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Hydrogeological and hydrogeochemical reassessment of selected potentially medicinal waters of the Sudetes (SW Poland, NE Bohemian Massif)

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Abstract

The Sudetes, like the other parts of the Bohemian Massif, are rich in medicinal waters, though the wealth of these resources have still not yet been sufficiently identified nor analysed. The Sudetes are characterised by extensive fractured and fractured-porous aquifers, significant depth of water infiltration and coexistence of fresh, medicinal and thermal waters. These often mix with ordinary groundwater under various geological and hydrogeological conditions, which results in complex groundwater chemistry. In this study, we analyse selected occurrences of potentially medicinal waters, i.e. radon, carbonic and acidulous ones among eight currently unused prospective areas and reassess their hydrogeological and hydrogeochemical properties. Physicochemical parameters of water were measured *in situ* in winter 2023 and 12 new samples were taken for laboratory analysis. The results were compared to historical hydrogeological and hydrochemical datasets from between 1968 and 2022. They help to understand the conditions of occurrence of potentially medicinal waters in the Polish Sudetes, and to some extent in the proximal parts of the Bohemian Massif showing similar geological and hydrogeological settings, including the hard-rock crystalline massif environment and the Bohemian Cretaceous Basin.

INTRODUCTION

Medicinal waters, also called therapeutic, healing and curative (Kirschner, 2005; Elster et al., 2022), belong to special types of groundwater which, because of their chemical composition, are beneficial to human health and wellbeing. These are used worldwide for balneology, health care and recreation and play an important role for economic development (Lund, 1996; Reimann and Birke, 2010). In this paper we focus on currently unused resources of potentially medicinal waters in the Polish part of the Sudetes, the mountains shared by the Czech Republic, Poland and Germany. The Sudetes, which are the marginal, north-eastern part of the Bohemian Massif, are characterised by the widespread presence of fractured and fractured-porous aquifers, significant depth of groundwater infiltration, the coexistence of fresh, medicinal and thermal waters, as well as their shallow occurrence. Here, radon-bearing waters and waters containing CO_2, i.e. carbonic and acidulous waters, occur. These often mix with ordinary groundwater under various geological and hydrogeological conditions, forming complex chemical groundwater types (Dominikiewicz, 1951; Ciężkowski, 1990; Paczyński and Płochniewski, 1996; Ciężkowski et al., 2010, 2011, 2016; Dowgiałło, 2012). The medicinal waters which occur in certain localities in the Sudetes (Ciężkowski, 2002; Ciężkowski et al., 2016) are connected with deep tectonic fault zones (Michniewicz, 1981).

The Sudetes occupy a small part of Poland's territory, yet they are rich in medicinal waters (Fistek, 1979). According to *Rejestr uzdrowisk i obszarów ochrony uzdrowiskowej wraz z kierunkami leczniczymi wg. stanu na 08.09.2025 r.* (Eng. Register of Health Resorts as of September 8th, 2025) altogether 47 municipalities in Poland hold the official status of a health resort municipality. Out of this number 11 are located in south-western Poland, in a region called Lower Silesia, including 10 communes in the Polish Sudetes. The two most popular spas in the Polish Sudetes, i.e. Jelenia Góra Cieplice Śląskie-Zdrój and Lądek-Zdrój, belong to the oldest spas in Central Europe (Banaś et al., 1975).

In the Czech part of the Bohemian Massif, due to abundance of medicinal waters, as well as because of their evident curative effects, these types of water have been well-known and studied by numerous researchers for several decades and in some localities for even longer (Laboutka and Vylita, 1983; Vrba, 1996; Hrkal, 1997). A modern comprehensive review of the medicinal waters of the Bohemian Massif was provided by Hynie (1963) and Krásný et al. (2012), while Květ (2011) contributed a detailed description of their selected occurrences. Medicinal waters occur in the eastern and central parts of the Sudetes, for instance along the major regional fault zone of Pořiči–Hronov–Czermna–Gorzanów. In locations such as Kudowa-Zdrój, Duszniki-Zdrój, Polanica-Zdrój, Nowa Łomnica, Gorzanów and Długopole-Zdrój (Fig.1) medicinal and potentially medicinal waters occur.

The term ‘potentially medicinal waters’, often used in this paper, refers to groundwater showing the same physicochemical features as those identified by Polish legal regulations, i.e. *Ustawa Prawo geologiczne i górnicze z dnia 10 lipca 2024 r.* (Eng. Geological and Mining Law Act of July 10th, 2024 (Journal of Law 2024 no 1290). Potentially medicinal waters, however, still require some research and administrative procedures to be officially recognized by the Ministry of Health. This issue is discussed in detail further below in this paper.

In research we conducted between 2021 and 2024 (Chudzik et al., 2024) 12 localities of potentially medicinal waters within eight prospective areas in the Polish Sudetes were sampled in 2023. Physicochemical parameters were measured *in situ* and groundwater samples were sent for laboratory analyses. In this paper we study 12 new groundwater samples, comparing them with a historical hydrogeological and hydrogeochemical dataset collected between 1968 and 2022, to analyse currently unexploited resources of potentially medicinal waters, reassessing them hydrogeologically and hydrogeochemically. These comparisons help to better understand the occurrence and eventual use of such waters in the Polish Sudetes and the proximal parts of the Bohemian Massif, especially the crystalline massifs and the Bohemian Cretaceous Basin.

STUDY AREA, GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

Geographically, the study area is located in south-western Poland, in the Sudetes (Solon et al., 2018) which comprise part of the Lower Silesian Block. The Sudetes themselves form a north-eastern component of the geologically complex Bohemian Massif, one of the most important old geological units of Central Europe (Franke and Żelaźniewicz, 2023). The Sudetes are characterised by a mosaic structure of folded, dislocated and fractured crystalline massifs, large synclinoria infilled with hard sedimentary rocks, and much evidence of volcanic activity (Oberc, 1972; Żelaźniewicz, 2005; Żelaźniewicz and Aleksandrowski, 2008; Żelaźniewicz et al., 2011). Most of the medicinal waters are associated with deep fault zones, their strike governed by the main Sudetic tectonic features, and a system of smaller, crossing, perpendicular dislocations (Hynie, 1963;

Dowgiałło and Fistek, 2007; Krásný et al. 2012). Recharge of deep aquifers takes place through outcrops and fault zones at the higher altitudes (Ciężkowski et al., 2016).

As regards regional classification of the medicinal and potentially medicinal waters of Poland, the Sudetes belong to the Sudetic province and its subunit, i.e. the Sudetic region, where the occurrence of these waters is specifically different from those in other areas of the country (Paczyński and Płochniewski, 1996; Dowgiałło and Paczyński, 2002). Depending on the lithology of aquifers, water retention time and circulation pathways, the potentially medicinal waters in the Sudetes are commonly characterised by elevated contents of the radon isotope ^{222}Rn, free CO_2 and concentrations of specific components as well as increased temperature. In the study area all medicinal waters derive, to a major extent, from infiltration of meteoric waters into the subsurface (Ciężkowski, 1990; Ciężkowski et al., 2016; Dowgiałło, 2012; Przylibski, 2005, 2011). Figure 1 depicts the study area, location of medicinal water intakes and groundwater sampling points. Figure 2 shows the geology of the study area with major tectonic features, as well as location of groundwater sampling points.

The prospective areas of Kowary and Sosnówka are located in the western part of the Sudetic Block within the geotectonic structural unit of the Karkonosze-Izera Massif composed of rock complexes of diverse ages and origins. The boundaries between the individual units are tectonic. The Karkonosze Granite Pluton built of coarse-grained porphyritic granites and emplaced during the Carboniferous (Słaby and Martin, 2008) constitutes the central part of the Karkonosze-Izera Massif. The Kowary-Wojków, Sosnówka *Źródło Anna* and Sosnówka *Źródło Magdalena* localities are within the outcrops of these granites. Farther to the south and south-east, a variously metamorphosed sedimentary-volcanogenic succession, including amphibolites, granite gneisses, hornfelses, gneisses, skarns, marbles and schists of Paleozoic and Proterozoic age occur (Mazur, 1995; Heflik et al., 2016) is present. There, the Kowary-Podgórze location is situated.

The prospective areas of Krosnowice, Stary Wielisław, Szczytna and Nowa Łomnica lie in the central part of the Sudetic Block, within the Intra-Sudetic Synclinorium and more specifically in the Upper Nysa Kłodzka Graben. This unit is a vast depression within the metamorphic basement that is composed mainly of gneisses and schists of the Orlica-Śnieżnik Dome. The sedimentary succession starts with Carboniferous to Lower Triassic conglomerates, sandstones and shales discordantly overlain by Upper Cretaceous marls and sandstones. The older strata are cut by intrusive igneous rocks of Carboniferous and Permian age. The Paleozoic sedimentary succession pinches out towards the south-west, where the Upper Cretaceous strata are deposited directly upon crystalline bedrock. The entire sedimentary succession is heavily fractured. The prospective area of Nowa Łomnica is located at the western limit of the Upper Nysa Kłodzka Graben, i.e. its western flexure, in the vicinity of the Orlica-Śnieżnik Dome crystalline basement. The contact between the units is tectonic. This prospective area covers both the Cretaceous strata and older Proterozoic schists and gneisses.

The prospective area of Stare Bogaczowice is located in the central part of the Sudetic Block on the north-western outskirts of the Intra-Sudetic Synclinorium. The bedrock is composed of Lower Carboniferous conglomerates, sandstones, greywackes and siltstones, constituting the Stare Bogaczowice Formation. These strata are partially overlain by Quaternary fluvial and fluvioglacial deposits.

The prospective area of Opolnica is located in the central part of the Sudetic Block, in the Bardo Fold Structure built by strata of the Upper Ordovician, Silurian, Devonian and Lower Carboniferous which do not show any strong effects of regional metamorphism. This unit is tectonically bounded. It includes the Lower Carboniferous Opolnica Formation built by the monotonous strata of interbedded siltstones, claystones, shales and greywackes, locally inlaid with pyrite (Wajsprych, 1995; Cymerman et al., 2015). Its top part is partially covered by Quaternary gravels, sands and muds of the Nysa Kłodzka River terraces and by coarser river valley infills. The geological setting strongly influences the hydrogeological and hydrogeochemical conditions. The crystalline rocks in the western part of the study area form strongly heterogeneous fractured aquifers where depth-dependent groundwater zonation occurs. The most shallow zone, up to 20-30 m b.g.l., is formed by weathered and fractured crystalline rocks partially overlaid by regolith, and by Quaternary fluvial deposits. Below, up to a depth of ~80 m b.g.l. the fissures are sparser and tighter. Groundwater flow occurs mostly in tectonically-formed vertical fractures. The deepest zone, between 200-300 m b.g.l., locally even deeper, is strictly limited to the larger faults and fracture zones (Staśko, 1996; Marszałek, 2010). Groundwater occurring in the crystalline rocks of the Sudetes shows low mineralisation and commonly shows elevated contents of radon ^{222}Rn.

The radon isotope ^{222}Rn originates from the radioactive decay of the radium isotope ^{226}Ra of the uranium-radium series. Uranium and radium are present in some minerals, for example, in the Karkonosze granites or older schists and gneisses. Emanations of gaseous ^{222}Rn are connected with circulation of groundwater throughout fractured crystalline rocks, especially granites. The highest ^{222}Rn contents usually occur in their topmost, strongly fractured and weathered, part (Przylibski, 2000, 2005, 2011; Goliáš et al., 2022). The radon isotope ^{222}Rn is radioactive, odourless, and water-soluble. Its migration is limited due to a short half-life period of 3.8224 days. Przylibski et al. (2007) indicated potential areas of radon waters in the crystalline rocks of the Izera-Karkonosze Massif and the Orlica-Śnieżnik Dome.

