

## Mineral and thermal waters of Poland

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*Abstract.* Definitions, history, resources, origin, and use of mineral and thermal waters in Poland are discussed. Mineral and some thermal waters have been used on the present territory of Poland for therapeutic purposes probably since the Roman times and according to documents since medieval ages. Nowadays, different types of mineral and thermal waters are exploited in a number of Spas for therapeutic purposes, whereas in some other areas thermal waters are exploited for recreation and heating purposes. Their occurrences, origin, chemical types, legal aspects of exploitation, potential vulnerability and bottling are presented.

**Keywords:** Poland, therapeutic waters, mineral waters, thermal waters, health resorts

The aim of the present paper is to present vast resources of therapeutic, potentially therapeutic and other mineral waters in Poland. Resources of thermal waters are rather poor and their uses are limited to therapeutic purposes, recreation and heating.

### Definitions of mineral, therapeutic and thermal waters

In the past, the term *mineral water* was used in Poland with a broad meaning including waters with specific hydro-chemical signatures or specific properties, independently of the concentration of total dissolved solids. Now, groundwater with the total dissolved solids (TDS) concentration of 1 g/dm<sup>3</sup> or higher is defined by law as mineral. *Therapeutic water* is defined as groundwater with natural variations of physical and chemical properties, being chemically and microbiologically clean, and satisfying at least one condition regarding its mineralisation, temperature or the content of a specific component. The mean concentration of a specific component reduced by a double value of its standard deviation should be not lower than a threshold value given in Table 1.

Therapeutic properties of different types of waters used in numerous spas have been proven by long-term medical observations as well as by clinical research. Water from a newly developed aquifer is regarded as potentially therapeutic if its chemical composition is similar to other known

therapeutic water(s). However, its inclusion into the category of therapeutic waters depends on the administrative regulations. Surveillance over the quality of therapeutic waters is carried out by the Polish Hygiene Institute. Four other laboratories are also licensed to certify therapeutic properties of groundwater.

Therapeutic waters are regarded as mineral resources, thus, their exploitation and protection are governed by the *Geological and Mining Act* (1994) and by the *Pharmaceutical Law* (2001). Geological formations containing therapeutical waters constitute mining areas, within which an investor is obliged to obtain a permission for exploitation, and the mining area is defined as that requiring protection and where negative impacts resulting from mining operations can occur.

Groundwater with a temperature of 20°C or higher at the discharge is also regarded as a mineral deposit. The actual fee for the exploitation of therapeutic and thermal waters is 1.1 PLN/m<sup>3</sup> and 0.26 PLN/m<sup>3</sup>, respectively. Abstracting therapeutic or thermal waters is licensed by the government, which issues certificates for prospecting and next for abstracting groundwater. The administrative authority responsible for this matter is the Ministry of Environment.

Problems related to licensing, geological documentations and groundwater resources are regulated by the Chief National Geologists and the Department of Geology and

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**Table 1. Classification of therapeutic groundwater based on their pharmaco-dynamic factors. In shadow minimal concentration or temperature required for therapeutic water**

Pharmaco-dynamic factors		
Total Dissolved Solids	Specific component	Temperature
≥1 g/dm <sup>3</sup>	2 mg F/dm <sup>3</sup> (fluoride water)	thermal ≥20°C
	1 mg I/dm <sup>3</sup> (iodide water)	
	1 mg S(II)/dm <sup>3</sup> (sulphide water)	
	70 mg H <sub>2</sub> SiO <sub>3</sub> /dm <sup>3</sup> (silica water)	
<1 g/dm <sup>3</sup>	10 mg Fe(II)/dm <sup>3</sup> (ferruginous water)	cold <20°C
	74 Bq Rn/dm <sup>3</sup> (radon or radioactive water)	
	1000 mg free CO <sub>2</sub> /dm <sup>3</sup> (CO <sub>2</sub> -rich water, carbonated water)	
	250 mg free CO <sub>2</sub> /dm <sup>3</sup> (carbonated water)	

Geological Licensing at the Ministry of Environment, with a help of the Commission for Hydrogeologic Documentations. The exploitation and protection of mineral groundwater is controlled by Regional Mining Offices.

### Beginnings of therapeutic waters

The oldest information about the use of mineral groundwater is associated with the prospecting and exploitation of salt beds. First archaeological information for the Ciechocinek area comes from the Bronze Age and next from 11th century, for the Kołobrzeg area from 7th century and for the Rabka-Zdrój and Szczawa area from 13th century (for localisations see Fig. 1). First intakes of carbonated waters existed the 1st and 2nd century in Szczawno-Zdrój. The legend about discovering thermal groundwater in Cieplice Śląskie-Zdrój (Germ. *Bad Warmbrunn*) in 1175 is presented in the first written information about mineral groundwater in Poland in the Henrykowska Book<sup>1</sup>. First bathing equipments over a thermal spring in Łądek-Zdrój (Germ. *Bad Landeck*) were destroyed in 1241 during the Mongolian invasion on Europe. Since the 16th century, the information on mineral waters appears more frequently.

In the earliest printed works, mineral waters from the following locations were described: Cieplice Śląskie-Zdrój in 1553, 1572, 1578 (*De Balneis...*, 1553), Wieliczka and Bochnia (Cracow area) in 1571, Szkló (now in Western Ukraine), Družbaki (now Ružbachy in Northern Slovakia), Swoszowice and others in 1578 (Oczko, 1578; see Fig. 2), Iwonicz-Zdrój in 1578, 1597. The first drawing originates from beginning of 17th century (Fig. 3).

An important event was the first analysis of mineral water from a spring in Łądek-Zdrój, which showed the existence of sulphur, alum, salt and cadmium (Conrad of Berg, 1498, according to Burghardt, 1774). This was probably the oldest chemical analysis of therapeutic water in Europe because famous Paracelsus performed his analyses of groundwater from Göppingen a quarter of a century later.

Early discoveries of mineral waters were usually associated with discoveries of springs, and exploitation of various mineral resources and fresh groundwater. Due to the introduction of drilling techniques, most of therapeutic groundwater are now abstracted with the aid of boreholes.

### Basic hydrogeologic works

The most extensive monographic descriptions of mineral and therapeutic groundwater in Poland include works by Dowgiałło (1969a, 1969b), Paczyński & Płochniewski (1996) and Paczyński & Sadurski (2007).

