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MEDICINAL CO_2-RICH WATER DEPOSITS IN THE POLISH PART OF THE SUDETES

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Abstract: The article presents characteristics of medicinal CO_2-rich water deposits occurring in different hydrogeological units of the Sudetes. The conditions of deposit formation in different and lithologically diverse rock media lead to the occurrence of waters varying in TDS (0.03–6.7 g/L) and CO_2 content (0.2–3.5 g/L) in a relatively small area of the Polish Sudetes. There are also CO2-rich water intakes with various total discharges in particular deposits: from 5216 m^3/year in Czerniawa-Zdroj to 250871 m^3/year in Duszniki-Zdroj. Particular attention has been paid to quantitative and qualitative parameters of Duszniki-Zdroj and Szczawno-Zdroj deposits. In Szczawno-Zdroj, the exploited intakes are springs with discharges in the range of 0.006–0.225 m^3/h, and in Duszniki-Zdroj – boreholes with discharges ranging from 4.2 to 18.0 m^3/h. The article presents the results of a statistical analysis of CO_2 content and intake discharge. Hydrogeochemical analyses have been performed with the use of AquaChem 2014.2 software.

Keywords*: *medicinal water, CO_2-rich water, carbonated water, Sudetes Mts

1. INTRODUCTION

The Polish part of the Sudetes are a distinct hydrogeological unit containing at least 20 deposits of waters exhibiting medicinal properties, including CO_2-rich waters. Barely half of these deposits are utilized in spa resorts for balneotherapeutic treatments and waters from only a few deposits are bottled.

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The block structure of the Sudetes determines the borders of hydrogeological units, often bounded by tectonic discontinuity zones. This is conducive to differentiation of water deposits despite their frequent close neighbourhood. Variety, both in terms of dynamics and physico-chemical parameters, is observed both within whole deposits and in particular intakes. Water outflows, including those of CO_2-rich waters, are generally located in dislocation zones crossing the main, so-called Sudetic fault systems (NW–SE). In the areas of main deep faults (often with fracture-like character), waters flowing from inside the orogen produce hydrochemical or geothermal anomalies in their drainage zones. As Ciezkowski et al. (1996) point out, the discussed waters are infiltration waters.

According to Polish geological and mining law, groundwaters with medicinal properties are a valuable group of minerals. Their exploitation by mining divisions of spa resorts is supervised by the Mining Board.

The vast majority of the discussed medicinal water deposits are located in mountain parts of the Sudetes near Jelenia Gora (Jelenia Gora-Cieplice, Świeradow-Zdroj and Czerniawa-Zdroj), Walbrzych (Szczawno-Zdroj and Jedlina-Zdroj) and Klodzko (Ladek-Zdroj, Duszniki-Zdroj, Polanica-Zdroj, Kudowa-Zdroj and Jeleniow). In general, these waters are characterized by distinctive properties such as high outflow temperature or increased concentrations of fluoride and ferrous ions, dissolved H_2S, CO_2 or radon.

2. DEPOSIT CHARACTERISTICS

A prominent group of Sudetic medicinal waters are CO_2-rich waters containing at least 1 g/L of dissolved CO_2. Deposits of such waters are found within the Karkonosze--Izera massif (Czerniawa-Zdroj and Świeradow-Zdroj), the intra-Sudetic basin (Szczawno-Zdroj and Jedlina-Zdroj), the upper Nysa Klodzka trough (Polanica-Zdroj and Gorzanow), the Kudowa depression (Kudowa-Zdroj and Jeleniow), and the massif of the Bystrzyckie and Orlickie Mountains (Dlugopole-Zdroj, Szczawina, and Duszniki-Zdroj). CO_2-rich waters are also naturally discharged in Stare Rochowice, Stare Bogaczowice, Bobrowniki Stare, Szalejow Gorny, Nowa Lomnica and Nowa Bystrzyca. In Gorzanow, there are outflows of both CO_2-rich and carbonated (with CO_2 content of 0.25–1 g/L) waters. The latter are currently extracted for bottling.). The location of deposits and springs of CO_2-rich waters in the Sudetic region is shown in Fig. 1.

The CO_2-rich waters of the Sudetes are fissure waters flowing out of crystalline Proterozoic massifs, pore-fissure waters related to strongly lithified Palaeozoic sedimentary rocks, or pore waters occurring in Mesozoic (Cretaceous) sandstones and mudstones (Table 1). Outflows of these waters are related to regional dislocation zones, often intersected by local faults, associated with the occurrence of springs. Intakes of medicinal CO_2-rich waters are encased wells of boreholes, usually operated as flowing wells. This operation method should secure both the quantity and quality of the extracted waters used mainly for balneotherapeutic purposes in spas resorts.

Varied hydrological conditions are observed in medicinal CO_2-rich water deposits in Duszniki-Zdroj and Szczawno-Zdroj.