In several locations in the Sudetic Synclinorium, emanations of dry CO_2 as well as carbonic and acidulous waters have been detected (Żak et al., 2008; Liber-Makowska and Kielczawa, 2021). The origin of the carbon dioxide has not been fully identified yet, and certainly is generated by several diverse processes. Commonly, endogenic CO_2 is connected with, for example, volcanism and occurrences of cooled thermal waters (Dowgiałło, 2002b). Another mechanism responsible for generation of CO_2 in the lithosphere may be connected with metamorphism and complex biogeochemical processes in sedimentary rocks (Ciężkowski et al., 2002; Dobrzyński et al., 2022). In the Sudetes CO_2 migrates with groundwater flow from the deeper parts of the lithosphere upwards, and its occurrence is associated with the regional fault zones of the main Sudetic strike and with smaller perpendicular dislocations.

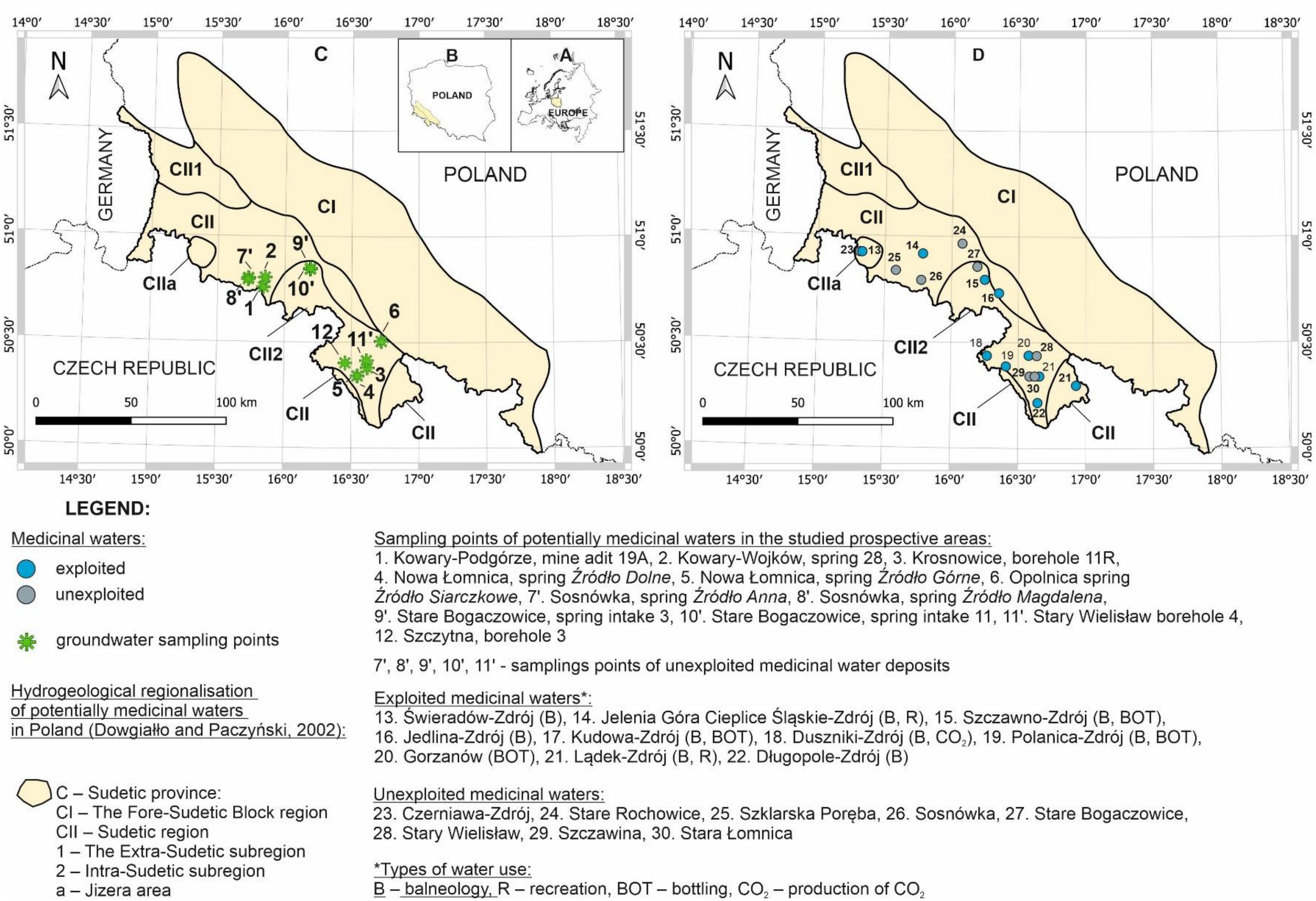
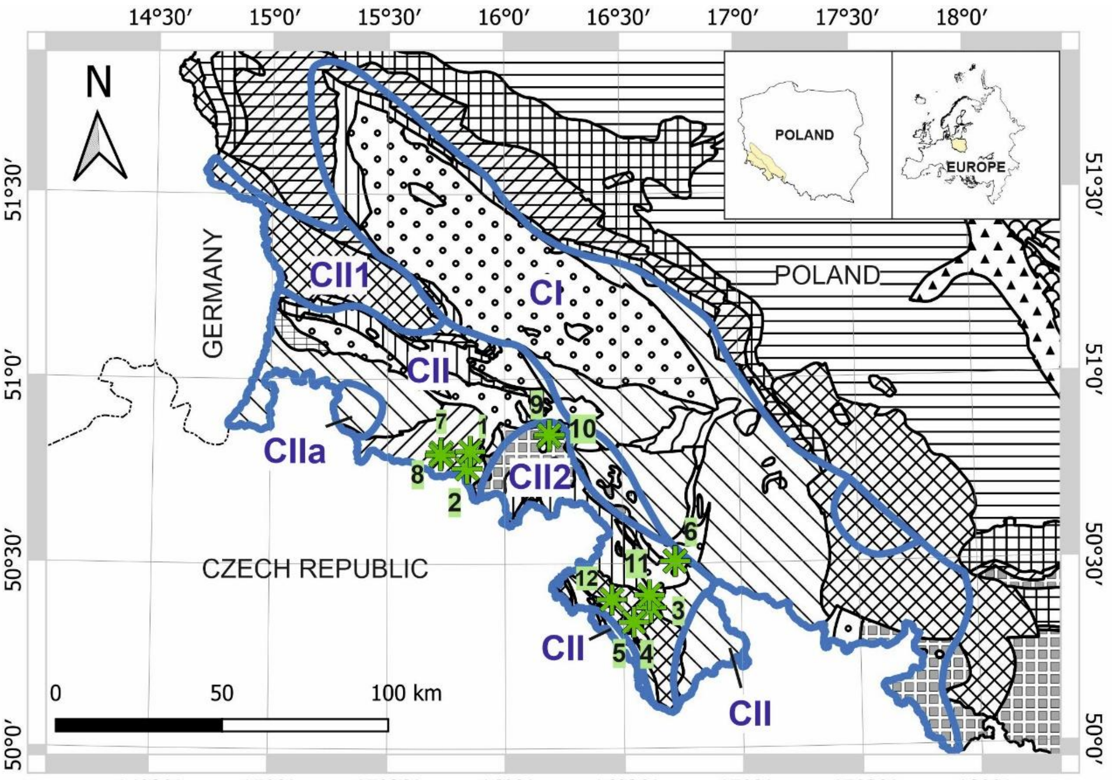


Fig. 1. Map showing research area and location of groundwater sampling points collected in 2023

Contour maps of: A – Europe, B – Poland, C – south-western Poland showing location of 12 sampling points of potentially medicinal waters and unexploited mineral waters collected in 2023, D – south-western Poland showing exploited and unexploited medicinal waters in the Sudetes



Legend:

Hydrogeological regionalisation of medicinal waters in Poland (Dowgiałło and Paczyński, 2002)
C – Sudetic province, CI – Fore-Sudetic Block region, CII –Sudetic region, 1 – Extra-Sudetic subregion, 2 – Intra-Sudetic subregion, a – Jizera area

Sampling points of potentially medicinal waters in the studied prospective areas:
1. Kowary-Podgórze, mine adit 19A, 2. Kowary-Wojków, spring 28, 3. Krosnowice, borehole 11R, 4. Nowa Łomnica, spring *Źródło Dolne*, 5. Nowa Łomnica, spring *Źródło Górne*, 6. Opolnica spring *Źródło Siarczkowe*, 7'. Sosnówka, spring *Źródło Anna*, 8'. Sosnówka, spring *Źródło Magdalena*, 9'. Stare Bogaczowice, spring intake 3, 10'. Stare Bogaczowice, spring intake 11, 11'. Stary Wielisław borehole 4, 12. Szczytna, borehole 3

Stratigraphy, lithology and selected tectonic features:

- Neoproterozoic - clay shales, mudstones and sandstones (Lusatian graywackes), locally hornfelses
- Neoproterozoic - Lower Ordovician - granitoides, orthogneisses, paragneisses and clay shales, locally hornfelses
- Neoproterozoic - Lower Carboniferous - meta-sedimentary and meta-volcanic rocks of the greenschist and amphibolite facies
- Silurian - clay shales, mudstones, graywacks and limestones
- Devonian - clastic rocks, carbonate rocks, quartzites, quartz schists and ophiolites
- Carboniferous - clastic rocks, carbonate rocks, hard coal, vulcanic and pyroclastic rocks
- Upper Carboniferous - granitoides
- Permian - evaporites, carbonate rocks, clastic rocks, vulcanic and pyroclastic rocks
- Lower Triassic - sandstones, mudstones, claystones, conglomerates and evaporites
- Middle Triassic - limestones, dolomites, claystones, mudstones and evaporites
- Upper Triassic - claystones, mudstones, sandstones, dolomites and evaporites
- Lower Jurassic - sandstones, mudstones, claystones and siderites
- Middle Jurassic - limestones, marls, mudstones, sandstones and gaizes
- Upper Jurassic - limestones, marls, claystones, dolomites and sandstones
- Upper Cretaceous - limestones, siliceous rocks, marls, sandstones and claystones

major faults

Fig. 2. Map of south-western Poland showing geological settings with major tectonic elements and location of 12 groundwater samples collected in 2023

MATERIAL AND METHODS

PROSPECTIVE AREAS OF POTENTIALLY MEDICINAL WATERS

The prospective areas were selected, taking into account several constraints. The most crucial was the occurrence of potentially medicinal water resources as indicated by previous studies and the lack of their exploitation during this research. Each area should allow for groundwater sampling and completion of basic *in situ* hydrogeological measurements, such as measurements of groundwater table depth, discharge of spring or artesian wells and measurements of the physicochemical parameters of the groundwater. The location of the prospective areas relatively far from existing spas, bottling plants, geothermal installations or any other facilities using medicinal or thermal waters was another important aspect to prevent any possible adverse interactions. The attitude of the local self-governing administration and the possibility to include development of medicinal water resources in their strategies was an important condition too. The selection of prospective areas turned out to be very challenging, because of the high number of already existing spas and well-known medicinal water deposits, commonly adjoining each other and located densely in geographically limited area.

Retrieving hydrochemically representative groundwater samples was of primary importance. This is why it was decided to choose the prospective areas allowing for groundwater sampling from springs and artesian wells with free outflow only. Groundwater sampling with the use of old boreholes showing the poorest technical condition affected by corrosion, obstruction or clogging, and where groundwater samples need be obtained by pumping only, was not taken into consideration. Nevertheless, differences in groundwater chemistry between historical datasets inferred in the case of groundwater sampling during the pumping tests and results of our research were somewhat different. The research concerned only selected locations within the study area. In spite of these constraints, the study covered the most significant hydrochemical types of potentially medicinal waters, as well as the major types of aquifers and their hydrogeological features. The water resources of the Sosnówka, Stare Bogaczowice and Stary Wielisław prospective areas, though they are currently not exploited, are still listed in the annual balance of mineral resources of Poland, (Lasota and Malon, 2025) and discussed in the explanaitions to a management map of waters qualified as mineral resources of Poland at the scale of 1:1 000 000 (Felter et al., 2022).