Origin and age of nearly all therapeutic waters were determined with the aid of environmental tracers as a result of investigations started in early seventies of the previous century (Dowgiałło, 1971; Dowgiałło & Tongiorgi, 1972). In the early stages of investigations only  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $^3\text{H}$  were analyzed, and in some cases also  $^{14}\text{C}$  and  $\delta^{13}\text{C}$ . During nineties of the previous century, within the Polish-German cooperation,  $^3\text{He}$ ,  $^4\text{He}$ ,  $^{40}\text{Ar}/^{36}\text{Ar}$ , Ne, Ar, Kr and Xe were measured in several systems of therapeutic waters. Recently, concentrations of He, Ne, Ar i SF<sub>6</sub> are measured by gas chromatography methods. Ages of modern waters, or ages of modern components in mixed waters, were determined from tritium records of different durations with the aid of the FLOWPC program (Małoszewski & Zuber, 1996). Ages of older waters were determined from the  $^{14}\text{C}$ ,  $^4\text{He}$  (or He) and  $^{40}\text{Ar}$  data as well as from the values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  interpreted in terms of the climatic period under which the recharge took place. Investigations of CO<sub>2</sub>-rich waters are limited to  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $^3\text{H}$ , because trace gases are stripped off by an independent flux of the deep-sited CO<sub>2</sub>, whereas for waters in carbonate rocks, the  $^{14}\text{C}$  method is rather of qualitative character due to the effective isotopic exchange between dissolved and solid carbonates, which delays the  $^{14}\text{C}$  movement. As mentioned, the methodology of the tracer methods and the results obtained in Poland are described in a guidebook (Zuber et al., 2007). Below a short summary of the most important findings is given.

Isotopic composition of C in CO<sub>2</sub> confirmed the magmatic origin of that gas in the Sudetes Mts. ( $\delta^{13}\text{C}$  from 11 to 4‰ and  $^3\text{He}/^4\text{He}$  abt. 2 R/R<sub>A</sub>), whereas, contrary to the expectations, a metamorphic origin was revealed in the Carpathians ( $\delta^{13}\text{C}$  abt. 1‰,  $^3\text{He}/^4\text{He}$  <1.0 R/R<sub>A</sub>) (Leśniak, 1985; Leśniak et al., 1997). Common CO<sub>2</sub>-rich waters in the Sudetes are of atmospheric origin of mostly modern age, whereas in the Carpathians their ages range from several years to more than 10 000 years.

<sup>1</sup>A 100-page long chronicle of the Henryków Cistercian Abbey in Lower Silesia, dated at 1270, written in Latin. It contains a sentence which is considered the oldest written in Polish



Fig. 1. Provinces of mineral and thermal waters in Poland according to Paczyński & Płochniewski (1996): A – Precambrian platform; B – Paleozoic platform; C – Sudetes Mts.; D – Carpathians

In the Sudetes,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of fresh waters reliably exhibit the altitude effect, which, together with age values, served for identifying the recharge areas of the majority of mineral water intakes. However, in the flysch Carpathians, the altitude effect appeared to be unreliable due to high scatter of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  data.

In the flysch Carpathians, besides numerous common  $\text{CO}_2$ -rich waters,  $\text{CO}_2$ -rich chloride waters and chloride waters also occur. Near the ground surface, they result from mixing between meteoric and non-meteoric waters, the latter ascending from deeper formations. Isotopic and hydrochemical investigations showed that in the western part of the Polish Carpathians this non-meteoric waters result

from dehydration of clay minerals in the final stages of diagenesis, with  $\delta^{18}\text{O} \cong 5\text{--}7\text{‰}$  and  $\delta^2\text{H} \cong -(25\text{--}30)\text{‰}$ . Chlorides are the remnants of the marine sedimentation water with concentrations ( $0.7\text{--}23 \text{ g Cl}^-/\text{dm}^3$ ) resulting from ultrafiltration and dilution processes accompanying the diagenesis (Zuber & Chowaniec, 2009). In the eastern part, waters representing intermediate stages of diagenesis often occur, with admixtures of sedimentation water (Porowski, 2006). In most cases they are also mixed with meteoric waters of different ages, with  $\delta^2\text{H}$  values often changed by generation of hydrocarbons (Zuber & Chowaniec, 2010).

Buried thermal brines related to meteoric waters of hot climates ( $\delta^{18}\text{O} \cong -2\text{‰}$ ,  $\delta^2\text{H} \cong -20\text{‰}$ ) occur in the bedrocks

of flysch, e.g. in Ustroń (Pluta & Zuber, 1995). Marine Badenian brines ( $\delta^{18}\text{O} \approx 0\text{‰}$ ,  $\delta^2\text{H} \approx 0\text{‰}$ , 19–110 g Cl/dm<sup>3</sup>) are known at several sites in the area of the Carpathian Foredeep (Zabłocie, Dębowiec and Łapczyca). They are

enriched in chlorides due to the ultrafiltration caused by compaction. Sulphide waters of meteoric origin occur in shallow Miocene formations, with TDS contents up to several g/dm<sup>3</sup> and ages from 50 to 8000 years, e.g. in Swozowice and Krzeszowice, and more than 10 000 years in Kraków-Mateczny.

In the north-central part of the foredeep (Busko-Zdrój), there are saline waters of interglacial origin with the salinity related to the leaching of Badenian chemical sediments which supposedly existed in the recharge area in the past ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  like in modern water, lack of <sup>3</sup>H and <sup>14</sup>C, <sup>4</sup>He  $\approx 130 \times 10^{-6}$  cm<sup>3</sup>STP/g, <sup>40</sup>Ar/<sup>36</sup>Ar  $\approx 301$ ). At the greater depths of that region, there are sulphide brines related to the pre-Quaternary post-Badenian recharge ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  significantly less negative than in modern water, <sup>4</sup>He  $\approx 350 \times 10^{-6}$  cm<sup>3</sup>STP/g, <sup>40</sup>Ar/<sup>36</sup>Ar  $\approx 310$ ) (Zuber et al., 1997).

According to the isotopic composition, therapeutic brines in the Polish Lowlands result either from mixing between sedimentation and meteoric waters (Dowgiałło, 1971; Dowgiałło & Tongiorgi, 1972), or rather from meteoric waters of warm pre-Quaternary climates and also cold Quaternary climates with salinity gained from leaching numerous Zechstein salt diapirs (Zuber & Grabczak, 1991; Krawiec, 1999; Krawiec et al., 2000; Zuber et al., 2007).

Isotope and noble gas studies showed that thermal waters in the Cieplice-Zdrój result mainly from recharge under cold climate, though some springs discharge modern water (Ciężkowski et al., 1992). Similar study showed that in the Łądek-Zdrój, the thermal water is several thousand years old (Zuber et al., 1995). For the both spas, the probable positions of the recharge areas of thermal waters were identified.