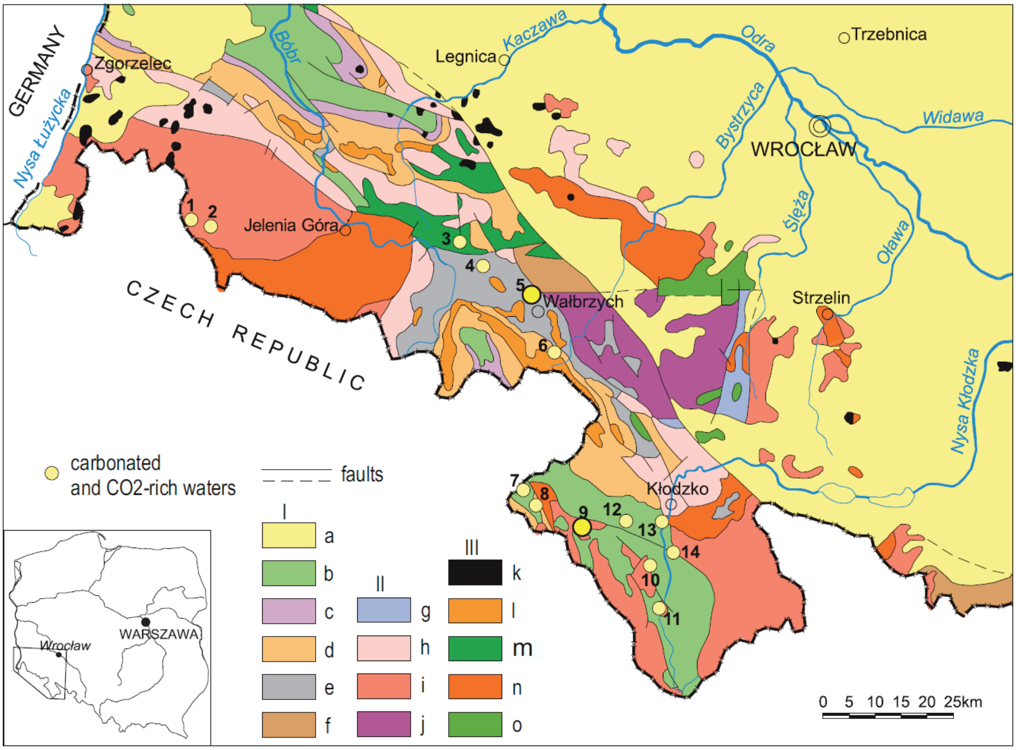

Fig. 1. Simplified geological map of the Sudetes and Fore-Sudetic Block
with carbonated and CO_2-rich waters locations.
Explanations: Carbonated and CO2-rich waters: 1 – Czerniawa-Zdroj, 2 – Świeradow-Zdroj, 3 – Stare Rochowice, 4 – Stare Bogaczowice, 5 – Szczawno-Zdroj, 6 – Jedlina-Zdroj, 7 – Kudowa-Zdroj, 8 – Jeleniow, 9 – Duszniki-Zdroj, 10 – Szczawina, 11 – Dlugopole-Zdroj, 12 – Polanica-Zdroj, 13 – Stary Wielislaw, 14 – Gorzanow; I – sedimentary series: a – Paleogene, b – Cretaceous, c – Triassic, d – Permian, e – Carboniferous, f – Carboniferous and Devonian; II – metamorphic series: g – mylonites and caaclasites of Paleozoic, h – phyllites, schists and conglomerates of Proterozoic-Lower Paleozoic, i – mica schists and gneisses of Lower Paleozoic, j – gneisses and migmatites of Proterozoic-Lower Paleozoic; III – magmatic seris: k – basalts of Cainozoic, l – volcanits o Pemian and Carboniferous, m – volcanites of Lower Paleozioc, n – granites of Upper Paleozoic, o – gabbros and serpentines of Upper Paleozoic

Duszniki-Zdroj are situated near the northern border of a tectonic unit referred to as the metamorphic complex of the Bystrzycke and Orlickie Mts. The dominant rocks in this area are Proterozoic and Old-Palaeozoic metamorphic rocks formed as various types of schists and gneisses (Zelazniewicz et al. 2011). Depressions and planation surfaces in summit parts of mountains are covered by Upper Cretaceous sedimentary rocks (marls interbedded with sandy and mudstone deposits) and Quaternary deposits (clays, gravels and sands).

Two Sudetic dislocation directions (with NW–SE strike) are noticeable here. The so-called waterhead fault running along the Bystrzyca Dusznicka valley is the most important for medicinal water occurrence (Fistek 1977).

Table 1. Characteristics of medicinal CO_2-rich water deposits in the Sudetes (based on: Ciezkowski 1990; Ciezkowski et al. 1996; 2016; Kielczawa 2001; Kielczawa, Liber-Makowska 2017; 2018; Kielczawa et al. 2018; Liber 2001; Liber-Makowska, Kielczawa 2019; *Bilans*... 2020 and on the latest available data)