At first, 13 prospective areas were selected for initial, general study. Out of this number, eight areas were chosen for further detailed analysis. In four areas studied, two groundwater sampling locations were identified, while in the remaining ones there was only one groundwater sampling location per area (Tab. 1). In Kowary, Stare Bogaczowice and Stary Waliszów diverse types of facility used to be operated for balneological purposes. Balneology in this paper is understood as health treatment, while recreation does not need to show any health treatment aspect (Lund, 1996). Based on the results of earlier hydrogeological and hydrochemical research, water in these locations showed certain pharmacodynamic coefficients beneficial for human health and wellbeing, which in the past allowed their authorisation by the Ministry of Health. Nowadays, in Kowary a small wellness and beauty centre is in operation, but on a limited scale. In Opolnica a bottling plant produced table water for few decades in the second half of the 20th century. These facilities are no longer in use. The remaining areas have never been used for balneological purposes, though they show such potential. The characteristics of the eight prospective areas are shown in Appendix 1.

FIELD MEASUREMENTS, WATER SAMPLING AND LABORATORY ANALYSES

The field measurements and groundwater sampling took place in winter 2023 and were preceded by field inspection and assessment of the technical condition of the wells and springs (Chudzik et al., 2024). Prior to water sampling, *in situ* field measurements of pH, electroconductivity (EC), temperature and dissolved oxygen content were conducted directly in the springs or in a flow cell in the case of extracting the water sample with a pump. The content of free carbon dioxide (CO_2) in the groundwater was determined *in situ* with a Karat apparatus. Here, we briefly provide only a basic outline of the test procedures: for further details see e.g. Dominikiewicz (1951), Ciężkowski et al. (2002) and Żak (2005). The apparatus comprises a glass cylinder with two openings, i.e. a smaller opening on its bottom end connected with a thin inner tube for discharging excess water, and a wider opening on the top end to fill in the apparatus with water. After pouring the sample into the cylinder it is shaken and free CO_2 from aqueous solution is emitted into the headspace. Its volume can be read out in ml. Finally, knowing this value and water temperature in °C, the content of free CO_2 in the water sample can be read out in mg/dm^3 using the calculation tables. This *in situ* procedure is simple and efficient but provides only estimated concentrations. As CO_2 solubility in water depends on several factors, such as temperature, the minimum detection limit for this method is different for each measured free CO_2 volume and water temperature. In general the minimum detection limit is <622.46 mg/dm^3 which corresponds to a water temperature of 11°C and 6 ml of free CO_2. This method can be only used with respect to CO_2 dissolved in water, being in aqueous solution and not chemically bonded. Only selected groundwater samples were tested, where earlier research showed that CO_2 is to be expected, in samples nos. 3, 4, 5, 9, 10, 11 and 12.

The groundwater was sampled to the chemically inert bottles which were provided by the laboratory. These were used in the following manner: 1 PE bottle of 1000 ml for determination of physicochemical parameters as well as anion and cation contents, 1 tinted glass bottle of 500 ml for determination of S^{2-} ions and H_2S content and 2 transparent glass bottles of 10 ml each for determination of radon isotope ^{222}Rn content. To preserve the water samples for determination of S^{2-} ions and H_2S content for chemical analyses the laboratory added 1 ml of 2N zinc acetate into each 500 ml bottle. The water samples for ^{222}Rn content were injected with a pipette to the bottom of each bottle, under a layer of glycerine preventing any gas losses. These two bottles were wrapped with bubble-wrap and put together with a pipette into a zip-lock bag for transportation back to the laboratory. Altogether, 12 groundwater samples were taken for laboratory analyses. All bottles were tightly closed and transported in an upright position in the cooling boxes ensuring a low and relatively stable temperature during transportation. The chemical analyses started not later than 24 hours after sampling and were carried out by the certified laboratory Eurofins OBiKŚ Polska Sp. z o.o. based in Katowice, Poland. The samples showing low contents of radon isotope ^{222}Rn were analysed by the laboratory of the Central Mining Institute – National Research Institute in Katowice, Poland. Cation content was analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Anion content was analysed with different analytical methods depending on the individual anion, including spectrophotometry, titration, and ion chromatography (IC). The content of H_2S and S^{2-} anions was analysed by titration. A brief transportation time was crucial for analyses of radon isotope ^{222}Rn and hydrogen sulphide H_2S content, which are impermanent water components.

Physicochemical parameters of the water samples analysed in this research are given in Table 1, the chemical type and Kurlov's formula are provided in Table 2, while the results of chemical analyses are given in Appendix 2. Results of laboratory analyses were compared with historical data in order to assess the stability of chemical composition with the help of Schoeller diagrams (Fig. 3). Results of chemical analyses and *in situ* measurements are few (n=12), but the set of data is homogeneous as regards time of collection and analytical techniques, allowing for credible statistical analysis, the results of which are illustrated in the form of a box and whisker plot (Fig. 4). The studies also take into account the historical data (n=21), i.e. the results of chemical analyses of exactly the same sampling locations, though derived from chemical analyses performed by a number of laboratories, often with different analytical methods over quite a wide time span, i.e. 1968-2022. All these results (n=33) were used to construct a Piper Diagram (Fig. 5).

Hydrogeochemical classification of the water samples was made according to the Priklonskiy-Shchukarev method (Tab. 2). This system categorises chemical types of water based on the dominant ion composition, i.e. ions exceeding 20% (meq/l) of the total content of ions. The formula used in this paper also provides mineralisation given as total dissolved solids (TDS) given in %, where 1000 mg/l equals to 0.1% of weight. Kurlov's formula is used to show the general chemical composition of a groundwater sample in the form of fractions (Tab. 2). The numerator shows anions, while cations are given by the denominator. Ions concentrations >1 mg/l are rounded to unity. Before the fraction, the selected specific components and mineralisation are provided, while after the fraction, the water temperature is given. The results of the chemical analyses of the water samples made in these studies are provided in Appendix 2. The chemical types of historical water samples and samples analysed in this study are illustrated by the Piper diagram (Fig. 5). This shows concentration, in % (meq/l), of cations and anions in two triangles and the corresponding water types in a diamond. General mineralisation, i.e. total dissolved mineral content, i.e. total dissolved solids (TDS), was expressed as a sum of all major anions and cations.

LEGAL REGULATIONS AND TERMINOLOGY

The umbrella term of mineral waters is commonly used in the legal acts of European countries and across the world (Porowski, 2019; Elster et al., 2022). The term mineral water has been commonly adopted, though its definitions differ from one country to another. Mineralisation of mineral waters in different European countries is usually <1 g/l (Elster et al., 2022). There still exists in general perception a somewhat lapsed definition setting out a limit value of 1 g/l as a minimum mineral content for water to be qualified as mineral water (Paczyński and Płochniewski, 1996; Dowgiałło, 2002a; Kirschner, 2005).

The primary legislation governing mineral resources management in Poland is *Ustawa Prawo geologiczne i górnicze z dnia 10 lipca 2024 r.* (Eng. Geological and Mining Law Act of July 10th, 2024 (Journal of Law 2024 no 1290). Interestingly, this act does not provide any definition of mineral water and qualifies medicinal waters as mineral commodities and their occurrences, under some constrains, as deposits. According to this act, medicinal waters present in the Sudetes are the water types listed below showing the following concentration limits of selected specific elements, and pharmacodynamic coefficients beneficial for human health and wellbeing:

- total solid dissolved mineral content of at least 1,000 mg/dm^3,
- ferrous ion content of at least 10 mg/dm^3, called ferruginous water,
- fluoride ion content of at least 2 mg/dm^3, called fluoride water,
- bivalent sulphur ion content of at least 1 mg/dm^3, called sulphide water,
- metasilicic acid content of at least 70 mg/dm^3, called silicic water,
- radon content of at least 74 Bq/dm^3, called radon water,
- carbon dioxide content of at least 250 mg/dm^3, for a content between 250 and 1,000 mg/dm^3, called carbonic water, and
- carbon dioxide content exceeding 1,000 mg/dm^3, called carbonated or acidulous water.

The terminology above is used in this paper, though with concentration units of mg/l instead of mg/dm^3, these being provided by the chemical laboratory for the analytical results. The term 'potentially medicinal waters', often used in this paper, refers to groundwater showing the same features as indicated in the act. These, however, are still not officially recognized as medicinal water deposits by the Ministry of Health and long-term consistent research is needed to demonstrate their chemical stability as well as their beneficial influence on human health and wellbeing.

SOURCES OF HISTORICAL INFORMATION AND DATA

Information and data on the individual medicinal water resources were inferred from the databases run by the Polish Geological Institute – National Research Institute, namely: *Bank Wód Mineralnych* (Eng. Mineral Water Resources Registry), which is accessible free of charge under the following Internet link: https://spd.pgi.gov.pl/en/mineral. The borehole data referring to mineral resources, geology and hydrogeology of the study area was retrieved from the following online databases, i.e.: *System Gospodarki i Ochrony Bogactw Mineralnych Polski MIDAS* (Eng. System of Management and Protection of Poland's Mineral Resources MIDAS) and *Centralna Baza Danych Geologicznych CBDG* (Eng. Central Geological Database). These are accessible free of charge following the Internet links: https://midas-app.pgi.gov.pl/ords/r/public/midas/start for mineral resources and https://baza.pgi.gov.pl/en for several types of geological data. Data from scientific publications and geological reports were also used.

RESULTS

PROSPECTIVE AREA OF KOWARY

This prospective area lies in the Izera-Karkonosze Massif, where near the town of Kowary two radon water occurrences, namely Kowary-Podgórze, mine adit 19A (groundwater sampling point no 1, Tab. 1, Fig. 1 and 2), and Kowary-Wojków, spring 28 (groundwater sampling point no 2, Tab. 1, Fig. 1 and 2), were sampled. Kowary is a small town well known for its former iron mining activities. Here, iron and polymetallic mineralisation is commonly accompanied by uranium ore-bearing rocks. Groundwater occurs mainly in the fractured aquifer of the crystalline basement, i.e. the Karkonosze granites and the Paleozoic and Proterozoic metamorphic rocks. These form an inhomogeneous medium where hydraulic conductivity varies in a wide range from 0.01 to 17.5 (m/d) (Grzegorczyk, 2002). The crystalline rocks are overlain by Quaternary deposits, especially within stream valleys. The porous and fractured aquifers remain in hydraulic contact forming a heterogeneous multi-aquifer system. The most characteristic feature of the fractured crystalline aquifer is depth-dependent zonation. In the prospective area of Kowary several springs, seepages, boreholes and mine adits with radon groundwater occur (Fistek, 1970). Adit 19A in Kowary-Podgórze and spring 28 in Kowary-Wojków were sampled on January 24, 2023. The water showed low mineralisation, of 86.98 and 207.99 mg/l, and elevated contents of radon isotope ^{222}Rn of 446.0 and 134.0 Bq/l, respectively. Normally, ^{222}Rn content in groundwater in the Sudetes is lower, especially in the sedimentary basins, where it commonly does not exceed 74 Bq/l which is the minimum content for water to be qualified as radon water (Przylibski, 2005; Przylibski et al., 2024). The chemical composition of both samples was distinctly different and allowed for classification of the water samples to two different chemical types, namely HCO_3–Ca and SO_4–Ca–Na, respectively. In 2023 measurement of discharge from the mine adit 19A and spring 28 were not technically possible. Values reported by Fistek (1970) varied between 28-47.5 m^3/h and 0.078-0.3 dm^3/h, respectively.

Spring 28 in Kowary-Wojków is a natural spring which has never been exploited. Between 1974-1989 the mine adit 19A was the only radon inhalatorium in Poland offering a specific microclimate for anthrotherapy, so-called speleotherapy, treatment. The patients were also given the radon water to drink. Between 1969-1990 the town of Kowary was officially registered as a spa by the Ministry of Health (Ciężkowski, 1990; Przylibski, 2005). Nowadays, in Kowary-Podgórze, another mine adit is used by a beauty and spa centre.