According to isotope and noble gas data, thermal waters of the Podhale Basin are recharged in the Tatras, in the low parts of outcrops of karstic formations at altitudes of about 1100–1300 m a.s.l. Tracer data indicating ages in the range from modern in wells near the Tatras to mid and late Holocene in the north-western part of the basin and pre-



Fig. 2. The oldest work in Polish on groundwater in Szkoło near Lwów (now Lvov in Ukraine) (Oczko, 1578)

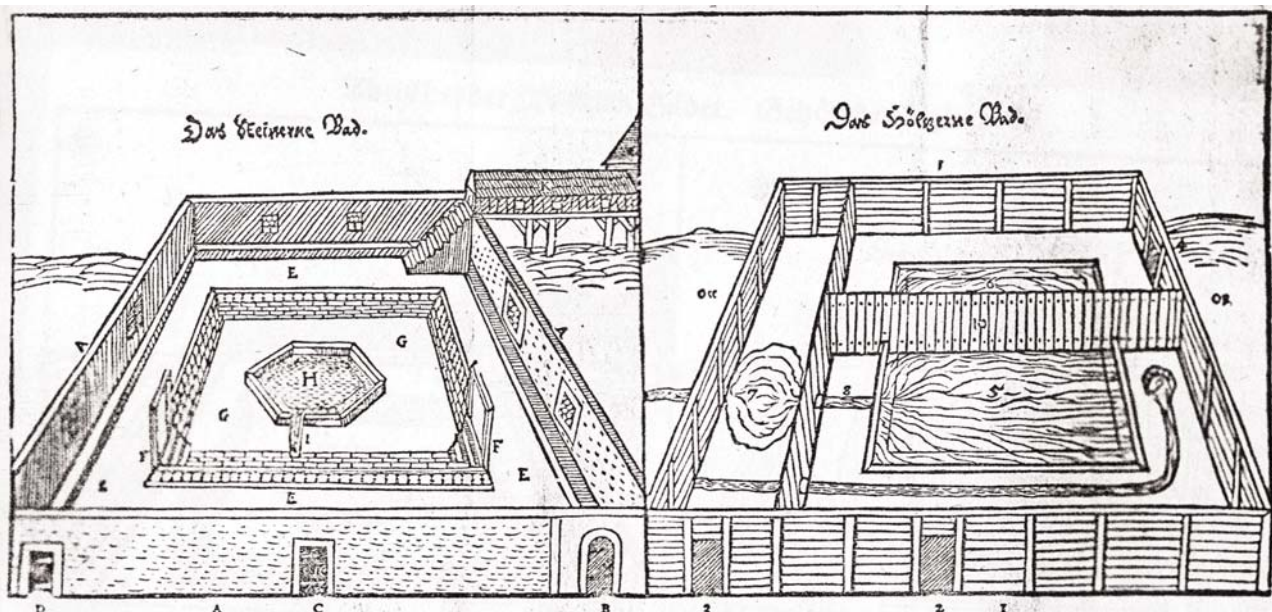


Fig. 3. The oldest print from the present Polish spas showing swimming pools of Kamienny and Drewniany in Cieplice Śląskie-Zdrój (Lower Silesia) (Schwenckfeldt, 1607)



Fig. 4. The Nałęczów Health Resort (SE Poland). Photo by J. Sokołowski

Holocene in the north-eastern part are of great importance for a proper management of the thermal system (Chowaniec et al., 2010).

#### Occurrences of therapeutic and thermal waters

Paczyński and Płochniński (1996) defined the following four provinces of occurrences of mineral waters (Fig. 1): Precambrian platform, Paleozoic platform, Sudetes Mts., and Carpathians. That classification is also applicable to therapeutic and thermal waters.

**Provinces A and B.** They cover the area of the Polish Lowlands, where mineral waters mainly occur in Cretaceous, Jurassic and Triassic formations. They are of meteoric origin as determined by environmental tracer methods, with ages ranging from the Holocene and Pleistocene to pre-Quaternary. The natural drainage area is at the Baltic coast though there are also some local drainage areas within the Lowland. Exploited therapeutic waters are usually of the Cl-Na and Cl-Na+I+Fe types, with TDS contents up to about 100 g/dm<sup>3</sup>. Their salinity mainly results from leaching of numerous Zechstein salt domes. Exceptions exist in Wieniec where water is of SO<sub>4</sub>-Cl-Ca-Na+H<sub>2</sub>S type, with TDS content of 3.5 g/dm<sup>3</sup>, and in Nałęczów (Fig. 4) where waters are of HCO<sub>3</sub>-Ca-Mg+Fe and HCO<sub>3</sub>-Ca types, with TDS contents of 0.6 to 0.7 g/dm<sup>3</sup>.

Some spas developed in the middle of the 19th century (Kołobrzeg, Świnoujście and Ciechocinek) at sites where brines ascended to the surface and served for the production of salt. The Spa in Ciechocinek developed on the production of salt from evaporated mineral water. In 1824–1828, two graduation towers and salt works were constructed and the



Fig. 5. Salt graduation tower in Ciechocinek (Central Poland). Photo from PGI-NRI archive

third one was completed in 1859 (Fig. 5). The historic salt works are still in operation and provide table salt, lye and therapeutic mud.

The principal resources of geothermal waters occur in the Mesozoic formations of the Polish Lowlands. They are mainly accumulated in the Lower Cretaceous and Lower Jurassic formations. Thermal waters in the Polish Lowland are usually of high salinity. However, some exceptions exist, for instance in Mszczonów (about 80 km to SW of Warsaw), water with temperature of 40.5°C and TDS content of only 0.49 g/dm<sup>3</sup> is exploited from a Cretaceous formation at the depth 1000 m. Similarly, in the area of the Łódź synclinorium, a thick zone of fresh water is also present, which reaches over 1600 m depth in its central area.

Total disposable resources accumulated within all Mesozoic and Paleozoic aquifers of the Polish Lowlands are estimated at  $6.28 \times 10^{18}$  J/year and  $2.93 \times 10^{18}$  J/year, respectively. Therefore, the total disposable resources of geothermal energy accumulated in 9 geothermal aquifers of the Polish Lowlands are  $9.21 \times 10^{18}$  J/year.

