the B-8b Michał intake

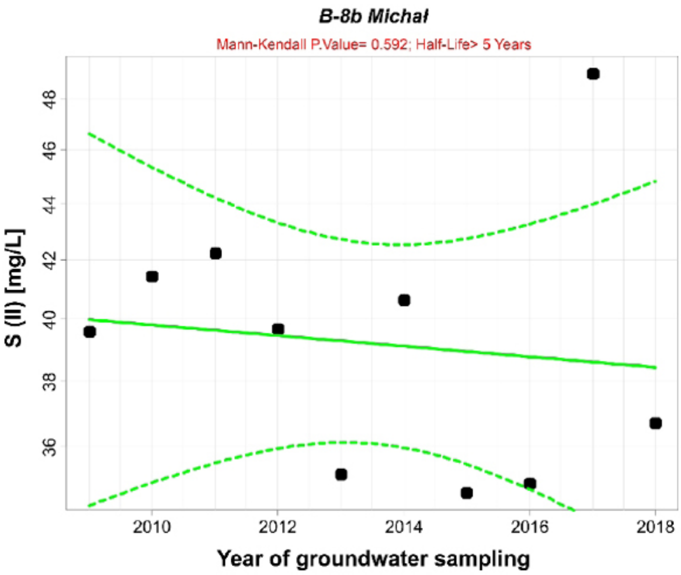

Fig. 5. Result of trend analysis for sulphur (II) compounds in groundwater from the B-8b Michał intake

For this purpose, the GWSDAT software (Kmiecik et al. 2004; Jones and Spence 2013; Mika and Korzec 2015; Wątor and Kmiecik 2015) was used. The analysis conducted showed no statistically significant monotonic trend (p=0.592, >0.05) (Fig. 5). This means that the concentration of sulphur (II) compounds in the water from the B-8b Michał intake is stable over time (Wątor et al. 2019).

Due to the unique properties of sulfidic water, it is important to assess correctly its chemical composition changes, especially concerning the components that give it its medicinal properties. Assessment of trends is very important in the case of medicinal water. The presence of a downward trend may result in the groundwater's loss of medicinal properties. Thus it is necessary to monitor and analyse the concentration of specific components in medicinal waters to quickly identify sources and causes, and to propose preventive strategies when a downward trend is detected (Rusiniak et al. 2017).

Summary and conclusion

This article contains an analysis of the stability of concentrations of sulphur (II) compounds in medicinal waters from the B-8b Michał intake in Busko-Zdrój. Gypsum and anhydrite are taken as the main source of sulphides in the groundwater from the Busko-Zdrój area. The sulphur contained in these minerals is, in the presence of microbes and under anoxic conditions, reduced to S (II) with the complicity of hydrocarbons (Kulikowska 1976; Łebkowska and Karwowska 2010; Deja-Sikora et al. 2019; Wątor et al. 2020). The general characteristics of the parameter examined were obtained by statistical analysis of data. The stability assessment conducted was based on control chart analysis. On the basis of this analysis, it was found that most results fall within the range set by warning limits, which demonstrates the stability of concentrations of sulphur (II) compounds over time. This stability was also confirmed by the absence of a statistically significant monotonic trend in the data series analysed.

Disclosure statement

No potential conflict of interest was reported by the authors.

Author contributions

Study design: IL, PR; data collection IL, PR; statistical analysis: IL, PR; result interpretation IL, PR; manuscript preparation IL, PR; literature review: IL, PR.

References

CIĘŻKOWSKI W, 2007, *Dopuszczalne wahania eksploatacyjnych i fizyczno-chemicznych parametrów wód leczniczych*. Oficyna wydawnicza Politechniki Wrocławskiej, Wrocław.

CHOWANIEC J, GĄGULSKI T, GORCZYCA G and OPERACZ T, 2014, Projekt robót geologicznych (Etap II) na wykonanie otworów hydrogeologicznych, rozpoznawczych OB-I, OB-II, OB-III, OB-IV, OB-V i OB-VI w rejonie Buska-Zdroju i Solca-Zdroju. PIG-PIB, Warszawa.