PROSPECTIVE AREA OF KROSNOWICE

This prospective area is located in the Intra-Sudetic Synclinorium and more specifically in the Upper Nysa Kłodzka Graben. About 500 metres south-west of the village of Krosnowice a hydrogeological test well R11 (groundwater sampling point no 3, Tab. 1, Figs. 1, 2) is located. Here, the Upper Cretaceous strata are discordantly deposited upon the supracrustal rocks of the Orlica-Śnieżnik Dome (Cwojdziński, 1979; Cymerman and Badura, 2019). The Upper Cretaceous succession is stratigraphically incomplete. The Lower Turonian strata are composed of mudstones and sandstones from a few metres to 120 m thick, while the thickness of the Upper Turonian marls and claystones ranges from 300 to 400 m. The Coniacian strata comprise marls interbedded with sandstones, not exceeding 80 m in thickness (Grzegorczyk et al., 1993).

In the prospective area of Krosnowice, two fractured-porous aquifers are present in the strata of the Upper Nysa Kłodzka Graben, the upper one, 20-150 m thick, of Coniacian and Upper Turonian age and the lower one, <20 m thick, in the Lower Turonian. The hydraulic parameters of both aquifers are variable. Normally, favourable zones are associated with tectonically affected rocks. Borehole R11 is screened in the lower aquifer, showing hydraulic transmissivity within the range of 5-30 m^2/d and up to 500 m^2/d in the tectonic zones (Grzegorczyk et al., 1993). Because of artesian conditions there is a constant groundwater outflow from the borehole which was measured by us on January 17th, 2023, as 0.97 m^3/h.

The groundwater samples were taken from the artesian outflow of the R-11 borehole on January 17, 2023. Water mineralisation amounted to 1134.72 mg/l and the water chemical type was HCO_3–Ca–Na. The content of free CO_2 was <622.46 m/dm^3. The water temperature measured at water outflow was 19.3°C. However, the historical data showed higher water temperature of 22°C (Liber and Kiełczawa, 2002; Ciężkowski et al., 2011), which was two degrees higher than the temperature limit for groundwater to be qualified as thermal water according to Polish legal regulations (Ciężkowski et al., 2010). In 1993, the water sample taken during the pumping test allowed for classification of water from the R11 borehole as acidulous and of increased temperature (Grzegorczyk et al., 1993).

The Krosnowice R11 borehole has never been exploited and water is dumped into a nearby stream. Nowadays, it is located in the area of a newly constructed dry flood storage area.

PROSPECTIVE AREA OF NOWA ŁOMNICA

This prospective area is located at the western edge of the Upper Nysa Kłodzka Graben, where the edge of the graben meets gneisses and schists of the metamorphic unit of the Orlica–Śnieżnik Dome (Fistek and Gierwielaniec, 1964; Żelaźniewicz et al., 2011). The graben structure is filled with the Upper Cretaceous sandstones and marls. Here, two locations with acidulous waters, namely *Źródło Dolne* (Eng. Lower Spring) and *Źródło Górne* (Eng. Upper Spring) (groundwater sampling points no 4 and 5, respectively, Tab. 1; Figs. 1, 2), were selected for this research. The occurrence of acidulous waters in this area is associated with the

Szczawina Fault and its transverse dislocations, along which all potentially medicinal water outflows concentrate. The most important fractured-porous aquifers occur in the Upper Cretaceous strata. The lower aquifer, is composed of Lower Turonian marls and Cenomanian sandstones, and the upper one comprises sandy marls of Coniacian and Middle to Upper Turonian age. The aquifers are divided by thick, less permeable clayey deposits. Locally, groundwater occurs in fractured metamorphic schists. The entire groundwater multiple aquifer system is very inhomogeneous and shows diverse hydrogeological parameters. The area is also known for dry exhalations of carbon dioxide (Fistek, 1977; Żak et al., 2008; Fillipovits et al., 2022).

The groundwater samples were taken on February 22, 2023 from both *Źródło Dolne* and *Źródło Górne*. Discharge from *Źródło Dolne* was 0.07 dm^3/s, though in the case of *Źródło Górne* it was not possible to measure for technical reasons. Water mineralisation was high and amounted to 903.75 and 1312.06 mg/l, while the content of carbon dioxide was 2442.33 and 2230.90 mg/l, respectively. Interestingly, both locations showed different concentrations of specific components, and also in the past, as corroborated by historical data (Krawczyk et al., 2010a, Fillipovits et al., 2022). The chemical type of water from the *Źródło Dolne* was HCO_3–Ca–Mg, with the following specific components: ferrous ions amounting up to 13.8 mg/l and increased contents of radon isotope ^{222}Rn reaching 89.3 Bq/l. The chemical type of water from the *Źródło Górne* was also HCO_3–Ca–Mg, whereas the specific components were different: ferrous ions amounted up to 118.0 mg/l and metasilicic acid (H_2SiO_3) content was 89.1 mg/l. This difference might be caused by the different mineralogical composition of aquifers in both locations and by diverse groundwater flow paths.

The springs of ferruginous acidulous water in Nowa Łomnica have been known since at least the 17th century, though they have been used only by the local residents and tourists. Approximately 1.7 km southeast of these springs, in the nearby village of Szczawina, there is a spring intake and a 51-metre-deep borehole extracting ferruginous acidulous waters showing a similar chemical composition, though with lower mineralisation. Based on these waters, a former bottling plant that operated in Szczawina between 1966 and 2007 produced water called *Długopolanka* (Krawczyk et al., 2010a; Krzonkalla-Maryniuk, 2015).

PROSPECTIVE AREA OF OPOLNICA

This prospective area is located in a small geotectonic unit called the Bardo Fold Structure. Here, occurs a spring called *Źródło Siarczkowe* (Eng. Sulphide Spring) (groundwater sampling point no 6 Tab. 1; Figs. 1, 2). The spring drains the top part of Paleozoic pyrite-impregnated quarzitic shales and is most probably associated with a groundwater circulation zone connected with deep fault zones. The unconfined groundwater table depth is usually shallow and varies between 1 and 5 m b.g.l., though occasionally it may be deeper. Discharge of the spring intake measured by Fistek et al. (1971) amounted to 0.6 m^3/h at a depression of 2.8 m; however, the hydrogeological parameters became more favourable after cleansing the spring in 1972. Inspection of the spring allowed its depth to be measured, which was then 5.5-6.0 m b.g.l. and confirmed the presence of sulphur bacteria.

A water sample from the spring intake *Źródło Siarczkowe* was taken on January 17, 2023, and showed mineralisation of 617.92 mg/l being of chemical type HCO_3–Na. A specific component was fluoride ions amounting up to 2.0 mg/l. The contents of S^{2-} ions and H_2S were elevated up to 0.41 and 0.26 mg/l, respectively, and the water sample had a moderate smell of hydrogen sulphide.

The spring was exploited for several decades by a small bottling plant producing table water called *Opolniczanka* which stopped to operate in the early 1990s. At present, the spring is enclosed by three stoneware casings and protected by a small building.

PROSPECTIVE AREA OF SOSNÓWKA

The prospective area of Sosnówka is placed in the Izera-Karkonosze Massif, in Sosnówka village, where two locations with radon water occurrences were selected, namely *Źródło Anna* (Eng. Ann Spring) and *Źródło Magdalena* (Eng. Magdalene Spring) (groundwater sampling points no 7 and 8, respectively, Tab. 1; Figs. 1, 2). Here, groundwater occurs mainly in the fractured aquifer formed by the Karkonosze granites of Carboniferous age (Bobiński, 2009; Bobiński, 2015). The fractured crystalline aquifer shows a characteristic depth zonation and a high degree of inhomogeneity. The groundwater table depth is usually shallow and unconfined, and hydraulic conductivity varies between 0.01 and 17.5 m^2/d (Kieńć, 2002). Discharge of *Źródło Anna* measured in 1963 varied between 0.33-0.41 dm^3/s, while in 1974 it was 0.81 dm^3/s. Discharge of *Źródło Magdalena* varied between 0.41 and 1,00 in 1963, while in 1974 it was 0.58 dm^3/s (Tęsiorowska, 1974). In winter 2023, measurements of discharge of *Źródło Anna* amounted to 0.23 dm^3/h; however, because of a leaking casing, this volume is an underestimate. Measurement of discharge in the case of *Źródło Magdalena* was not possible for technical reasons. Radon waters in the Sosnówka area were initially described already in the 1970s in several springs and seepages (Tęsiorowska, 1974). The value of the local radon hydrochemical background of groundwater, determined based on 465 measurements, ranged from 37 to 296 Bq/l. These refer to shallow circulation waters of infiltrative origin age typically varying from approximately one to several years (Przylibski, 2005).

Groundwater samples from both *Źródło Anna* and *Źródło Magdalena* were taken on January 23, 2023. These showed low mineralisation, of 86.40 and 57.04 mg/l, and increased contents of radon isotope ^{222}Rn, of 223.0 and 157.0 Bq/l, respectively. In both locations, the major anions were sulphates though with different cation contents. The chemical types of water samples from *Źródło Anna* and *Źródło Magdalena* were: SO_4–HCO_3–Ca–Na–Mg and SO_4–Cl–Ca–Na, respectively.

The *Źródło Anna* is a well-known tourist attraction of the Sudetes. Its outflow is situated in a stone enclosure below the chapel of Saint Anna. The *Źródło Magdalena* is currently used for water supply of a holiday house.

PROSPECTIVE AREA OF STARE BOGACZOWICE

This prospective area is located in the village of Stare Bogaczowice, on the north-western outskirts of the Intra-Sudetic Synclinorium. The oldest rocks identified are conglomerates, sandstones, greywackes and siltstones of Lower Carboniferous age, classified as part of the Stare Bogaczowice Formation. Their total thickness is as much as 1200 m (Kozdrój et al., 2009, 2017). The Lower Carboniferous strata show poor hydrogeological parameters which increase in the vicinity of the Struga Fault zone, striking E-W, with small transverse dislocations. The Struga Fault is the major tectonic feature of the area, forming a boundary between the Intra-Sudetic Synclinorium and the Świebodzice Fold Structure (Żelaźniewicz et al., 2011). The fractured-porous Lower Carboniferous aquifer is only partly overlain by semipermeable Quaternary deposits, thus it is vulnerable to contamination from the ground surface. The groundwater table is rather shallow and only locally confined. The potentially medicinal waters in this area are carbonic and acidulous waters, commonly showing a total mineralisation of >1000 mg/l (Fistek et al., 1968; Fistek, 1976; Poprawski and Jasiak, 1999). Springs and spring intakes are situated within the narrow valley of the Strzegomka River, over a distance of ~0.5 km, in the central part of the village. Numerous dry CO_2 exhalations were detected (Żak et al., 2008), the origin of which have not yet been fully identified.

Groundwater samples were taken on February 27, 2023, from the spring intakes 3 and 11 (groundwater sampling points no 9 and 10, respectively, Tab. 1; Figs. 1, 2). These showed elevated mineralisation of 2200.83 and 2345.31 mg/l, respectively. Content of free CO_2 was determined *in situ* for the groundwater sample from spring intake 3 only, and was 1093.75 mg/l, while in the spring intake 11 it was negative. Chemical types of the water samples from the spring intakes 3 and 11 were generally similar, i.e. HCO_3–Na–Ca–Mg and HCO_3–Ca–Mg–Na, respectively.

Stare Bogaczowice has been well-known for occurrences of medicinal waters since the 19th century. In the beginning of the 20th century, a small spa with a bathhouse and a drinking hall was created in the village. Between 1968 and the early 1990s, a bottling plant extracting water from numerous spring intakes produced water called *Anna*, though its operation ended in the 1990s.