The calculated disposable resources of geothermal energy in the Polish Lowlands can be correlated with geothermal energy resources obtained for the whole Europe by Cataldi (1994), who quoted geothermal reserves of  $6.00 \times 10^{19}$  J/year. According to his opinion, geothermal resources in Europe can be utilized in relatively limited areas of several thousands of square kilometres, where about 5–10% of these resources are accumulated. In these areas, properties of geothermal aquifers are particularly favourable and the heat markets are attractive for potential investors. Utilization of geothermal resources will depend on numerous factors discussed in detail by Górecki et al. (2006a, 2006b).

**Province C.** It includes the Polish Sudetes Mts. and the Fore-Sudetic Block. These two units are separated by the Sudetic Boundary Fault differ their geological structures

(Fig. 6). In the Polish part of the Sudetes, three main types of therapeutic waters occur: the most common CO<sub>2</sub>-rich (carbonated) waters, thermal waters, and radon waters, which often are mixed. They are found in three regions: western part of the Sudetes (Izera Mts.), along the north-eastern margin of the mid-Sudetes basin, and the central and western part of the Kłodzko Land.

The most westward area of CO<sub>2</sub>-rich waters is located in the metamorphic Izera Mts. Waters of that area are of HCO<sub>3</sub>-Ca-Mg+Fe+F+Rn types with TDS up to about 3 g/dm<sup>3</sup>, and the highest Rn content of 3 kBq/dm<sup>3</sup>. They are present in springs and wells deep up to 360 m. The second area with numerous occurrences of CO<sub>2</sub>-rich waters, however with low outflow rates, is situated in elongated belt (~45 km long) extending in NW-SE direction along the mid-Sudetes basin. Abundant CO<sub>2</sub>-rich waters occur within Kłodzko Land; they are of HCO<sub>3</sub>-Na-Ca, HCO<sub>3</sub>-Ca-Mg, HCO<sub>3</sub>-Ca-Na and HCO<sub>3</sub>-Ca-Na-Mg types, with TDS contents in the range of 1.1–6.0 g/dm<sup>3</sup>. All CO<sub>2</sub>-rich waters of the Sudetes province are of meteoric origin, dominantly with ages below 100–200 years.

Thermal waters regarded as therapeutic occur in Cieplice Śląskie-Zdrój and Łądek-Zdrój, where they were used already in 12th century. In Cieplice, thermal water of SO<sub>4</sub>-HCO<sub>3</sub>-Na+F+H<sub>2</sub>SiO<sub>3</sub> type with TDS content of about 0.6 g/dm<sup>3</sup> outflows from a horst of the Karkonosze granite. In 1997, the warmest groundwater in Poland (87 °C) with the yield of 45 m<sup>3</sup>/h was reached at the depth of 2000 m.

In Łądek, thermal waters are of HCO<sub>3</sub>-F-Na type with TDS content of 0.2 g/dm<sup>3</sup>. Fluoride content reaches 13 mg/dm<sup>3</sup>, hydrogen sulphide up to 3.6 mg/dm<sup>3</sup>, and radon up to 1350 Bq/dm<sup>3</sup>. Their temperature at the surface is 20–29°C;

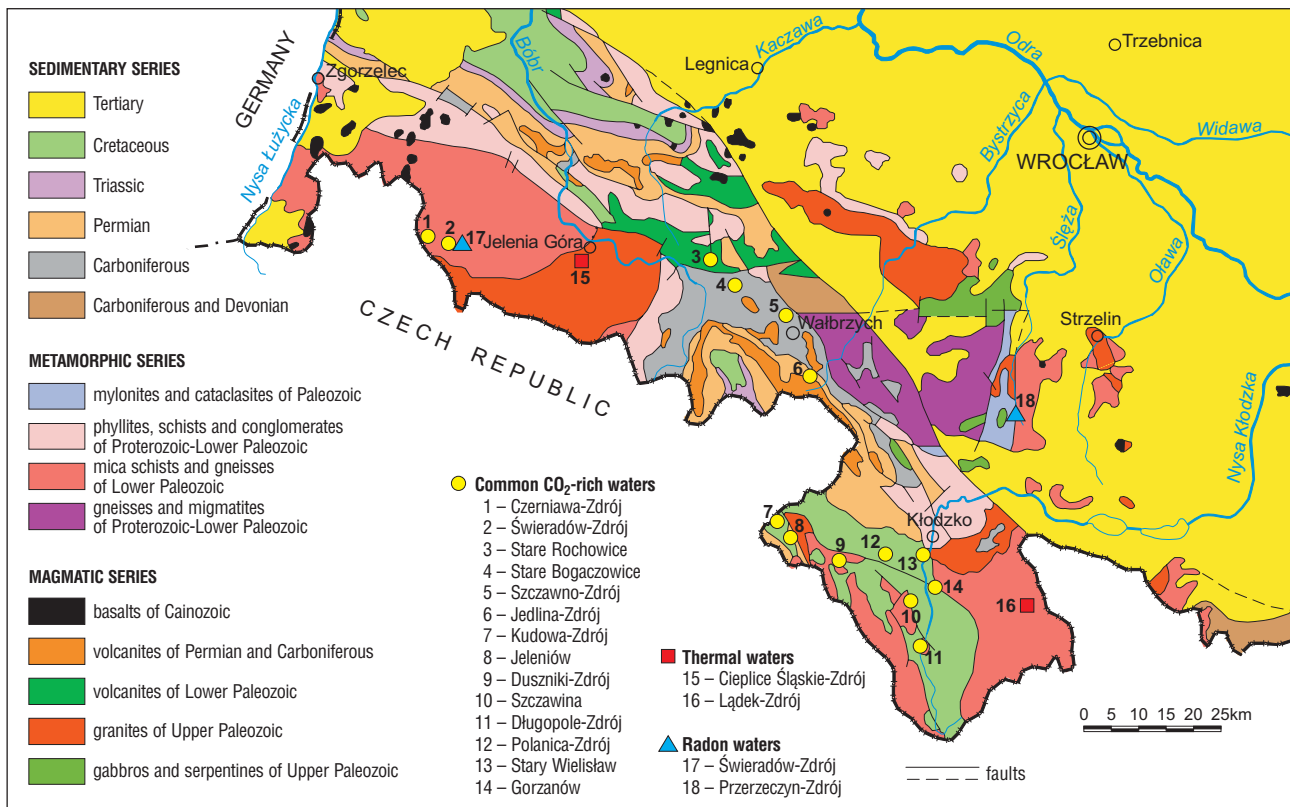


Fig. 6. Simplified geological map of the Sudetes province with most important occurrences of therapeutic and thermal waters

however, a well drilled down to 700 m depth reached groundwater with temperature of 45°C.