Water deposit	Type of rock (age)	Total admissible volume or discharge*	TDS	CO_2	Type of water
		m^3/h	g/L	g/L	
1	**2**	**3**	**4**	**5**	**6**
Czerniawa-Zdroj	mica schit (Proterozoic)	1.17	0.6–3.3	1.06–3.5	CO_2-rich waters: HCO_3-Ca-Mg, Fe
Dlugopole-Zdroj		1.95	0.9–1.5	1.3–2.6	CO_2-rich waters: HCO_3-Ca-Mg, Fe, Rn
Duszniki-Zdroj	mica schit, gneiss (Proterozoic)	42.7	0.8–3.9	1.2–2.8	CO_2-rich waters: HCO_3-Ca-Mg; HCO_3-Ca-Na, Fe, Si; HCO_3-Ca-Na-(Mg), Fe, Rn
Bobrowniki Stare		0.72*, not exploited	0.2–0.9	0.9–2.5	CO_2-rich waters: HCO_3-Ca-Mg, Fe,
Świeradow-Zdroj	gneiss, mica schit (Proterozoic)	1.31	0.03–3.02	1.3–2.6	CO_2-rich waters: HCO_3-Ca-Mg, Fe, F
Szczawina		3.4, not exploited	0.5–0.7	2.1–2.8	CO_2-rich waters: HCO_3-Ca-Mg, Fe
Nowa Lomnica		0.15*, not exploited	1.2	1.6–2.6	CO_2-rich waters: HCO_3-Ca-Mg, Fe
Nowa Bystrzyca		6.12*, not exploited	1.1	0.8–2.2	CO_2-rich waters: HCO_3-Ca-Mg, Fe
Stare Rochowice	limestone, sericite schist (Cambrian-Ordovician)	41.04, not exploited	2.0–6.7	up to 2.26	CO_2-rich waters: SO_4-HCO_3-Na-Ca
Szczawno-Zdroj	conglomerate, sandstone, mudstone (Carboniferous)	0.454	0.8–4.7	0.6–2.5	CO_2-rich waters: HCO_3-Na, Rn; HCO_3-Na-Mg; HCO_3-Na-Ca; HCO_3-Ca-Na, Fe; carbonated waters: HCO_3-Ca-Na-Mg

1	2	3	4	5	6
Stare Bogaczowice	conglomerate (Carboniferous)	0.62, not exploited	0.6–2.7	0.35–1.3	CO_2-rich waters: HCO_3-Na-Ca-Mg, Rn
Jedlina-Zdroj	porphyry, sandstone (Carboniferous)	5.0	0.6–2.1	2.2–2.4	CO_2-rich waters: HCO_3-Ca-Mg-Na, Fe, Rn
Kudowa-Zdroj	sandstone, mudstone (Cretaceous)	8.5	1.3–3.3	1.5–2.3	CO_2-rich waters: HCO_3-Na-Ca, Fe, Rn; HCO_3-Ca-Na, Rn
Jeleniow		11.4	0.6–2.6	1.4–2.78	CO_2-rich waters: HCO_3-Na-Ca, Fe, Rn
Polanica-Zdroj	Sandstone (Cretaceous)	68.22	0.9–2.6	0.5–2.75	carbonated and CO_2-rich waters: HCO_3-Ca
Szalejow Gorny		0.36*, not exploited	1.3–1.8	0.6–1.5	carbonated and CO_2-rich waters: HCO_3-Ca-Na
Stary Wielislaw Dolny		20.8, not exploited	1.6–2.4	1.0–2.5	carbonated and CO_2-rich waters: HCO_3-Ca-Na
Gorzanow		65.4	1.0–1.3	0.2–0.5	carbonated waters: HCO_3-Ca-Na
		29.8, not exploited	1.6–1.7	0.6–1.3	CO_2-rich waters: HCO_3-Ca-Na

In the latter half of the 19th century, there were 14 known medicinal water springs in Duszniki, captured at small depths. As a result of reconstruction and drilling, 10 medicinal water intakes are known currently, out of which only Pieniawa Chopina, Jan Kazimierz and well No 39 (with depths of 78 to 180 m) are exploited. These intakes are located in the spa zone occupying the southern part of the town. All of them are flowing wells (Liber-Makowska, Kielczawa 2019).

The medicinal water deposit in Szczawno-Zdroj is situated in the north-western part of the intra-Sudetic basin. It is one of the major geologic units in the Sudetes and it is filled with a Carboniferous sedimentary rock complex. The CO_2-rich waters in Szczawno circulate within poorly permeable Lower-Carbonic sediments forming cyclic series of conglomerates, sandstones and mudstones (Haydukiewicz et al. 1982). South of Walbrzych lies the Upper-Carboniferous Walbrzych formation with coal seams, which were mined until 1996. The mining activity affected the deposit parameters of Szczawno waters (Kielczawa, Liber-Makowska 2017; 2018).

Specific properties of waters occurring here were studied as early as the 16th century and the current intakes (brass bell-type wells) were executed in the early 19th century.

CO_2-rich water outflows are found along the Szczawnik fault running perpendicular to the principal dislocation of the discussed region, i.e., the Struga tectonic zone with a NW–SE strike. Numerous water outflows are grouped, depending on their chemical composition and location, into 9 multiple-well intakes, 5 out of which are currently exploited. These are Marta, Dabrowka, Mlynarz, Mieszko and Mieszko 14 springs.

The total available reserves of medicinal CO_2-rich water intakes oscillate from 0.454m^3/h for Szczawno-Zdroj intakes to 68.22 m^3/h for Polanica intakes. Small reserve values are characteristic of springs with small discharges, while the largest reserves have been estimated for boreholes, mostly operating as flowing wells. The reserves assessed for pumped wells relate only to individual intakes in Jedlina, Kudowa-Zdroj, Jeleniow and Polanica-Zdroj intakes. Table 1 presents total available reserves of currently utilized CO_2-rich intakes for which production reserves (i.e., reserves that could be extracted in specific economic and technical conditions) have been determined. Additionally, the table specifies estimated total reserves of unused intakes or intake discharges where such estimations are lacking.