PROSPECTIVE AREA OF STARY WIELISŁAW

The prospective area of Stary Wielisław is located in the Upper Nysa Kłodzka Graben, which is part of the Intra-Sudetic Synclinorium. There, an identified but currently unexploited deposit of carbonic and acidulous waters has been documented by two hydrogeological boreholes (Fistek, 2010). In the 1970s and 1980s, two boreholes, 3 and 4, showing depths of 100 and 268 m b.g.l. respectively, were drilled. They captured the confined aquifer with acidulous waters showing artesian hydraulic conditions. This study focused on borehole 4 (groundwater sampling point no 11, Tab. 1, Fig. 1 and 2). The Upper Cretaceous aquifer is built of sandstones of Middle and Lower Turonian ages. Zones of numerous tectonic dislocations and fractures, stretching in a narrow strip along the Bystrzyca Dusznicka and Wielisławka river valleys, allow for enhanced circulation of potentially medicinal waters and determine the location of springs. The aquifer is very inhomogeneous and hydraulic conductivity varies from 100 to 300 m^2/d in the tectonically affected areas. In the prospective area of Stary Wielisław, numerous dry exhalations of carbon dioxide have been detected (Żak et al., 2008).

A groundwater sample was taken on February 22, 2023 from a pipeline a few tens of metres long discharging water from the artesian outflow of the borehole 4 to the Bystrzyca Dusznicka river. Groundwater sampling directly at the borehole was not technically possible. Discharge of the free artesian outflow as measured by us amounted to 4.89 m^3/h. The water showed mineralization of 1695.87 mg/l and was of chemical type of HCO_3–Ca. Water temperature measured *in situ* at water outflow was slightly increased compared to water temperature in the nearby springs, being 12.4°C. The free CO_2 content in the water was below the detection limit of <622.46 mg/dm^3. Our laboratory test results did not indicate an elevated level of ferrous ions. Contents of free CO_2 and ferrous ions were underestimated because the water was sampled at the outlet of the pipeline where their concentrations may change because of degassing and Fe^{2+} precipitation processes. Rust-coloured sediment is visible around the discharge point. According to historical data (Fistek, 2010) this water is expected to be classified as ferruginous and acidulous.

The springs of carbonated water in Stary Wielisław have been known since at least the beginning of the 20th century and have been used by the local residents. A bottling plant operating here since 1972 produced water, initially called *Polaniczanka*, and since 1997 *Polanica Zdrój*. Production ended in 2008 (Fistek, 2010; Krawczyk et al., 2010b). None of the boreholes is exploited at present.

PROSPECTIVE AREA OF SZCZYTNA

The prospective area of Szczytna lies in the Intra-Sudetic Synclinorium and its subunit, the Upper Nysa Kłodzka Graben. Here, the potentially medicinal waters occur in Lower Turonian sandstones and Upper Cenomanian sandstones and conglomerates, especially in areas located near the fault zones. The geological features of the Upper Cretaceous succession determine the confined conditions of groundwater circulation. In the case of this prospective area, groundwater samples from borehole 3 (groundwater sampling point no 12, Tab. 1; Figs. 1, 2) were studied. This is located in the north-eastern part of Szczytna and has a total depth of 253.5 m b.g.l. In the profile of this well, a fault zone was detected at a depth between 159-163 m b.g.l. from which a strong inflow of acidulous water was observed. In winter 2023, due to artesian conditions, the groundwater table stabilised ~0.5 m a.g.l. The most important fractured-porous aquifers of this prospective area occur in the Upper Cretaceous strata. The lower one is built of Lower Turonian marls and Cenomanian sandstones, while the upper one consists of the sandy marls of Coniacian and Middle to Upper Turonian age. The aquifers are divided by thick, less permeable clayey intervals.

The groundwater samples were taken from the artesian water outflow on January 17, 2023. Discharge of the free artesian outflow amounted to 0.46 m^3/h. Mineralisation was 2208.9 mg/l, while the content of free CO_2 was 2450 mg/l. The laboratory test indicated an elevated content of arsenic ions, i.e. 0.19 mg/l. The water temperature measured *in situ* at the water outflow was 10.3°C. According to historical data, it increased with growing pumping rate, up to 17.3°C, during the pumping test performed in 2009 (Fistek, 2009).

The borehole was constructed in 2009 to capture acidulous water to be used by a bottling plant or health resort. The arsenic ion concentrations in the groundwater in 2023 reached 0.189 mg/l, which exceeds the permissible concentration in drinking water. The content of radionuclides was also elevated, and α radiation ranged between 2.34 and 2.85 Bq/l, while β radiation between 2.01 and 2.34 Bq/l, which disqualified the water for bottling purposes. The water may be used for balneological purposes, though it requires additional testing. Borehole 3 has never been exploited, and for the time being water is dumped into a ditch.

Table 1

Physicochemical characteristics of 12 new groundwater samples collected in 2023 and results of *in situ* measurements

#	Prospective area Sampling point	Sampling date	EC (μS/cm)	pH	T °C	O_2 ppm	CO_2* (mg/l)	Comments
1	Kowary (Kowary-Podgórze) Mine adit 19A	January 24, 2023	242.8	7.8	10.3	ND	N/A	Water sample colourless and odourless
2	Kowary (Kowary-Wojków) Spring 28	January 24, 2023	123.9	6.5	4.8	ND	N/A	Water sample colourless and odourless
3	Krosnowice Borehole 11R	January 17, 2023	1171	6.51	19.3	0.15	<622.46	Water sample colourless with moderate feeling of CO_2, precipitation of $CaCO_3$ and reddish Fe compounds on well casing and on the ground near the outflow
4	Nowa Łomnica Spring intake *Źródło Dolne*	February 22, 2023	884	5.73	5.3	ND	2442.33	Water sample colourless with detection of CO_2, precipitation of Fe compounds of reddish colour on the ground near the water outflow
5	Nowa Łomnica Spring intake *Źródło Górne*	February 22, 2023	1030	5.73	7.3	ND	2230.90	Water sample strongly reddish with detection of CO_2, precipitation of reddish Fe compounds on the ground near the outflow, abundant CO_2 emanations
6	Opolnica Spring intake *Źródło Siarczkowe*	January 17, 2023	718.00	9.16	8.6	5.28	N/A	Water sample colourless with moderate smell of H_2S
7	Sosnówka Spring intake *Źródło Anna*	January 23, 2023	118.4	6.9	6.8	ND	N/A	Water sample colourless and odourless
8	Sosnówka Spring intake *Źródło Magdalena*	January 23, 2023	68.7	6.3	6.8	ND	N/A	Water sample colourless and odourless
9	Stare Bogaczowice Spring intake 3	February 27, 2023	1880	6.41	8.2	ND	1093.75	Water sample colourless and odourless with detection of CO_2
10	Stare Bogaczowice Spring intake 11	February 27, 2023	1030	6.93	8.6	ND	NEG	Water sample colourless and odourless
11	Stary Wielisław Borehole 4	February 22, 2023	1515.00	6.37	12.4	ND	<622.46	Water sample colourless with weak indications of CO_2, precipitation of reddish Fe compounds near the outflow
12	Szczytna Borehole 3	January 17, 2023	2006.0	6.10	10.3	0.07	2450.24	Water sample colourless with detection of CO_2, precipitation of reddish Fe compounds near the outflow

– numbering according to figures 1 and 2; * content of free CO_2 determined *in situ* using the Karat device; ND – no data; N/A – not applicable, NEG – negative, <622.46 mg/dm^3 – below detection limit

DISCUSSION

Differences in lithology, mineralogical composition and tectonics among the studied aquifers determine the hydrogeological and hydrogeochemical properties of the prospective areas studied. Potentially medicinal groundwater occurring in the Upper Cretaceous strata showed elevated mineralisation varying between 903.75 and 2208.90 mg/l. Due to prevailing carbonates, including a high calcite content in the rock matrix and cement, as well as elevated contents of free CO_2, the dominant anions were bicarbonate ions (HCO_3^-), while the major cations were the most commonly calcium ions (Ca^{2+}). Except for the increased total solid dissolved mineral content, the specific component which allows qualifying these waters as potentially medicinal ones was the elevated content of free CO_2. This, due to the methodology of *in situ* measurements with Karat apparatus, was detected only at four of the sampling points studied and amounted to 1093.75, 2230.90, 2442.33, and 2450.24 mg/l for the Stare Bogaczowice intake 3, Nowa Łomnica *Źródło Górne*, Nowa Łomnica *Źródło Dolne* and Szczytna borehole 3, respectively (Tab. 1 and App. 2). The groundwater samples in Nowa Łomnica showed increased concentrations of other specific components which may allow for classification as medicinal water, namely: at the Nowa Łomnica *Źródło Dolne* ferrous ions (Fe^{2+}) amounted to 13.80 mg/l and radon isotope ^{222}Rn was 89.3 Bq/l, while at the Nowa Łomnica *Źródło Górne* ferrous ions (Fe^{2+}) amounted to 118.00 mg/l and metasilicic acid (H_2SiO_3) to 89.1 mg/l (App. 2).

The hydrogeochemistry of groundwater occurring in the crystalline bedrock, composed mainly of silicate minerals, was recognizably different. Mineralisation of four groundwater samples analysed from the prospective areas of Kowary and Sosnówka was low and varied between 86.40 and 207.99 mg/l. The specific component allowing for qualification of these waters as potentially medicinal was the radon ^{222}Rn isotope which amounted to 134.0 and 446.0 Bq/l for the locations of Kowary-Podgórze, mine adit 19A and Kowary-Wojków, spring 28, respectively, while at the Sosnówka *Źródło Magdalena* and *Źródło Anna* these were 157.0 and 223.0 Bq/l, respectively (App. 2).

Groundwater in the prospective area of Stare Bogaczowice showed the highest mineralisation among all groundwater samples analysed and varied between 2200.83 and 2345.31 mg/l for the spring intakes 11 and 3, respectively. Except for high mineralisation, the specific component which may allow these waters to be classified as medicinal ones is again the elevated content of free CO_2, which in the case of spring intake 3 was 1093.75 mg/l (Tab. 1 and App. 2).

Mineralisation of the groundwater sample from the spring intake *Źródło Siarczkowe* in the prospective area of Opolnica was 617.92 mg/l. Here, the specific element detected in the groundwater sample which may allow classification as potentially medicinal water was the content of fluoride (F^-) ions amounting to 2.0 mg/l. There were also slightly elevated concentrations, compared to other wells in this area, of bivalent sulphur ions (S^{2-}), amounting to 0.41 mg/l, and a hydrogen sulphide (H_2S) content of 0.26 mg/l (App. 2), with a moderate smell characteristic for this gas, These concentrations, however, cannot allow classification of the water sample to sulphide water.

In Poland, the criteria that drinking water must meet are given by the *Rozporządzenie Ministra Zdrowia z 7 grudnia 2017 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi* (Eng. Regulation of the Minister of Health of December 7th, 2017 on the quality of water intended for human consumption). According to this regulation, ordinary drinking water should contain no more than 250 mg/l of chloride, 0.05 mg/l of manganese, 200 mg/l of sodium, and 0.2 mg/l of ferruginous ions, while the magnesium ion content should be between 7 and 125 mg/l. There is no specified permissible concentration of hydrogen sulphide, though the odour of the water must be “acceptable to consumers and free from abnormal changes”.

In the case of the prospective areas located within the carbonate sedimentary rocks of the Upper Nysa Graben, the chemical types were rather similar, i.e.: HCO_3–Ca for Stary Wielisław, borehole 4, and Szczytna, borehole 3, HCO_3–Ca–Na for Krosnowice, borehole R11, and HCO_3–Ca–Mg for Nowa Łomnica, *Źródło Dolne* and *Źródło Górne*, and HCO_3–Ca–Mg–Na and HCO_3–Na–Ca–Mg for Stare Bogaczowice, intakes 3 and 11. However, in the case of the groundwater samples from the crystalline bedrock, the following locations showed a wide variety of chemical types, i.e.: HCO_3–Ca for Kowary-Podgórze mine adit 19A, SO_4–Ca–Na for Kowary Wojków springs 28, as well as SO_4–HCO_3–Ca–Na–Mg for *Źródło Anna* and SO_4–Cl–Ca–Na for spring *Źródło Magdalena* in Sosnówka. The differentiated chemical composition of these groundwater samples derived, most probably, from the diverse lithology and mineral composition of the aquifer material. Chemical types of the groundwater samples studied, according to the classification of Priklonskiy-Shchukarev, as well as their chemistry and contents of specific elements and temperature, are shown in Table 2.