**Province D.** It includes the Outer Carpathians, the Inner Carpathians and the Carpathian Foredeep (Fig. 7). The province is rich in great variety of mineral waters and shows coexistence of fresh groundwater together with mineralized and thermal waters.

The Inner Carpathians include the Tatra Mts., the Podhale basin, and the Pieniny Klippen Belt. The thermal water occurs in karstic Eocene and Mesozoic carbonate formations (Fig. 8). The recharge area are in the Tatras and the general flow direction is to the north up to the impermeable barrier of the Pieniny Klippen Belt. Here, groundwater partly discharges by upward seepage; however, majority of flow is directed westwards and eastwards, and then southwards, where it reaches the Danube catchment basin in Slovakia. Water temperature reaches abt. 85°C in the north-eastern part of the basin whereas the TDS content is from abt. 0.2 up to 3 g/dm<sup>3</sup>. This groundwater is commonly used for recreation (Bukowina, Zakopane and Biały Dunajec) and for heating.

The Outer Carpathians are built of Cretaceous and Paleogene flysch formations (shales and sandstones of variegated thickness) which were overthrust from the south and folded in a number of orogenic cycles during the Paleogene and Neogene up to the late Miocene.

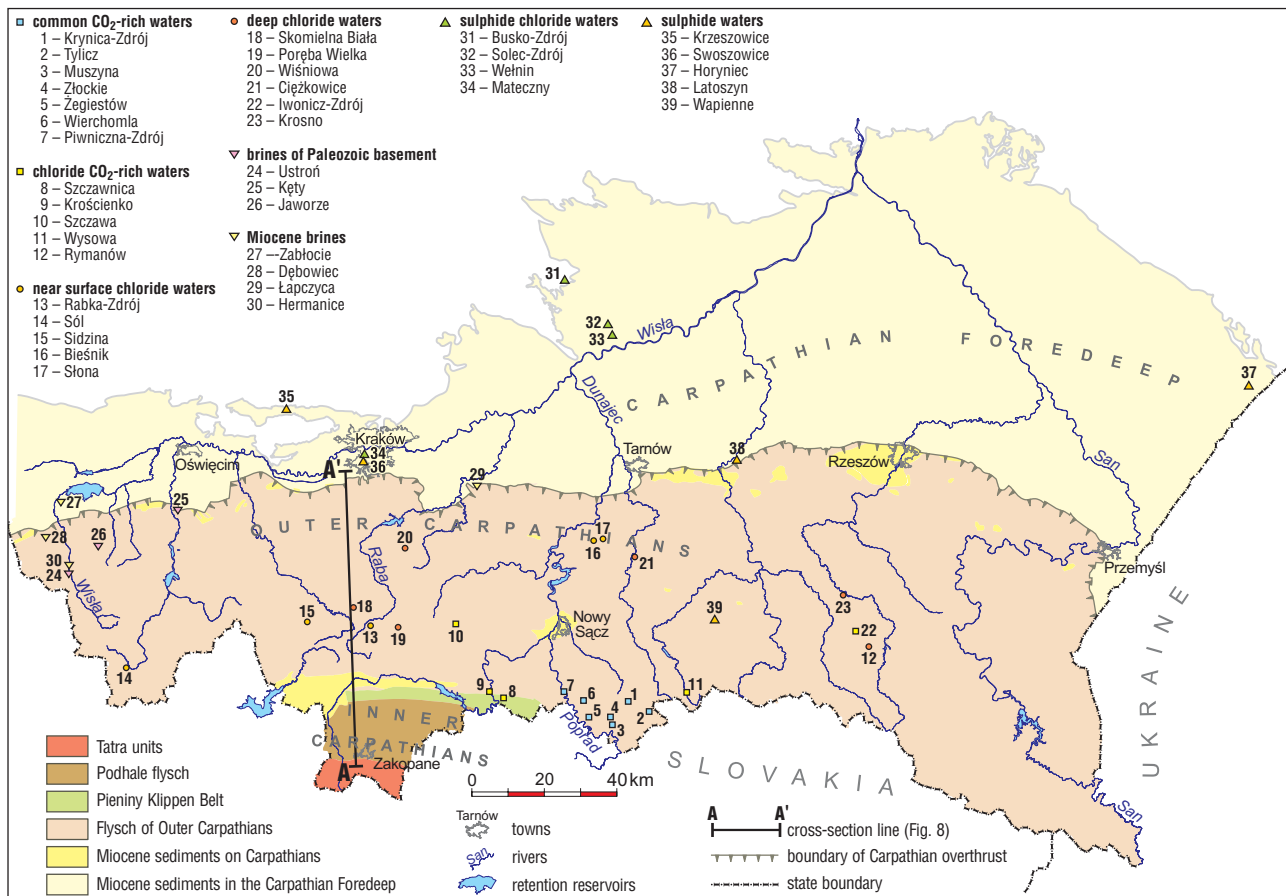
Within the Outer Carpathian flysch, common and chloride CO<sub>2</sub>-rich waters, saline waters and brines occur. Chlorides in these waters are the remnant of the sedimentary water that was isotopically and chemically altered during

the processes of diagenesis (Zuber & Chowaniec, 2009; Zuber et al., 2010).