Available reserves do not fully reflect the possibility of obtaining CO_2-rich waters from particular intakes. In order to obtain a fuller assessment of usable amounts of CO_2--rich waters, the total mean annual discharge from intakes exploited as flowing wells was calculated. The calculations were mostly based on 2020 data, and in their absence – data from an earlier period (2019 for Świeradow-Zdroj and Jedlina-Zdroj intakes and 2016 – for intakes in Dlugopole-Zdroj). In the case of pumped wells (6 out of 24 exploited intakes), annual water withdrawal was taken into account. This concerns the following intakes: J-300 in Jedlina-Zdroj, J-150a in Jeleniow, Gorne and Moniuszko in Kudowa-Zdroj, and PL-1 and PL-2 in Polanica-Zdroj (two out of five operating wells).

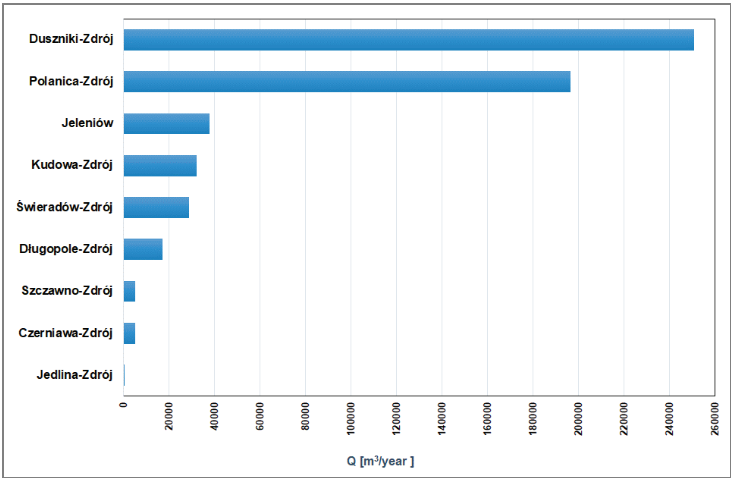

Fig. 2. Total mean discharges from exploited medicinal CO_2-rich water intakes in Sudetic deposits

The calculated mean total discharges from exploited intakes for particular deposits are shown in Fig. 2. The highest mean total discharge, 250 871.04 m^3/year, was calculated for intakes in the Duszniki-Zdroj deposit, and the lowest total amount, 700 m^3/year, was pumped out of the J-300 intake in Jeleniow-Zdroj. A similarly high total discharge from three wells (Wielka Pieniawa, Pieniawa Jozefa 1 and Pieniawa Jozefa 2) plus water withdrawn from two wells (PL-1 and PL-2), amounting to 196 554.52 m^3, was recorded in 2020 in Polanica-Zdroj intake, where additionally 50 153.0 m^3 of other waters, used for bottling purposes, are extracted. The lowest mean total 2020 discharges were measured at borehole No 4 in Czerniawa-Zdroj (5216.3 m^3/year) and in Szczawno-Zdroj intakes (5293.22 m^3/year).

The variation in total discharges from medicinal CO_2-rich water intakes and the diverse chemical types of their waters reflect the varied conditions found in different hydrogeological units of the Sudetes, in which the Sudetic deposits were formed. What is particularly important is the duration and the depth at which these waters circulate in diverse crystalline and sedimentary deposits.

Among the analysed medicinal water deposits, the highest relative proportions of sodium ions are characteristic of CO_2-rich waters of Szczawno-Zdroj, Kudowa-Zdroj and Jeleniow, and Duszniki-Zdroj. Waters richest in calcium ions are CO_2-rich waters from Gorzanow, Czerniawa, Duszniki-Zdroj and Polanica-Zdroj (Fig. 3). It should be noted here that waters varying in cation composition co-occur in some places, forming slightly varied chemical types depicted in Fig. 3 by smaller plots corresponding to particular intakes within particular deposits (e.g., Szczawno, Duszniki, Kudowa and Gorzanow). In all likelihood, this is due to the mixing of waters from different circulation systems varying in chemical composition and TDS content. Considerable amounts of dissolved CO_2 (c. 2.8 g/L at the most – Table 1) confirm the possibility of the inflow of waters from deep circulation systems to drainage zones.