The chemistry of the groundwater samples studied is well illustrated by their statistical parameters of chemical composition shown by Figure 3A-C, where Figure 3A shows statistical characteristics for all 12 samples analysed, Figure 3B for 7 groundwater samples from the Intra-Sudetic Synclinorium and Figure 3C shows 4 groundwater samples from the Karkonosze-Izera Massif. The individual elements showing the highest range are mineralisation expressed as TDS, bicarbonate ions (HCO_3^-) and free CO_2 for Figure 3A and 3B, while for Figure 3C, the highest range shows mineralisation (TDS), bicarbonate ions (HCO_3^-) and the radon ^{222}Rn isotope. The difference in mineralisation and concentration of bicarbonate ions (HCO_3^-) between the groundwater samples from the fractured-porous Cretaceous sedimentary aquifers (Fig. 3B) and the fractured Carboniferous and Paleozoic-Proterozoic aquifers (Fig. 3C) is profound and reaches one order of magnitude. For the possible classification of groundwater as a potentially medicinal water, a crucial factor is the stability of its chemical composition over a certain period of time. The concentration of major anions, cations and specific components in the 12 groundwater samples of potentially medicinal water we studied compared to 21 historical results of chemical analyses are shown by Schoeller diagrams (Fig. 4A-H). The chemical stability varies significantly depending on location and the element studied. The most stable chemical composition occurred at Kowary-Wojków spring 28 (Fig. 4A2), both springs in the prospective area of Nowa Łomnica (Fig. 4C1 and C2), borehole 4 in the prospective area of Stary Wielisław (Fig. 4G) and borehole 3 in the prospective area of Szczytna (Fig. 4H). By contrast, the maximum differences in concentration of major ions and specific elements over time, for example: SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+} and ^{222}Rn, reaching up to 80-87%, were observed for the Kowary-Podgórze mine adit 19A (Fig. 4A1), borehole R11 (Fig. 4B) and *Źródło Siarczkowe* in Opolnica (Fig. 4D). These differences could be caused by factors including the presence or absence of an impermeable cover on the aquifer, and the influence of geo- or anthropogenic factors on groundwater chemistry. Another reason may be groundwater sampling techniques. In the case of the boreholes historical datasets show chemistry of samples taken during pumping tests, while our research covers groundwater samples collected from free artesian outflow. The total dataset of results of chemical analyses of 33 groundwater samples is quite inhomogeneous, i.e. the samples were analysed by different laboratories, with different techniques and according to different standards in the time span between 1968 and 2023.

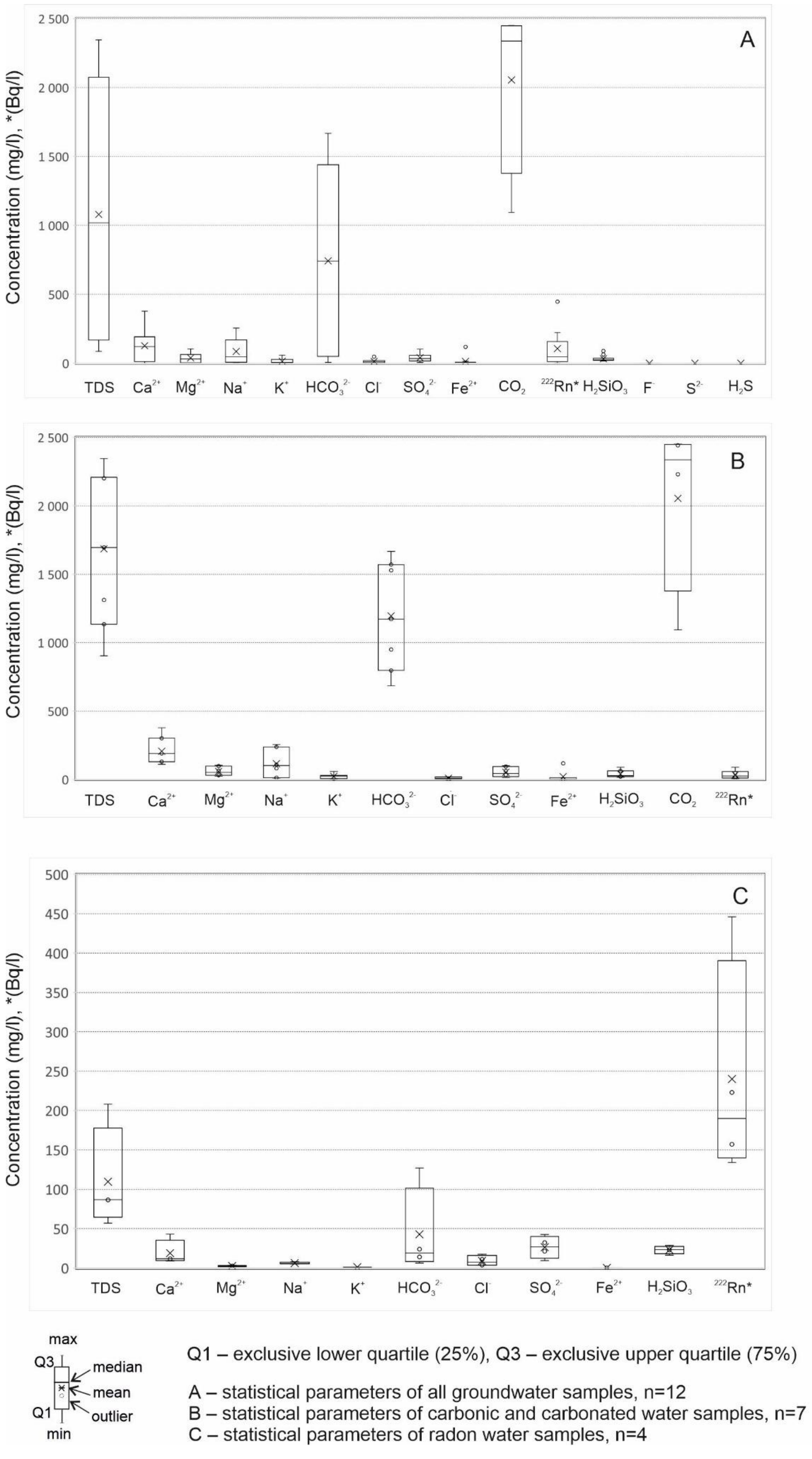
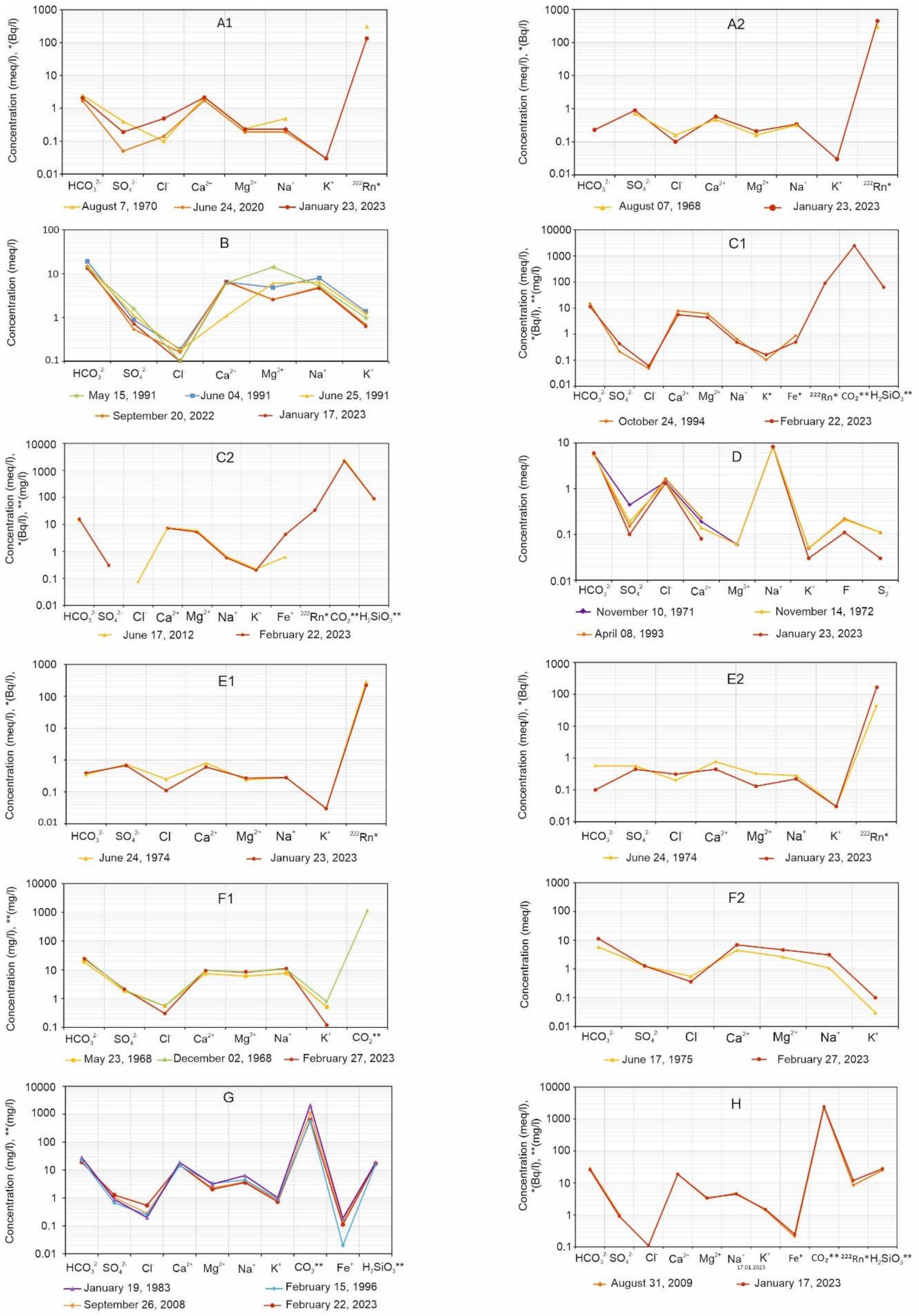