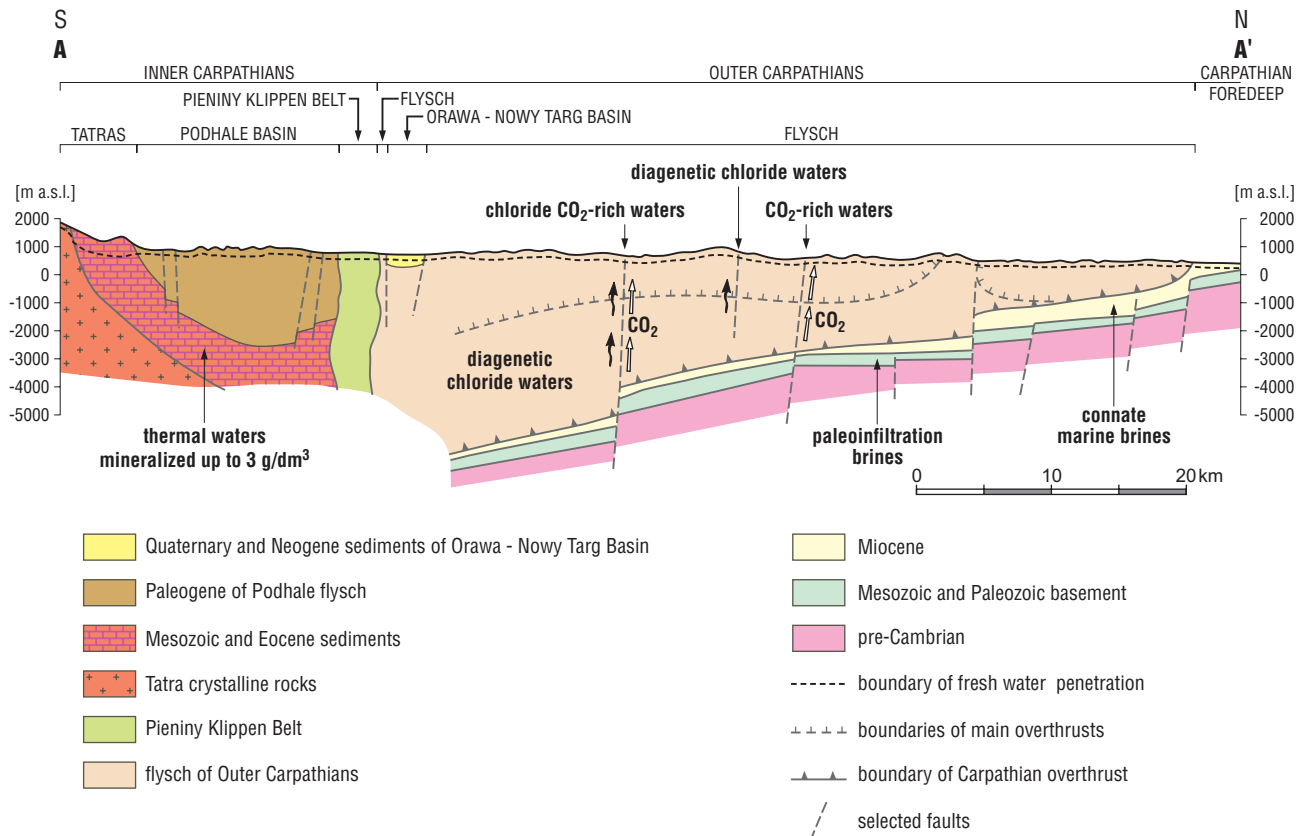
CO<sub>2</sub>-rich waters discharge in a number of springs and are also in wells up to 400 m deep located along the Poprad River valley and valleys of its tributaries (e.g. in Krynica-Zdrój, Tylicz, Muszyna, Złockie, Żegiestów, Wierchomla and Piwniczna-Zdrój). Modern CO<sub>2</sub>-rich waters are usually of HCO<sub>3</sub>-Ca type, with TDS up to about 3 g/dm<sup>3</sup>. Older waters are usually of HCO<sub>3</sub>-Na-Mg or HCO<sub>3</sub>-Mg-Na type, with TDS reaching even about 12 g/dm<sup>3</sup>. All these waters occur in fault zones, where a deep penetration of meteoric water and upward migration of CO<sub>2</sub> are enhanced. In that area, numerous dry CO<sub>2</sub> exhalations are also present. The nicest example of dry CO<sub>2</sub> exhalation in Poland occurs in Złockie, and is protected as a National Nature Monument, under the name of Prof. Henryk Świdziński.

Surface and subsurface occurrences of chloride CO<sub>2</sub>-rich waters are associated with fault zones enhancing the ascension of both CO<sub>2</sub> and diagenetic water, but with relatively shallow penetration of meteoric waters like it is schematically shown in Fig. 8. They are usually of Na-HCO<sub>3</sub>-Cl-I or Na-Mg-HCO<sub>3</sub>-Cl-I type, with TDS contents up to abt. 25 g/dm<sup>3</sup>, in cases of 100% domination of the diagenetic water. They occur in Szczawnica, Krościenko, Szczawa, Wysowa, and Rymanów-Zdrój.

An unusual type of chloride CO<sub>2</sub>-rich water is called the zuber water in the memory of its discoverer, Prof. Rudolf Zuber. It occurs in some areas of Krynica-Zdrój and Złockie, where small amounts of very old meteoric waters of pre-Holocene age meet at the depth of 400–900 m with



**Fig. 7.** Simplified geological map of the Carpathians and the Carpathian Foredeep with discussed occurrences of different mineral waters



**Fig. 8.** Schematic cross-section through the Carpathians along the line shown in Fig. 7, with the projection of genetic types of waters (Zuber & Chowaniec, 2009)

also small amounts of ascending diagenetic water in the presence of a very strong CO<sub>2</sub> influx. They are of HCO<sub>3</sub>-Na+I or HCO<sub>3</sub>-Na-Mg+I types, with TDS contents up to about 30 g/dm<sup>3</sup> (Oszczypko & Zuber, 2002; Zuber & Chowaniec, 2009).

Surface and near-surface presence of saline waters are known in areas where ascending diagenetic waters mix in various proportions with meteoric waters, with no CO<sub>2</sub> influx (Rabka-Zdrój, Sól, Sidzina, Bieśnik, Słona). They are of Na-Cl+I and Na-Cl-HCO<sub>3</sub>+I types, with TDS contents up to about 45 g/dm<sup>3</sup>. These waters were also found in a number of deep wells at sites with no signs of near-surface presence of mineral water (e.g., Skomielna Biała, Poręba Wielka, Wiśniowa, Ciężkowice, Iwonicz-Zdrój and Krosno).

Brines of Cl-Na-Ca+I type, with TDS content between about 30 and 150 g/dm<sup>3</sup>, and temperature of about 50°C, occur in karstic Devonian formations and Carboniferous sandstones of the flysch basement in the Outer Carpathians (e.g. in Ustroń, Kęty and Jaworze). They are regarded as buried waters of meteoric origin, and are mainly used for medical treatments. Only Ustroń brine is used for therapeutic purposes both as mineral and thermal water. In general, both the basement and flysch formations of Outer Carpathians do not contain significant resources of thermal waters.

The Carpathian Foredeep is a geologic structure of a piedmont rift, filled with the Miocene sediments reaching a thickness of 100 to 3000 m. Below the marine Miocene sediments, the Mesozoic and the Paleozoic strata are present. Chemical sediments (gypsum, anhydrites and salts) among Miocene formations are a characteristic feature of the area, which has a significant impact upon the chemistry of groundwater.