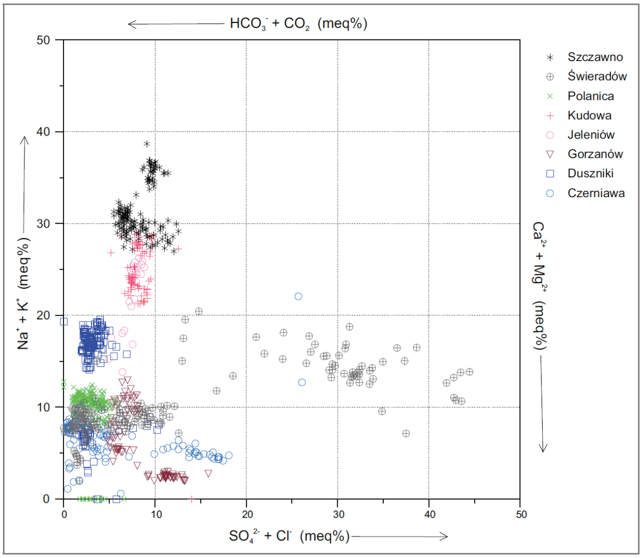

Fig. 3. Langelier-Ludwig diagram for carbonated and CO_2-rich waters of the Sudety Mts (based on: Ciezkowski et al. 2016; modified)

In order to perform a more thorough analysis of changes in selected quantitative and qualitative parameters, the authors chose deposits in Duszniki-Zdroj and Szczawno--Zdroj varying in hydrogeological conditions (fissure and pore water deposits respectively), quantitative parameters (maximum and minimum discharges from wells and springs), and qualitative parameters (various chemical types).

3. ANALYSIS OF CHANGES IN SELECTED DEPOSIT PARAMETERS

The analysis of changes in the most important deposit parameters of medicinal CO_2--rich waters from the Sudetes was based on available monitoring data obtained chiefly from spa-resorts' mining divisions. These data are related to both quantitative parameters such as available reserves and intake discharge and results of chemical analyses of waters, and to selected additional qualitative parameters (water temperature, CO_2 and HCO_3^- ion content). Measurements of discharge and selected physico-chemical parameters are usually conducted once a week, while chemical composition analyses – once a year or every other year, depending on the deposit. The data that were taken into account covered the period of at least 10 recent years, and for some parameters – several decades.

The research focuses on deposit parameters of medicinal waters from Duszniki-Zdroj and Szczawno-Zdroj. Currently, the only utilized wells in Duszniki are boreholes with mean long-term (of about 40 years) discharges oscillating from 4.2 m^3/h in Jan Kazimierz intake to 18.0 m^3/h in Pieniawa Chopina well. Much lower mean long-term discharges (over a period of over 50 years) are characteristic of Szczawno springs, and they vary from 0.006 m^3/h for Mlynarz spring to 0.225 m^3/h for Mieszko spring.

Alongside discharge, CO_2 content in water is measured once a week. Long-term mean values of this parameter for Duszniki intakes vary from 1593.5 mg/L (in intake No. 39) to 1681.3 mg/L (in Jan Kazimierz intake). Throughout all the monitoring period, the amount of CO_2 dissolved in water from this deposit did not fall below the limit value of 1000 mg/L characteristic of CO_2-rich waters (Table 2). The mean CO_2 content in waters from Szczawno springs measured over a long-term period varies from 810.4 mg/L in Mieszko 14 spring to 2023.6 mg/L in Mieszko spring. For most intakes (4 out of 5) in this deposit, drops below the threshold value of 1000 mg/L of CO_2 dissolved in water was observed. Particularly changeable and the lowest CO_2 content is characteristic of water from Mieszko 14 spring, where values between 237.0 mg/L and 1434.0 mg/L have been recorded. Therefore, water from this intake should be classified as carbonated water (the median of 845.0 mg/L).

High CO_2 content in waters from Duszniki-Zdroj wells causes pulsating changes in discharge from these intakes. As water is withdrawn, gas separation enables simultaneous extraction of CO_2. Throughout all the period of intake exploitation, a weak correlation between discharge variation and CO_2 content has been observed (with correlation coefficient of 0.2–0.4). At the time of deposit survey in 2011, simultaneous increases in discharge and CO_2 content were recorded in water from Jan Kazimierz intake (correlation coefficient of 0.8). The character of these changes is shown in Fig. 4.

Table 2. Characteristics of changes in CO_2 content in medicinal water from exploited intakes in Duszniki-Zdroj and Szczawno-Zdroj

Water intake	Observation period	Number of measurements	CO_2 content in water mg/L			
			Min.	Average	Max.	Median
Szczawno-Zdroj						
Mieszko	1967–2021	2893	1253.0	2023.6	2530.0	2023.0
Mieszko-14	1967–2021	2469	237.0	810.4	1434.0	845.0
Dabrowka	1967–2021	11 271	899.0	1762.5	2293.0	1789.0
Mlynarz	1965–2021	2975	635.0	1426.8	2302.0	1423.0
Marta	1965–2021	2965	940.0	2013.1	2686.0	2017.0
Duszniki-Zdroj						
Pieniawa Chopina	1987–2020	1667	1291.0	1638.0	1958.0	1650.0
Jan Kazimierz	1975–2020	1873	1047.0	1681.3	2000.0	1696.0
39	1999–2020	1118	1251.0	1593.5	1928.0	1617.0