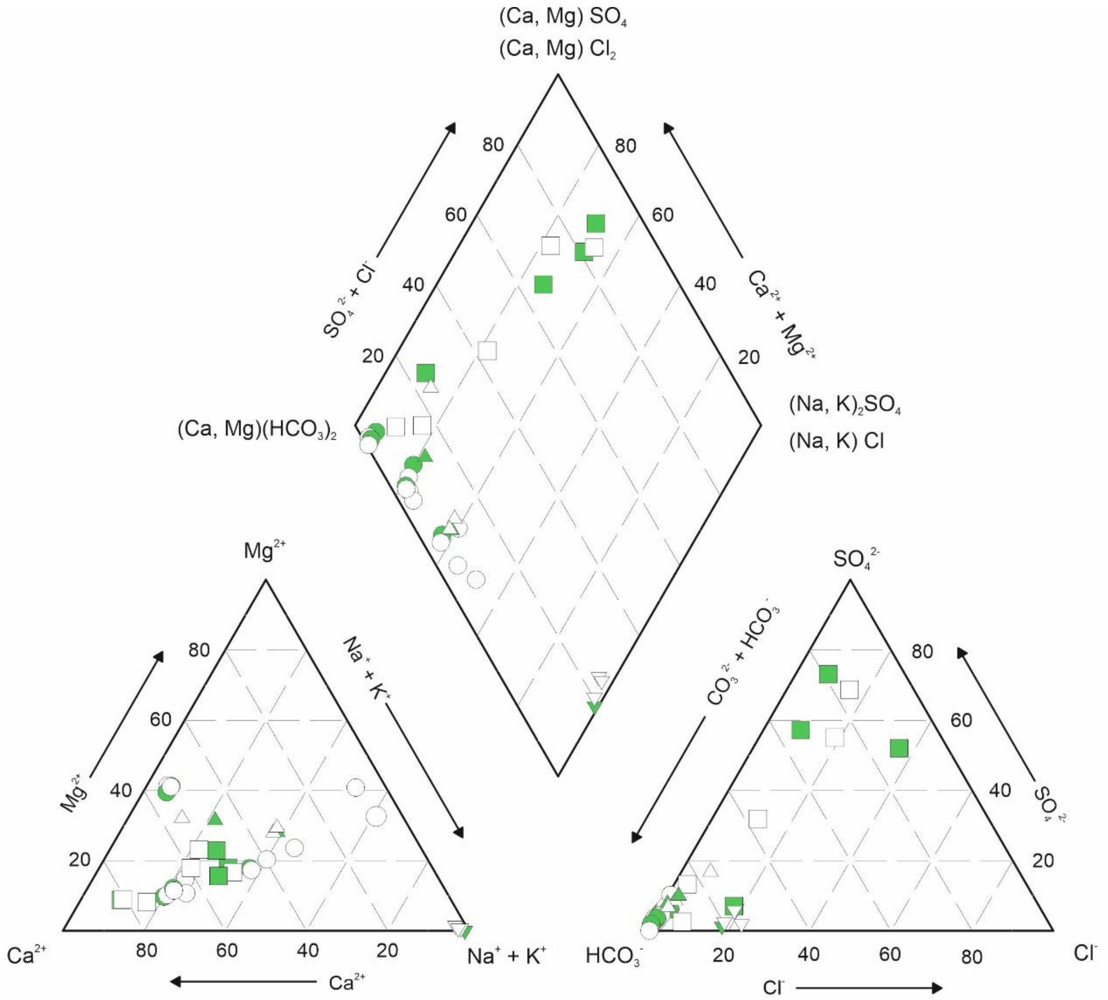
Fig. 3. Box and whisker plots showing selected statistical parameters of the chemical composition of 12 groundwater samples collected in 2023



A1 – Kowary-Podgórze, mine addit 19A, A2 – Kowary-Wojków, spring 28, B – Krosnowice, borehole 11R, C1 – Nowa Łomnica, spring *Źródło Dolne*, C2 – Nowa Łomnica, spring *Źródło Górne*, D – Opolnica, spring *Źródło Siarczkowe*, E1 – Sosnówka, spring *Źródło Anna*, E2 – Sosnówka, spring *Źródło Magdalena*, F1 – Stare Bogaczowice, spring intake 3, F2 – Stare Bogaczowice, spring intake 11, G – Stary Wielisław, borehole 4, H – Szczytna, borehole 3

Fig. 4. Schoeller diagrams showing the groundwater chemical composition of 33 groundwater samples: 12 collected in 2023 and 21 collected between 1968 and 2022

The relation between the rock types and the groundwater composition of the individual groundwater samples, including 12 samples analysed for this research and 21 historical ones, is displayed in a Piper diagram (Fig. 5). This, in addition to the Priklonskiy-Shchukarev designation, is another approach to hydrogeochemical classification (Appelo and Postma, 1996; Ganvir, 2023). The diagram shows the concentration, in % (meq/l), of anions and cations in two triangles and the corresponding water types in a diamond. The groundwater samples taken from the Intra-Sudetic Synclinorium (circles) show high mineralisation, a diverse composition of cations with prevailing calcium cation (Ca^{2+}), and a strong domination of bicarbonate anions (HCO_3^-). These show primarily the alkaline-earth bicarbonate chemical water type ($Ca\text{-}HCO_3$). By contrast, the groundwater samples taken from the crystalline bedrock of the Karkonosze-Izera Massif (squares) show low mineralisation. The major cations are calcium ions, while the anions are bicarbonates, sulphate ions (SO_4^{2-}) and, to smaller extent, chloride ions (Cl^-). Most of these groundwater samples belong to the alkaline-earth elevated alkaline bicarbonate to sulphate chemical water type ($Ca\text{-}HCO_3$ / SO_4), and a smaller group to the alkaline-earth bicarbonate type ($Ca\text{-}HCO_3$). The groundwater samples, some of them containing free CO_2, retrieved from the Paleozoic fractured-porous aquifer (triangles) show diverse mineralisation, moderate to high contents of calcium and some sodium (Na^+) cations. Among the anions, both bicarbonates and sulphates are present. These water samples belong mainly to the alkaline-earth elevated alkaline bicarbonate chemical water type ($Ca\text{-}Na\text{-}HCO_3$). The last group of groundwater samples comes from the Paleozoic fractured-porous aquifer (inverted triangles), where the groundwater samples showed elevated fluoride concentrations. Here, compared to the other locations analysed, mineralisation is moderate. The major cations are sodium ions, while the dominating anions are bicarbonates. These show a distinct alkaline, mainly $(H)CO_3$ water type.



○ – fractured-porous aquifer of Cretaceous sedimentary series of the Upper Nysa Kłodzka Graben, prospective areas of Krosnowice, Stary Wielisław, Szczytna and Nowa Łomnica (includes also groundwater circulation through Proterozoic metamorphic series of the Orlica-Śnieżnik Dome), number of samples n=15

□ – fractured aquifer of Carboniferous and Paleozoic-Proterozoic crystalline bedrock of the Karkonosze-Izera Massif, prospective areas of Kowary and Sosnówka, number of samples n=9

△ – fractured-porous aquifer of Paleozoic sedimentary series of the Intra-Sudetic Synclinorium, the Świebodzice Fold Structure, prospective area of Stare Bogaczowice, number of samples n=5

▽ – fractured-porous aquifer in Paleozoic sedimentary series of the Bardo Fold Structure, prospective area of Opolnica, number of samples = 4

● ■ ▲ ▼ – 12 groundwater samples ghatered in 2023

Concentration values are given in %(meq/l)
Size of each symbol corresponds to mineralization (mg/l), mineralisation: min = 57.04 and max = 2425.00 (mg/l)

Total number of groundwater samples n=33, number of groundwater samples taken in the framework of this research n=12 (taken in 2023), number of historical groundwater samples n=21 (taken between 1968-2022)

Source of historical data for the prospective areas of: Kowary – Fistek (1970), Krosnowice – Grzegorczyk et al. (1993), Nowa Łomnica – Krawczyk et al. (2010a), Opolnica – Fistek et al. (1971), Sosnówka – Tęsiorowska (1974), Stare Bogaczowice – Fistek et al. (1968) and Fistek (1976), Stary Wielisław – Fistek (2010); Szczytna – Fistek (2009)

Fig. 5. Piper diagram showing chemical composition and chemical types of 12 groundwater samples collected in 2023 and 21 historical groundwater samples collected between 1968 and 2022

Table 2

Chemical characteristics of 12 groundwater samples collected in 2023

#	Prospective area Sampling point	Groundwater chemical type of Priklonskiy-Shchukarev*	Kurlov's formula**
1	Kowary, Kowary-Podgórze Mine adit 19A	0.021% HCO_3–Ca, Rn	$Rn(222)^{134}\ M^{0.21}\frac{HCO_3^{80}Cl^{18}\ SO_4^{7}}{Ca^{80}\ Na^{9}\ Mg^{9}}T^{10.3}$
2	Kowary, Kowary-Wojków Spring 28	0.009% SO_4–Ca–Na, Rn	$Rn(222)^{446}\ M^{0.09}\frac{SO_4^{69}\ HCO_3^{19}\ Cl^{8}}{Ca^{50}\ Na^{29}\ Mg^{18}}T^{8.6}$
3	Krosnowice, Borehole 11R	0.11% HCO_3–Ca–Na, CO_2	$CO_2^{<0.62}M^{1.1}\frac{HCO_3^{94}SO_4^{5}}{Ca^{45}Na^{32}Mg^{18}K^{4}}T^{19.3}$
4	Nowa Łomnica Spring intake *Źródło Dolne*	0.09% HCO_3–Ca–Mg, CO_2, Rn, Fe	$Fe^{13.8}Rn(222)^{89.3}{CO_2}^{2.44}M^{0.9}\frac{HCO_3^{96}SO_4^{4}}{Ca^{50}Mg^{39}Na^{4}K^{1}}T^{5.3}$
5	Nowa Łomnica Spring intake *Źródło Górne*	0.13% HCO_3–Ca–Mg, CO_2, Fe, H_2SiO_3	$H_2SiO_3^{89.1}Fe^{118}{CO_2}^{2.23}M^{1.3}\frac{HCO_3^{98}SO_4^{2}}{Ca^{41}Mg^{30}Na^{3}K^{1}}T^{7.3}$
6	Opolnica Spring intake *Źródło Siarczkowe*	0.062% HCO_3–Na, H_2S, F	$F^{2.0}H_2S^{0.3}M^{0.62}\frac{HCO_3^{80}Cl^{17}SO_4^{1}}{Na^{98}\ Ca^{1}}T^{8.6}$
7	Sosnówka Spring intake *Źródło Anna*	0.009% SO_4–HCO_3–Ca–Na–Mg, Rn	$Rn(222)^{223}M^{0.09}\frac{SO_4^{55}HCO_3^{32}Cl^{9}}{Ca^{51}Na^{24}Mg^{23}K^{3}}T^{6.8}$
8	Sosnówka Spring intake *Źródło Magdalena*	0.006% SO_4–Cl–Ca–Na, Rn	$Rn(222)^{157}M^{0.06}\frac{SO_4^{50}Cl^{35}HCO_3^{11}}{Ca^{54}\ Na^{27}Mg^{15}K^{3}}T^{6.8}$
9	Stare Bogaczowice Spring intake 3	0.22% HCO_3–Na–Ca–Mg, CO_2	$CO_2^{1.0}M^{2.2}\frac{HCO_3^{92}SO_4^{8}}{Na^{38}Ca^{33}Mg^{28}}T^{8.2}$
10	Stare Bogaczowice Spring intake 11	0.11% HCO_3–Ca–Mg–Na	$M^{1.1}\frac{HCO_3^{84}SO_4^{10}Cl^{3}}{Ca^{47}Mg^{31}Na^{21}}T^{8.6}$
11	Stary Wielisław Borehole 4	0.17% HCO_3–Ca	${CO_2}^{<0.62}M^{1.7}\frac{HCO_3^{91}SO_4^{6}Cl^{3}}{Ca^{70}Na^{16}Mg^{10}K^{3}}T^{12.4}$
12	Szczytna Borehole 3	0.22% HCO_3–Ca, CO_2	${CO_2}^{2.45}M^{2.2}\frac{HCO_3^{96}SO_4^{3}}{Ca^{66}Na^{16}Mg^{12}K^{5}}T^{10.3}$

– numbering according to figures 1 and 2; * – formula shows: mineralization (TDS) given in %, providing 1000 mg/l = 0.1% of weight percentage, major anions and cations ≥20% meq/l, specific components allowing for classification as medicinal water; ** – formula shows all present major anions and cations mg/l rounded to unity, concentration of free CO_2, Fe, F and H_2SiO_3 in mgl/l, M (mineralization = TDS) in g/l, content of Rn in Bq/l and T in °C

CONCLUSIONS

Most of the medicinal waters we studied occur in the Upper Cretaceous fractured-porous aquifers mostly comprising marls and sandstones of the Upper Nysa Kłodzka Graben, part of the Intra-Sudetic Synclinorium. There, the prospective areas of Krosnowice, Nowa Łomnica, Stary Wielisław and Szczytna were designated. The tectonic setting of Nowa Łomnica means that the aquifer is composed of both the Upper Cretaceous sedimentary strata and metamorphic rocks of the Orlica-Śnieżnik Dome. The individual groundwater samples derived from these locations showed commonly elevated contents of total solid dissolved minerals and of free CO_2. Several showed increased concentrations of such specific elements as ferrous ions and metasilicic acid which may allow for future classification as potentially medicinal water.