In the south-west part of the Carpathian Foredeep (Zabłocie and Dębowiec) and in the south-central part (Łapczyca), sedimentary brines of the Badenian age occur. They are of Cl-Na+Br+I type and are completely devoid of sulphides; with TDS ranging from 35 to 185 g/dm<sup>3</sup>, with the enrichment in some chemical components resulting from ultrafiltration caused by compaction. They are used primarily for the production of medical salts. Such brines occur also in the Badenian deposits, which are partly covered by overthrust flysch formations (Dębowiec, Hermanice and Kęty); however, at depths greater than 1500 m, they are diluted by dehydration waters of diagenetic origin released from clay minerals in further compaction process (Zuber & Chowaniec, 2009).

In the north-central part of the foredeep (Busko-Zdrój, Solec-Zdrój, Welńin and recently also found near Busko, in Las Winiarski and Dobrowoda) occur therapeutic sulphide waters mainly of Cl-SO<sub>4</sub>-Na+S type, with TDS content of about 12 to about 40 g/dm<sup>3</sup>. They are old meteoric waters of interglacial and pre-Quaternary ages, with chemical composition resulting from dissolution of gypsum and salt intercalations within the Badenian sediments (Zuber et al., 1997). More probably the salinity of these waters results from the dissolutions of salt layers which presumably existed in that area in the geological past (Chowaniec et al., 2009).

Sulphide waters with elevated chloride concentrations are also present in Kraków-Mateczny (SO<sub>4</sub>-Cl-Ca-Na-Mg+S and similar types, TDS of 1.4–4.5 g/dm<sup>3</sup>). Their age is related to recharge at the end stages of the last glacial period with a small admixture in one borehole of modern water (Zuber et al., 2004). Besides medical use, they were also used for



the production of tasty bottled water, after removal of H<sub>2</sub>S and saturation with CO<sub>2</sub>.

Numerous sulphide waters of meteoric origin and free of chlorides are present in Kraków-Swoszowice (SO<sub>4</sub>-Ca-Mg+S type, TDS of 2.8–2.9 g/dm<sup>3</sup>), Horyniec (HCO<sub>3</sub>-Ca-Na+S type, TDS of 0.5–0.7 g/dm<sup>3</sup>) and Latozsyn (SO<sub>4</sub>-Ca+S type, TDS of 2.8 g/dm<sup>3</sup>). Their ages are in the range of 50 to 100 years. Similar waters in Krzeszowice (SO<sub>4</sub>-HCO<sub>3</sub>-Ca-Mg+S type and TDS of 2.6 g/dm<sup>3</sup>) are 5–8 thousand years old.

### Resources and exploitation

Withdrawals of mineral and thermal waters used for medical treatments, recreation and heating in specific provinces are presented in Table 2.

A groundwater intake cannot be operated without a licence in which the permissible exploitation rate and estimated disposable resources are defined. For specific geological structures with renewable groundwater, disposable resources were determined with the aid of different methods, usually assuming that they equal 20–30% of the underground discharge. For geological structures that do not contain renewable waters, disposable resources were determined from the dimensions of the structure, porosity and specific yield.

Chloride waters and chloride CO<sub>2</sub>-rich waters that are mixtures of meteoric and ascending diagenetic components are regarded as renewable within the limit resulting from the inflow rate of the ascending diagenetic water.

### Vulnerability and protection of therapeutic waters

Long term hydrogeologic and hydrochemical observations, that cover periods of several tens or even more than 100 years, as well as environmental tracer data, indicate that some therapeutic waters are of modern ages or contain mineralised or fresh components of modern ages. Such waters require special attention and their protection areas must be well defined and controlled. In spite of a great effort in that field, some accidents happen from time to time which lead to temporary or final closures of endangered intakes.

The largest losses of therapeutic waters were caused by the development of hard coal industry (disappearance of springs in Jastrzębie-Zdrój, Jedlina-Zdrój and Stary-Zdrój), lignite coal mining (disappearance of springs in Opolna-Zdrój) and salt mining (disappearance of springs in Inowrocław). The total or partial decline of spring discharges were also caused by the development of new drilled intakes

(Ciechocinek, Cieplice-Zdrój, Duszniki-Zdrój, Kołobrzeg, Łądek-Zdrój and Polanica-Zdrój). Temporary negative impacts (decrease of mineralisation) on near-surface therapeutic waters may result from a breakdown of communal water supply systems, like it happened once in Krynica-Zdrój. The decline of the flow rate can be caused by excessive exploitation of nearby intakes of fresh groundwater (Jeleniów and Łądek-Zdrój), regulation of rivers (Polanica-Zdrój and Rymanów-Zdrój), and road construction or excavations works carried out on slopes above springs (Szczawnica).

The entire management and protection of thermal and therapeutic groundwater in particular spas are carried out by the Mining Departments (*Uzdrowiskowe Zakłady Górnicze*). The management of spas is also controlled by several local authorities (Association of Spa Communities and Union of Polish Spas) and economical associations (Chamber of Commerce „Polish Spas” and National Chamber of Commerce „Bottling Industry”).

### Monitoring and databases

Information regarding groundwater resources is collected in a central database (Bank HYDRO), which run is by the Polish Geological Institute – National Research Institute (PGI-NRI) ([www.psh.gov.pl/bankhydro.html](http://www.psh.gov.pl/bankhydro.html)). One of its components is a database called Bank HYDRO – MINERAL GROUNDWATER. The database contains basic information about groundwater intakes, including their hydrogeologic parameters, water chemistry and licenses.

Detailed data related to particular intakes are available in the Mining Departments (*Uzdrowiskowe Zakłady Górnicze*) in spas and other entrepreneurs abstracting therapeutic and thermal waters. They include results of detailed chemical analyses usually performed once a year and the results of monitoring of main components and of hydrodynamics, which is usually based on everyday observations.

### Use of therapeutic and thermal waters

**Balneogeology.** In balneology water is used for medical treatment, rehabilitation and prevention. Balneologic resources comprise of therapeutic water, medical gases (CO<sub>2</sub>, H<sub>2</sub>S and Rn), and therapeutic peat and mud. These resources are used in spas for medical treatment in baths and swimming pools, drinking treatment (crenotherapy), inhalation, irrigation and rinsing. Among therapeutic treatments they are also radon inhalations (Łądek-Zdrój and Świeradów-Zdrój) and dry baths in gaseous CO<sub>2</sub> (Krynica-Zdrój and Długopole-Zdrój).