DEJA-SIKORA E, GOŁĘBIEWSKI M, KALWASIŃSKA A, KRAWIEC A, KOSOBUCKI P and WALCZAK M, 2019, Comamonadaceae OTU as a remnant of an ancient microbial community in sulfidic waters. *Microbial ecology* 78(1): 85–101.

GORCZYCA G and TOTT M, 2010, Projekt prac geologicznych w celu ustalenia zasobów dyspozycyjnych wód leczniczych, siarczkowych w rejonie Buska-Zdroju i Solca-Zdroju. Etap I. Przedsiębiorstwo Geologiczne S.A. Kraków.

JĘDRZEJCZAK M, BŁOŃSKA E and JĘDRZEJCZAK M, 2010, Wstępna ocena kuracji pitnej wodą siarczkową ze źródła Zuzanna Las Winiarski k. Buska-Zdroju u pacjentów z hiperlipidemią. VI międzynarodowa konferencja naukowo-szkoleniowa farmaceutów „Aktualne możliwości terapii chorób o podłożu miażdżycowym", 25–27 listopada 2010, Warszawa.

JONES W and SPENCE M, 2013, *Ground Water Spatio-Temporal Data Analysis Tool (GWSDAT Version 2.1 User Manual*, Shell Global Solution (UK).

KMIECIK E, 2018a, The impact of human errors on the estimation of uncertainty of measurements in water monitoring. In: Boring R (ed.), *Advances in human error, reliability, resilience, and performance*. AHFE 2017. Advances in Intelligent Systems and Computing, 589. Springer, Cham.

KMIECIK E, 2018b, Analytical procedures for ion quantification supporting water treatment processes. In: *Geothermal Water Management*: 83–112. CRC Press.

KMIECIK E, STEFANIAK S, SZCZEPANSKA J and TWARDOWSKA I, 2004, Evaluation of temporal and spatial trends of groundwater quality alteration in the area of mining waste disposal site. *In Advanced Environmental, Chemical, and Biological Sensing Technologies II* 5586: 126–135. International Society for Optics and Photonics.

KMIECIK E and KORZEC K, 2015, Ocena stabilności składu chemicznego wód termalnych ujmowanych otworem Bańska PGP-1 w Bańskiej Niżnej, Podhale. *Przegląd Geologiczny* 63(10/1): 830–833.

KONDRACKI J, 2009, *Geografia regionalna Polski*. Wydawnictwa Naukowe PWN, Warszawa.

KRAWCZYK J, MATEŃKO D, MĄDRY J and PORWISZ B, 1999, Wody lecznicze Buska-Zdroju w świetle dotychczasowych badań. In: Krajewski S and Sadurski A (eds), *Współczesne Problemy Hydrogeologii* IX, Państw. Inst. Geol., Warszawa, 159–164.

KUCHARSKI K and ŚLIWIŃSKA J, 2006, Poszukiwania badawcze z ostatniego 40-lecia nad działaniem leczniczym wód siarczkowych w Busku-Zdroju (1965–2005). *Balneologia Polska* 48(3): 142–149.

KULIKOWSKA J, 1976, Przyczyny do poznania genezy wód mineralnych rejonu Buska i Solca oraz możliwości zwiększania ich zasobów. *Problemy uzdrowiskowe* 6/8: 191–212.

LEGWANT Z, GAWĘDA J, LEGWANT-WÓJCICKA M and KORNECKI W, 2013, Ocena skuteczności kompleksowego leczenia uzdrowiskowego choroby zwyrodnieniowej stawu kolanowego w Sanatorium „Włókniarz" w Busku-Zdroju. *Studia Medyczne* 29(2): 167–170.

LEGWANT Z, 1995, Możliwości wykorzystania buskich wód siarczkowo-siarkowodorowych w lecznictwie. *Balneologia Polska* 37(1): 28–30.

ŁEBKOWSKA M and KARWOWSKA E, 2010, Bakterie redukujące siarczany na tle badań paleobiologicznych. In: Lisik R (ed.), Wody siarczkowe w rejonie Buska, Wyd. XYZ, Kielce, 185–193.