The second groundwater group comprises samples retrieved from fractured aquifers formed by the igneous crystalline rocks of the Karkonosze-Izera Massif. These lie in two prospective areas, Kowary and Sosnówka. The crystalline bedrock is composed mostly of granites, as well as granite gneisses, gneisses, mica schists, amphibolites, hornfelses, skarns and locally marbles. For these locations, the specific element is radon isotope ^{222}Rn.

The prospective area of Stare Bogaczowice is located on the north-western outskirts of the Intra-Sudetic Synclinorium. Here, the fractured-porous aquifer is mainly built of a thick Paleozoic sedimentary succession, including conglomerates, sandstones and greywackes, though showing poor hydraulic properties. The groundwater commonly shows increased total solid dissolved mineral content and elevated contents of free CO_2.

A distinct location is the prospective area of Opolnica located in the Bardo Fold Structure where potentially medicinal waters occur in a fractured-porous aquifer composed primarily of Paleozoic siltstones, claystones, shales and greywackes forming the Opolnica Formation. The specific component of these waters is the fluoride anion.

The eight prospective areas we studied form an exemplary group and dataset source of potentially medicinal water in the Polish Sudetes and can be treated as a study case. This small group represents the major types of potentially medicinal waters, chemical water types and types of aquifers of this region. Occurrences of potentially medicinal waters are, to a large extent, determined by the complex geological settings, especially by the lithology, tectonics and mineral composition of the rocks. The results of these studies clearly show that the places especially predisposed to the occurrence of medicinal waters are associated with the major tectonic features, i.e. the deep tectonic zones with the major Sudetic strike and smaller perpendicular dislocations. Another crucial factor is the ability of the subsurface to collect and conduct groundwater, thus such properties as the intergranular and fracture porosity of the rocks. The groundwater chemistry is to a major extent dominated by the mineralogy of the rock environment as well as by biogeochemical processes. Research focusing on such issues as the origin and flux of ^{222}Rn, CO_2 and other gases in the groundwater should be continued. A crucial issue are measurements of temperature, especially its profiling in the hydrogeological boreholes.

The occurrences of potentially medicinal waters should be regularly monitored for their quality and quantity. Their possible future utilisation, due to a high number of already existing facilities using medicinal water in the studied area, should ultimately reflect market needs and available investment measures. However, several of them can become at least a tourist attraction.

The selected prospective areas represent geological and hydrogeological conditions, as well as the chemical types of medicinal waters, characteristic of the Polish Sudetes. Therefore, these research findings are regionally significant and may contribute to reassessment of hydrogeological and hydrogeochemical data in the proximal parts of the Bohemian Massif, including its Czech parts. The results may help to determine new sources of medicinal waters in the region within geological units that have similar tectonic, geological and hydrogeological settings.

Data availability statement

The great majority of the original research findings of this study are provided in this paper. For further details and inquiries, please contact the corresponding author.

Author contributions

MRK: Writing – review and editing; Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Field research, Supervision, LC: Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, AK: Writing – original draft, Visualization, Methodology, Formal analysis, Data curation, Field research. All authors have read and agreed to the submitted version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix 1
General characteristics of prospective areas and groundwater sampling points

#	Prospective area Sampling point	Coordinates GPS: N & E	Altitude (m a.s.l.)	Borehole or intake depth (m b.g.l.)	Discharge: (dm^3/s)** (m^3/h)***	Geological unit	Major rock types	Age of aquifer	Type of aquifer
1	Kowary (Kowary-Podgórze) Mine adit 19A	50° 45' 31.4'' 15° 50' 23.8''	727.1	0.0	1: 28-47.5 (Fistek, 1970) 2: N/A	Karkonosze-Izera Massif, Karkonosze Granite Pluton	Granites, granite gneisses, gneisses, mica schists, amphibolites, hornfelses, skarns, marbles	C, Pz-Pt, Q	F
2	Kowary (Kowary-Wojków) Spring 28	50° 48' 16.8'' 15°51' 11.7''	553.4	0.0	1: 0.078-0.3 (Fistek, 1970) 2: N/A	Karkonosze-Izera Massif, Karkonosze Granite Pluton	Granites	C, Q	F
3	Krosnowice Borehole 11R	50° 22' 47.6'' 16° 37' 03.1''	312.8	525.0	1: 4.0, depr. 140 (Grzegorczyk et al., 1993) 2: 0.97	Intra-Sudetic Synclinorium Upper Nysa Kłodzka Graben	Marls, sandstones	K	F-P
4	Nowa Łomnica Spring intake *Źródło Dolne*	50° 20' 29.4'' 16° 32' 38.9''	596.6	0.0	1: N/A 2: 0.07	Intra-Sudetic Synclinorium Upper Nysa Kłodzka Graben Orlica-Śnieżnik Dome	Marls, sandstones, schists	K, PZ-Pt	F-P
5	Nowa Łomnica Spring intake *Źródło Górne*	50° 20' 28.3'' 16° 32' 38.2''	599.5	0.0	1: N/A 2: N/A	Intra-Sudetic Synclinorium Upper Nysa Kłodzka Graben Orlica-Śnieżnik Dome	Marls, sandstones, schists	K, PZ-Pt	F-P
6	Opolnica Spring intake *Źródło Siarczkowe*	50° 30' 19.4'' 16° 43' 15.1''	268.5	5.5-6.0	1: 0.6, depr. 2.8 m (Fistek et al., 1971) 2: N/A	Bardo Fold Structure	Siltstones, claystones, shales, greywackes	Pz	F
7	Sosnówka Spring intake *Źródło Anna*	50° 48' 05.2'' 15° 43' 47.4''	666.2	0.0	1: 0.33-0.41 av. in 1963 0.81 av. in 1974 (Tęsiorowska, 1974) 2: 0.23	Karkonosze-Izera Massif, Karkonosze Granite Pluton	Granites	C	F

#	Prospective area Sampling point	Coordinates GPS: N & E	Altitude (m a.s.l.)	Borehole or intake depth (m b.g.l.)	Discharge: (dm³/s)** (m³/h)***	Geological unit	Major rock types	Age of aquifer	Type of aquifer
8	Sosnówka Spring intake *Źródło Magdalena*	50° 47' 42.0'' 15° 43' 37.3''	710.1	0.0	1: 0.41-1,00 av. in 1963 0.58 av. in 1974 (Tęsiorowska, 1974) 2: N/A	Karkonosze-Izera Massif, Karkonosze Granite Pluton	Granites	C	F
9	Stare Bogaczowice Spring intake 3	50° 50' 55.6'' 16° 11' 25.2''	363.6	2.73	1: N/A 2: N/A	Intra-Sudetic Synclinorium Świebodzice Fold Structure	Conglomerates, sandstones, greywackes	Pz	F-P
10	Stare Bogaczowice Spring intake 11	50° 50' 57.2'' 16° 11' 27.9''	363.7	5.28	1: N/A 2: N/A	Intra-Sudetic Synclinorium Świebodzice Fold Structure	Conglomerates, sandstones, greywackes	Pz	F-P
11	Stary Wielisław Borehole 4	50° 24' 42.9'' 16° 36' 00.9''	310.1	268	1: upper aquifer: 3.1, depr. 8.8 lower aquifer: 15.0, depr. 9.3 (Fistek, 2010) 2: lower aquifer: 4.89	Intra-Sudetic Synclinorium Upper Nysa Kłodzka Graben	Marls, sandstones	K	F-P
12	Szczytna Borehole 3	50° 24' 10.1'' 16° 27' 07.5''	470.3	253.5	1: 12.0, depr. 31.0 (Fistek, 2009) 2: 0.46	Intra-Sudetic Synclinorium Upper Nysa Kłodzka Graben	Marls, sandstones	K	F-P

– numbering according to figures 1 and 2; * – discharge of natural springs in dm³/s; ** – discharge of boreholes and mine adit in m³/h; 1 – discharge value derived from archive hydrogeological report; 2 – discharge value measured *in situ* in this research; depr. – depression; av. – average; N/A – not applicable or not available; Q – Quaternary, K – Cretaceous, C – Carboniferous; Pz – Paleozoic; Pz-Pt – Paleozoic-Proterozoic; F – fractured, F-P – fractured-porous. In the case of boreholes: Krosnowice R11, Stary Wielisław 4 and Szczytna 3 historical discharge was measured with pumping tests.

Appendix 2

Chemical characteristics of 12 groundwater samples collected in 2023 including TDS, major ions and selected specific components

#	Prospecting area Sampling point	Sampling date	TDS (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	HCO_3^{-} (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	Fe^{2+} (mg/l)	F^{-} (mg/l)	S^{2-} (mg/l)	CO_2 * (mg/l)	^{222}Rn (Bq/l)	H_2S (mg/l)	H_2SiO_3 (mg/l)
1	Kowary (Kowary-Podgórze) Mine adit 19A	January 23, 2023	86.98	11.60	2.50	7.76	1.06	14.00	3.44	42.52	0.027	<0.1	0.23	N/A	446.0	<0.2	28.7
2	Kowary (Kowary-Wojków) Spring 28	January 23, 2023	207.99	43.00	2.78	5.37	1.21	127.00	17.54	9.35	0.181	0.29	<0.2	N/A	134.0	<0.2	16.4
3	Krosnowice Borehole 11R	January 17, 2023	1134.72	130.00	31.10	108.00	25.10	797.00	3.48	34.7	1.19	0.70	0.29	<622.46	6.4	<0.2	38.0
4	Nowa Łomnica Spring intake *Źródło Dolne*	February 22, 2023	903.75	111.00	52.60	11.10	6.31	685.00	2.14	20.72	13.80	<0.1	<0.2	2442.33	89.3	<0.2	63.1
5	Nowa Łomnica Spring intake *Źródło Górne*	February 22, 2023	1312.06	144.00	63.00	13.20	7.86	950.00	<2	14.52	118.00	<0.1	<0.2	2230.90	33.7	<0.2	89.1
6	Opolnica Spring intake *Źródło Siarczkowe*	January 17, 2023	617.92	1.62	<0.005	190.00	1.31	370.00	47.04	4.77	0.062	2.00	0.41	N/A	2.4	0.26	19.4
7	Sosnówka Spring intake *Źródło Anna*	January 23, 2023	86.40	12.10	3.31	6.52	1.18	24.00	3.84	32.12	BDL	<0.1	<0.2	N/A	223.0	<0.2	23.6
8	Sosnówka Spring intake *Źródło Magdalena*	January 23, 2023	57.04	8.81	1.54	5.14	1.02	6.20	10.92	21.31	0.036	<0.1	<0.2	N/A	157.0	<0.2	23.2

#	Prospecting area Sampling point	Sampling date	TDS (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	HCO_3^{-} (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	Fe^{2+} (mg/l)	F^{-} (mg/l)	S^{2-} (mg/l)	CO_2 * (mg/l)	^{222}Rn (Bq/l)	H_2S (mg/l)	H_2SiO_3 (mg/l)
9	Stare Bogaczowice Spring intake 3	February 27, 2023	2200.83	192.00	98.40	255.00	4.66	1529.00	10.51	101.60	0.019	0.15	<0.2	1093.75	47.9	<0.2	23.7
10	Stare Bogaczowice Spring intake 11	February 27, 2023	2345.31	190.46	104.00	237.95	30.00	1667.00	19.66	94.60	0.124	<0.1	<0.2	NEG	19.1	<0.2	21.0
11	Stary Wielisław Borehole 4	February 22, 2023	1695.87	302.00	25.10	81.80	28.70	1172.00	19.27	61.59	3.11	<0.1	<0.2	<622.46	<2.0	<0.2	17.0
12	Szczytna Borehole 3	January 17, 2023	2208.90	378.00	41.40	103.00	58.50	1571.00	4.05	43.81	7.01	0.33	<0.2	2450.24	12.0	0.54	28.0

– numbering according to figures 1 and 2; * – free CO_2 determined *in situ* using the Karat apparatus; N/A – not applicable, NEG – negative, < – below detection limit, TDS – total dissolved solids, i.e. a sum of all major anions and cations