**Table 2. Exploitation resources (Q<sub>e</sub> in m<sup>3</sup>/h) and intake (ΣQ in m<sup>3</sup>/yr) of therapeutic and thermal groundwater in Poland in 2008**

Provinces		A & B	C	D			Total
		Lowlands	Sudetes	Carpathians Foredeep	Outer Carpath.	Inner Carpath.	
Medical waters	Q <sub>e</sub>	1 038	259	88	323	–	1.708
	ΣQ	640 069	496 249	100 099	449 326	–	1 685 743
Thermal waters	Q <sub>e</sub>	817	224*	–	–	1 328*	2 369
	ΣQ	1 617 336	718 603*	–	–	3 358 425*	5 694 364

\* thermal water also used as therapeutic

Surface and near surface intakes of therapeutic waters are of different types. The most common are springs which in large numbers occur in Cieplice Śląskie-Zdrój, Krynica-Zdrój, Łądek-Zdrój, Szczawnica and Świeradów-Zdrój. They have special constructions to ensure undisturbed outflow and prevent direct inflow of meteoric and surface water. In several locations, uptakes made by the *Scherrer Company of Bad Ems* (Fig. 9) have been operational for nearly 100 years. The most common are boreholes with artesian outflows and outflows enhanced by CO<sub>2</sub>, with pumps in boreholes or oil-field type pumps (Fig. 10). The most common depths do not exceed 100 m, but boreholes with depths of several hundred metres are quite common. The deepest is the C-1 borehole in Cieplice Śląskie-Zdrój (2002 m).

Very unusual constructions of intakes of CO<sub>2</sub>-rich waters are in water galleries in Długopole-Zdrój (Emilia, Kazimierz and Renata springs), Szczawnica (Jan-14), Cieplice Śląskie-Zdrój (Marysieńka and Nowe springs), and Szczawnica (Pitoniakówka). The most picturesque are swimming pools constructed directly over the springs like in Łądek-Zdrój (Wojciech – shown in Fig. 11; Jerzy) and in Cieplice Śląskie-Zdrój (Basenowe Damskie, Basenowe Męskie).

In balneology and recreation, thermal groundwater is used with a great success. Seven Polish spa resorts – Cieplice, Cieplice Śląskie-Zdrój, Łądek-Zdrój, Iwonicz-Zdrój, Ustroń and Konstancin – use thermal water abstracted from natural springs or drilled wells. Thermal water for recreational and rehabilitation purposes are used in the area of Podhale Basin (Zakopane, Biały Dunajec and Bukowina, Fig. 12) and in central Poland (Uniejów).

**Bottled waters.** In difference to hydrogeological meaning of mineral waters, a new term of natural mineral waters was introduced in the bottling business. The current classification of bottled waters was introduced by the regulation of the Polish Health Ministry in 2004. All bottled waters must be produced only from groundwater intakes.

Natural mineral water and natural spring water is a groundwater that is extracted by one or more natural or drilled boreholes and is naturally unpolluted with regard to groundwater chemistry and bacteriology, has stable mineral content and has physiological properties that have positive impact on human health (natural mineral water), its properties and mineral composition is no different from composition of water destined for human consumption (natural spring water).

Potable water is achieved by adding natural mineral water or mineral salts containing at least one or more components of physiological importance (Na, Mg, Ca, Cl, SO<sub>4</sub> or CaCO<sub>3</sub>) to a natural spring water.

At present there are some 130 bottling companies in Poland; however, most of them are located in south of the country. The biggest producers are the following companies:

- ❑ Danone (*Zywiec-Zdrój*) – 23%;
- ❑ Nałęczów Zdrój S.A. (*Cisowianka*) – 8%;
- ❑ Nestle (*Nałęczowianka*) – 7%;
- ❑ Coca Cola (*Kropla Beskidu*) – 6%;
- ❑ S.P. Muszynianka and others (*Muszynianka, Muszyna*) – 3%;
- ❑ Zespół Uzdrawisk Kłodzkich S.A. (*Staropolanka*) – 2%.

The average yearly consumption of bottled waters in Poland is 67 litres per person (2009).

A specific group of bottled mineral waters are therapeutic waters. An institution that is competent to decide whether water is therapeutic or not is the National Institute for



Fig. 9. An example of Scherrer system in Szczawno-Zdrój (beginning of the XXth century). Photo by E. Liber



Fig. 10. An old pump abstracting saline water from a borehole in Rabka-Zdrój. Photo by L. Rajchel



Fig. 11. Marble swimming pool of the XIX century over a thermal spring in Łądek-Zdrój. Photo by W. Cieżkowski



Fig. 12. Complex of swimming pools with thermal water in Bukowina Tatrzańska. Photo by J. Chowaniec

Public Health in Warsaw, which must respect legal regulations specific for pharmaceutical industry. Bottled water that is destined for commercial sale in individual packaging must be clean, untreated water from one aquifer, whose chemical composition and physical properties guarantee specific therapeutic effects that are certified by results of pharmacological and clinical tests. Such waters are bottled in their natural state in Krynica-Zdrój (waters of Jan, Słowinka and Zuber), Polanica-Zdrój (Wielka Pieniawa), Szczawno-Zdrój (Dąbrówka and Mieszko) and Wysowa (Franciszek, Henryk and Józef).

**Liquid CO<sub>2</sub>.** About 3% of natural CO<sub>2</sub> that is extracted with CO<sub>2</sub>-rich waters is liquefied. Two plants in Duszniki-Zdrój and in Krynica-Zdrój produce in total some 1200 t of liquefied CO<sub>2</sub>. That gas is used mostly for saturating bottled waters and for medical treatments in dry CO<sub>2</sub> baths.

**Other Spa products.** Therapeutic waters are used also for producing other spa products like table and bath salts (Ciechocinek, Iwonicz-Zdrój and Zabłocie), lye and therapeutic mud (Ciechocinek), cosmetics like creams, emulsions, gels and foams, facials and others (Busko-Zdrój, and Iwonicz-Zdrój).

**Power industry.** The first geothermal power plant was opened in Poland in 1993 within Podhale Basin, in the Inner Carpathians. As the exploitation intake, Bańska PGP-1 borehole is used, with a depth of 3240 m, water temperature of ca. 86°C and flow rate of 550 m<sup>3</sup>/hr. Abstracted water supplies energy of 15.5 MW to Zakopane town and a few villages. At present, thermal groundwater is utilised also in three other geothermal plants in the Polish Lowlands: in Pyrzyce (since 1996, now under closing, water temperature 64°C, power 13.5 MW), in Mszczonów (since 1999, 40°C, power 1.1 MW) and in Uniejów (2001, 67°C, power 3.2 MW). Under construction there are plants in Skierniewice and Toruń.

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