ŁYCZEWSKA J, 1972, Objaśnienia do szczegółowej mapy geologicznej Polski, skala 1:50 000, arkusz Busko-Zdrój (917). PIG, Wyd. Geol., Warszawa.

MIDAS, 2019, System Gospodarki i Ochrony Bogactw Mineralnych MIDAS - baza danych www.pgi.gov.pl

MIKA A and KORZEC K, 2015, Ocena stabilności kwasu metakrzemowego w wodach termalnych ujmowanych otworem Bańska PGP-1 w Bańskiej Niżnej. Technika Poszukiwań Geologicznych – Geotermia, *Zrównoważony Rozwój*. Wyd. IGSMiE PAN 2: 89–96.

PACZYŃSKI B and SADURSKI A (eds), 2007, *Hydrogeologia regionalna Polski*. Wydawnictwo Geologiczne, Warszawa.

PGG, 2017, Ustawa z dnia 9 czerwca 2011 r. Prawo geologiczne i górnicze (Dz. U. z 2017 r., poz. 2126).

PN, 1981, Woda i ścieki – Badania zawartości siarki i jej związków – Oznaczanie sumy siarkowodoru i siarczków rozpuszczalnych z użyciem elektrody jonoselektywnej (PN-C-04566-05:1981).

PN, 1982, Woda i ścieki – Badania zawartości siarki i jej związków – Oznaczanie siarkowodoru i siarczków rozpuszczalnych metodą tiomerkurymetryczną (PN-C-04566-03:1982).

PORWISZ B, CHOWANIEC J, GORCZYCA G and KOWALSKI J, 2002, *Dokumentacja hydrogeologiczna zasobów dyspozycyjnych wód leczniczych i towarzyszących im lub występujących odrębnie wód potencjalnie leczniczych na obszarze Karpat i zapadliska przedkarpackiego*. Przedsiębiorstwo Geologiczne, Kraków.

POŻARYSKI W, 1974, *Budowa geologiczna Polski*. T.4. Tektonika cz. 1. Niecka Nidziańska. Wyd. Geologiczne Warszawa, 316–322.

RUSINIAK P, WĄTOR K and PLATA J, 2017, Deterministic and probabilistic approaches to the denomination of the hydrochemical type of potentially medicinal groundwater from the "Zdrój Główny" intake (Krzeszowice, Poland). *Geology, Geophysics and Environment* 43(4): 303–309.

WĄTOR K, KMIECIK E and TOMASZEWSKA B, 2016, Assessing medicinal qualities of groundwater from the Busko-Zdrój area (Poland) using the probabilistic method. *Environmental Earth Sciences* 75: 804. DOI: https://doi.org/10.1007/s12665-016-5538-0

WĄTOR K, DOBRZYŃSKI D, SUGIMORI K and KMIECIK E, 2020, Redox potential research in the field of balneochemistry: case study on equilibrium approach to bioactive elements in therapeutic waters. *International Journal of Biometeorology* 1–12. DOI: https://doi.org/10.1007/s00484-020-01871-7

WĄTOR K and KMIECIK E, 2015, Analiza trendów zmian składu chemicznego wód leczniczych z ujęcia B-13 w Busku Zdroju z wykorzystaniem program GWSDAT. *Przegląd Geologiczny* 63(10/2): 1125–1130.

WATOR K, KMIECIK E and RUSINIAK P, 2018, An Influence of Research Methodology on the Results of Determination of a Chemical Composition of Curative Water. *Acta Balneologica* 60(4): 272–276.

WĄTOR K, KMIECIK E and LIPIEC I, 2019, The use of principal component analysis for the assessment of the spatial variability of curative waters from the Busko-Zdrój and Solec-Zdrój region (Poland)–preliminary results. *Water Supply* 19(4): 1137–1143.

ŻELAŹNIEWICZ A, 2011, *Regionalizacja tektoniczna Polski*, Komitet Nauk Geologicznych PAN, Wrocław.

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