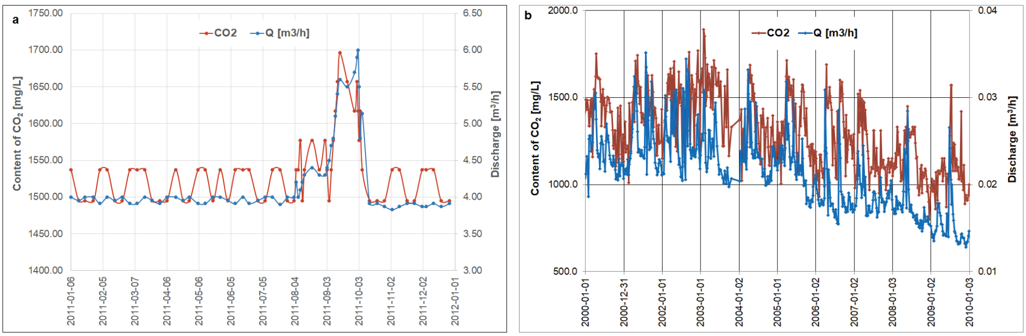

Fig. 4. Variations in discharge and CO_2 content in waters from Jan Kazimierz intake in Duszniki-Zdroj (a) and Mlynarz intake in Szczawno-Zdroj (b)

Simultaneous changes in discharge and CO_2 content are also observed in Szczawno-Zdroj springs. In this case, changes in both parameters are of seasonal nature (Fig. 4b). Like in Duszniki-Zdroj intakes, increasing discharge co-occurs with rising CO_2 content in most springs throughout all the exploitation period (the correlation coefficient is 0.2–0.5 for 4 out of 5 intakes). Such a correlation is the most apparent in Mlynarz spring for the years 2000-2009 (correlation coefficient of 0.7).

The observed changeable CO_2 concentrations in waters from the studied deposits are associated with varied inflow of deep circulation waters and the discussed gas.

Detailed characteristics of other deposit parameters in Duszniki-Zdroj and Szczawno-Zdroj have been presented in works by: Kielczawa, Liber-Makowska (2017; 2018) Liber-Makowska, Kielczawa (2019), Romanova et al. (2021).

The waters of Duszniki-Zdroj represent the Ca-Na-(Mg)-HCO_3 type. Their TDS content varies from c. 0.5 to c. 3.9 g/L, at pH of 5.2 to 7.0 for all intakes. The outflow temperatures of the discussed waters range between 10 and c. 35°C (Liber-Makowska, Kielczawa, 2019). The dominant anion in the chemical composition is the HCO_3^- ion (from 86% meq to 96% meq). Cations are dominated by calcium ions (from 40% meq to c. 70% meq), followed by sodium and magnesium ions. Analyses of relative concentrations of particular ions have also demonstrated considerable significance of Mg^{2+} (up to 29% meq) and Na^+ ions (up to 68% meq in Pieniawa Chopina intake). Among specific components, metasilicic acid, ferrous ions, CO_2 and Rn occur in concentrations enabling classification of the discussed waters as medicinal (Table 3).

Table 3. Variation ranges of TDS, carbon dioxide and main ion content in the exploited medicinal water intakes in Duszniki-Zdroj and Szczawno-Zdroj expressed by a simplified version of Kurlov's formula (based on 1990–2020 data from particular intakes depending on data availability CO_2 and TDS content in g/L; specific components in m/L; Rn in Bq; T in °C; principal ions in % meq)

Duszniki-Zdroj	
Pieniawa Chopina	$Fe^{10-19}H_2SiO_2^{1.5-2.1}TDS^{2.0-2.8}\dfrac{HCO_3^{92-96}}{Ca^{41-68}Na^{41-68}Mg^{16-29}}T^{15-19}$
Jan Kazimierz	$CO_2^{1.2-2.6}TDS^{1.0-1.8}\dfrac{HCO_3^{86-96}}{Ca^{40-70}Na^{22-31}Mg^{16-27}}T^{11-18}$
Nr 39	$CO_2^{1.3-1.8}TDS^{1.9-2.0}\dfrac{HCO_3^{93-95}}{Ca^{43-49}Na^{20-24}Mg^{20-23}}T^{18-19}$
Szczawno-Zdroj	
Mlynarz	$CO_2^{0.6-1.7}M^{1.9-2.7}\dfrac{HCO_3^{75-89}}{Na^{52-70}Mg^{18-24}Ca^{16-23}}$
Mieszko	$CO_2^{0.8-2.2}M^{2.4-4.2}\dfrac{HCO_3^{76-82}}{Na^{65-77}}$
Marta	$Rn^{2.4-82}CO_2^{1.26-2.3}M^{1.6-2.8}\dfrac{HCO_3^{83-92}}{Na^{55-66}Ca^{17-21}Mg^{15-22}}$
Dabrowka	$CO_2^{0.8-2.2}M^{1.3-2.6}\dfrac{HCO_3^{76-89}}{Na^{45-65}Ca^{20-29}Mg^{14-24}}$

In Szczawno-Zdroj, the extracted waters can be classified as Na-HCO_3 CO_2-rich waters varying in the proportions of Mg^{2+} and Ca^{2+} cations, which periodically affects the hydrochemical types of particular springs (Na-HCO_3 – Mieszko, Na (Ca, Mg)--HCO_3 – Marta and Dabrowka, Na (Mg, Ca)-HCO_3 – Mlynarz). On the deposit scale, relative concentrations of the dominant HCO_3^- and Na^+ ions reach 75–92% meq and 45–77% meq, respectively. The TDS content in these waters varies in the range of 1.3–2.8 g/L. The medicinal character of waters from this deposit is determined by the presence of dissolved CO_2 (from 0.6 to 2.3 g/L) and Rn (Table 3).

