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title: **Occurrences, origin and vulnerability of therapeutical waters in the western part of the Polish Carpathians**

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In Poland, the most abundant resources of different types of therapeutical waters occur in the western part of the Carpathians and in their fore-deep area. Mineral waters (i.e. with TDS > 1000 mg/L), specific waters (e.g. with I⁻, Fe²⁺, H₂S or H₂SiO₃ in required contents), CO₂-rich waters (with free CO₂ > 1000 mg/L) and thermal waters (>20°C) can be regarded as therapeutical by law, if they are free of pollutants and characterized by satisfactorily constant physical and chemical parameters. Typical examples of such waters are presented below.

Common CO₂-rich waters are of purely meteoric origin and occur in flysch Carpathians, mainly along the Poprad river valley where deep seated CO₂ of metamorphic origin travels along fault zones to the ground surface. Their mean ages range from less than 10 years for small springs to pre-Holocene ages in some wells several hundred meters deep. The most common age values of exploited waters are between several tens and 300 years. Elevated concentrations of nitrates are observed only in some small springs whereas all other intakes are free of pollutants. The youngest waters are of HCO₃-Ca types with TDS up to 3 g/L whereas in the oldest ones Mg²⁺ and Na⁺ dominate among cations with TDS usually in the range of 3 to 5 g/L, and in extreme cases up to 12 g/L. CO₂-rich chloride waters also occur only in the flysch formations. They differ from common CO₂-rich waters by admixtures of ascending chloride waters which result from dehydration of clay minerals during diagenesis. These waters are of Na-Cl type (mNa⁺/mCl⁻ >1); their chemical constituents being remnants of the sedimentation marine water modified mainly by ultrafiltration and chemical reactions accompanying the burial diagenesis. In areas without CO₂ flux, the diagenetic waters, if travel to the ground surface, mix with fresh waters. In Rabka Spa the TDS contents in diagenetic waters reach abt. 20 g/L.

Within the area of the Outer Carpathians, Devonian and Carboniferous carbonates and sandstones of the flysch bedrock contain brines of paleometeoric origin with TDS contents exceeding 100 g/L. However, the bedrock of flysch in the Podhale Basin (Inner Carpathians) is represented by Eocene and Mesozoic carbonates, which outcrop in the Tatra Mts. at altitudes of abt. 1100–1800 m. These fissured and karstified formations contain waters with ages ranging from modern to pre-Holocene. They are thermal with temperatures up to abt. 85°C and TDS up to 3 g/L.

Flysch formations are characterized by numerous sulfide springs with mean ages up to 200–300 years, which are related to occurrences of diffused pyrites and organic matter. Only waters of one site (Wapienne) are regarded as therapeutical with H₂S contents up to 6 mg/L (HCO₃-Ca type with TDS up to 0.4 g/L).

Quite different sulfide waters situation occur in the area of the Carpathian fore-deep which is filled-in by Miocene (Badenian) marine sediments. Sulfide waters in marls and gypsum formation of Kraków-Swoszowice are very young (described by exponential model with the mean age of 50 years). They are of SO₄-HCO₃-Ca-Mg type with H₂S contents of 60–80 mg/L and TDS of 2.6 g/L. Confined sulfide waters in Neogene sands of Kraków-Mateczny are of glacial age with admixture of modern water in one well. They are of SO₄-Cl-Na-Mg-Ca type with H₂S up to 6 g/L and TDS up to about 4.5 g/L. Their mineralization is related to the dissolution of salt and gypsum inclusions in Miocene clays. Sulfide water in Krzeszowice occur in a confined formation of Badenian gypsum; in the Main Spring, it is of SO₄-HCO₃-Ca type with TDS of about 3 g/L and H₂S content of 4 mg/L.

The most valuable sulfide waters occur over a large area in the region of Busko Spa. Confined Cenoman sands and sandstones are the main water bearing formation with unknown recharge area somewhere at the north-west, whereas natural drainage area is at Busko Spa. They are of Cl-Na and Cl-SO₄-Na types with H₂S contents of 20–40 mg/L and TDS of about 12–14 g/L. The chemistry of these waters evidently results from leaching of salt and gypsum formations. Environmental tracers strongly suggest their meteoric origin related to the last interglacial.

Jurassic limestones in Busko Spa contain Cl-Na brines of pre-Quaternary age, which were recharged after the last sea regression in the Badenian. Cl-Na and Cl-SO₄-Na sulfide brines of presumably similar age occur in the area of Solec Spa which is situated to the south-east of Busko Spa, in the direction of the Vistula river valley.

Abundant presence of highly mineralized waters of the post-Badenian ages is the only remnant of Badenian salt and gypsum deposits which presumably existed in the recharge area(s). Gypsum formations are preserved only in the south-east part of the area where no conditions for the recharge existed.

Hydrogeology and ages of all discussed waters indicate that most of them are not susceptible to potential anthropogenic pollutants, if properly managed and not over exploited. Only the youngest waters can be endangered, especially those in Swoszowice and Wapienne.



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