When analysing variation in the concentration of bicarbonate ions compared with that of sodium (Fig. 5a) and calcium (Fig. 5b) ions in waters from Szczawno-Zdroj intakes, one can distinguish two water groups varying in the character of relations between the concentrations of the above ions. One of these groups comprises waters from Dabrowka, Marta, and Mlynarz intakes. The other group, clearly distinguishable from other waters in the entire deposit, is made up of waters from Mieszko intake. Here, variation is the result of higher concentrations of the discussed ions, and not the character of their changes (~1:1). In Duszniki-Zdroj, waters in the analysed intakes constitute a compact group in Fig.5a which points to greater deposit stability and a far bigger resistance of the rock medium containing the deposit (crystalline rocks of the Orlica-Bystrzyca metamorphic complex) to weathering. When it comes to Duszniki waters, one can clearly observe a higher proportion of Ca^+ ions compared to Szczawno-Zdroj waters (Fig. 5b).

It must be noted that the amount of CO_2 dissolved in waters of the discussed deposits falls within the range of 0.6 to 2.7 g/L. The inflow of large amounts of CO_2 to water undoubtedly results in an increase in the number of HCO_3^- ions. Therefore, it is reasonable to think that the obtained image is the result of varied lithology of aquifers, and consequently – their varied resistance to chemical weathering. The rising effect of the rock medium on the waters in Duszniki-Zdroj has been noted by Liber-Makowska and Kielczawa (2019).

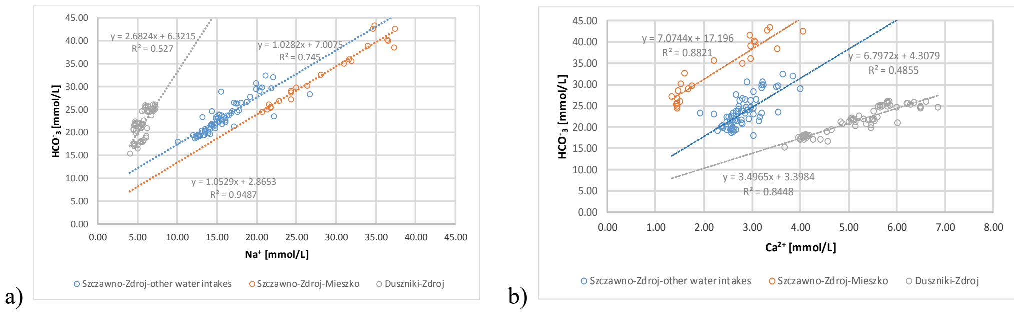

Fig. 5. Variation in HCO_3^- ion concentration depending on Na^+ (a) and Ca^{2+} (b)

Moreover, in the Duszniki deposit, one can distinguish three groups of waters slightly differing in the character of relations between the concentrations of the above ions (Fig. 5a). As mentioned before, waters from Mieszko intake in Szczawno-Zdroj are clearly distinct from other waters (Fig. 5b). What occurs in both deposits is the mixing of waters from different circulation systems (Ciezkowski et al. 2016). It should be emphasized that in Szczawno-Zdroj waters are captured from small depths using a bell-type well, which surely facilitates their mixing.

When analysing the saturation degree of the discussed waters in relation to the rock medium, considerable oversaturation with clayey minerals, gibbsite, potassium and sodium feldspars, calcium carbonates, and calcium and magnesium minerals has been observed. Calcium and magnesium aluminosilicates and silicates are largely dissolved (Table 4). The studied waters are generally in equilibrium with amorphic silica and magnesium carbonates. The presence of secondary calcite in drilling core samples from Duszniki-Zdroj suggests that the above calcites are secondary minerals formed as a result of aluminosilicate decomposition co-induced by CO_2 (Appelo, Postma 2007).

Considerable concentrations of silica in waters from Duszniki-Zdroj (Table 4) are probably also due to the above processes.

Table 4. Values of saturation indices with respect to selected rock-forming minerals (based on available recent physico-chemical analyses of waters)

Intake mineral	Marta	Mieszko	Dabrowka	Mlynarz	Nr 39	Jan Kazimierz	Pieniawa Chopina
Albite	0.8	0.99	0.46	0.09	0.44	0.29	0.99
Analcime	–1.41	–1.2	–1.73	–2	–1.98	–1.99	–1.52
Anorthite	–1.81	–1.85	–2.21	–2.42	–1.87	–1.7	–1.21
Calcite	0.62	0.66	0.47	0.52	0.66	0.5	0.82
Dolomite	1.27	1.37	0.9	1.12	0.97	0.64	1.23
Magnesite	0.09	0.15	–0.14	0.03	–0.25	–0.41	–0.15
Chalcedone	0.42	0.4	0.4	0.3	0.61	0.47	0.7
Si(aq)	–0.43	–0.45	–0.46	–0.55	–0.25	–0.4	–0.16
Quartz	0.87	0.85	0.85	0.75	1.06	0.92	1.15
Gibbsite	1.57	1.6	1.4	1.4	1.35	1.6	1.53
Illite	4.16	4.14	3.67	3.35	4.73	4.84	5.52
Kaolinite	5.69	5.7	5.29	5.1	5.61	5.92	6.16
Ca-montm.	5.09	5.07	4.6	4.23	5.25	5.4	6.03
Phlogopite	–6.69	–6.86	–7.19	–7.15	–6.07	–6.51	–5.47
Talc	–1.33	–1.54	–1.69	–1.75	–1.33	–2.23	–0.85
Adularia	1.51	1.47	1.28	0.98	2.67	2.52	3.2
K-mica	10.24	10.25	9.66	9.37	10.93	11.37	11.83
K-feldspar	1.51	1.47	1.28	0.98	2.67	2.52	3.2
Laumontite	3.42	3.33	2.97	2.56	3.83	3.75	4.66

High relative concentrations of Na^+ ions in Szczawno waters are the product of sodium aluminosilicate dissolution and the exchange of Na^+/Ca^{2+} ions from clayey minerals found in Carboniferous mudstone series.

As Romanova et al. (2021) report, $[Mg^{2+}]/[Ca^{2+}]$ ion ratios demonstrate, according to Hunslow's (1995) classification, that calcite and dolomite dissolution is the principal source of Ca^{2+} and Mg^{2+}ions present in Szczawno-Zdroj waters. However, the rock medium in which the waters from this deposit are formed are mainly built of clastic material originating in the rock massifs neighbouring on the Intra-Sudetic depression. The authors believe that like in Duszniki-Zdroj, the main source of the discussed ions is probably dissolution of aluminosilicates and silicates (e.g., amphiboles or biotite; Hem, 1985) with a considerable participation of CO_2 ensuring significant concentrations of HCO_3^- ions. What is more, dolomite is gradually dissolved in solutions which are heavily undersaturated with respect to this mineral (Drever 2002). Waters in both deposits exhibit oversaturation with respect to both calcite and dolomite (Table 4), which implies a possibility of secondary calcium and magnesium carbonate precipitation. in Duszniki, such processes are probably due to calcite enclosures observed in fractures and fissures in the rock medium. On the other hand, precipitation of secondary dolomite is complicated, owing to the ordered crystal structure in this mineral (Appelo, Postma 2007). Therefore, if the "drainage" of Mg^{2+} ions from water by secondary dolomite precipitation is impeded, the concentration of this ion in the discussed waters increases. As a result, high $[Mg^{2+}]/[Ca^{2+}]$ ion ratios are observed, apparently pointing to dolomite as the main source of the discussed ions.

5. SUMMARY AND CONCLUSION

The Sudetic region abounds in numerous occurrences of CO_2-rich waters and carbonated waters varying in qualitative and quantitative parameters resulting from varied conditions of deposit formation in different hydrogeological units. These are fissure waters flowing out of Proterozoic crystalline massifs and pore waters associated with sedimentary complexes of different ages. Medicinal CO_2-rich water intakes are related to dislocation zones intersecting Sudetic fault systems. For instance, waters of the Duszniki deposit circulate within the crystalline massif of the Orlica-Bystrzyca metamorphic complex. The Szczawno-Zdroj deposit is formed within sedimentary deposits of the intra-Sudetic basin.

The studied waters are characterized by TDS content in the range of 0.5–4.2 g/L and the general chemical type of Na-HCO_3^- in Szczawno and Ca-Na-HCO_3^- in Duszniki. In both deposits, varying proportions of Mg^{2+}ions are observed. Apart from TDS content, these are dissolved gases (CO_2 and Rn) that determine the medicinal properties of these waters. Additionally, waters from Duszniki contain increased concentrations of metasilicic acid. Among waters extracted in Szczawno-Zdroj, waters from Mieszko intake clearly stand out, owing to their highest TDS content and the highest concentrations of Na^+ and HCO_3^- ions. Waters from Duszniki are characterized by higher concentrations of calcium ions, compared to Szczawno waters.

Waters from both deposits demonstrate strong similarity in respect of TDS content and the amount of dissolved CO_2. Larger fluctuations of the latter parameter are observed in Szczawno-Zdroj waters, where individual measurements below the threshold value of 1g/L have been recorded in 3 out of 5 intakes. Based on long-term mean CO_2 content of 0.8 g/L, water from Mieszko 14 spring should be categorised as carbonated water.

A statistical analysis has demonstrated a similar relationship between discharge variation and CO_2 content in waters from most intakes in Duszniki-Zdroj and Szczawno--Zdroj. High CO_2 content in waters from Duszniki-Zdroj wells causes pulsating changes in discharge from these intakes. Outflows of CO_2-rich water from Szczawno springs have the character of annual seasonal changes.

In terms of chemistry, waters from Mieszko intake in Szczawno-Zdroj are clearly distinguishable. The main source of sodium and calcium ions, and of silica, are aluminosilicates (plagioclases) weathering with the participation of CO_2. The presence of Mg^{2+} ions is, in all likelihood, supplied by weathering amphiboles, and in the case of Duszniki waters, additionally by biotite and magnesium silicates. Wider variation ranges of major ion concentrations in Szczawno-Zdroj waters suggest more intensive inflow of waters from a shallow circulation system to intakes. It is also indicated by seasonal variation in spring discharge in this deposit revealed by clear discharge increases during rainy periods in spring and summer.

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