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REVIEW ARTICLE

NATURAL GROUNDWATERS IN POLAND - OCCURRENCE, PROPERTIES AND CHEMICAL TYPES*

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ABSTRACT
Chemical composition, organoleptic and physicochemical properties of natural groundwaters are varied and dependent on their geological environment. Determining the basic organoleptic properties – such as colour, taste, odour – as well as physical properties – such as electrical conductivity or redox potential – allow us to assess the stability of water chemical composition. Based on their origin, groundwaters can be divided into infiltration, as well as condensation, juvenile, metamorphic and relic groundwaters, which are currently of lesser value. Groundwaters sourced in Poland belong to various chemical types and play an important role in balneotherapy and the bottling industry. Of particular importance are thermal, bicarbonate, chloride or sulphate type waters. There is also a growing interest in humic waters found in the Wielkopolska region.

Key words: *infiltration waters, thermal waters, electrical conductivity of water, humic waters, chemical types of water*

STRESZCZENIE
Skład chemiczny, właściwości organoleptyczne i fizykochemiczne naturalnych wód podziemnych są zróżnicowane i uwarunkowane środowiskiem geologicznym, z którego pochodzą te wody. Określenie podstawowych właściwości organoleptycznych, takich jak barwa, smak, zapach, a także fizycznych jak np. przewodność elektryczna czy potencjał redoks pozwalają ocenić stałość składu chemicznego wody. Wody podziemne ze względu na ich pochodzenie można podzielić na infiltracyjne, a także kondensacyjne, juwenilne, metamorficzne i reliktowe, mające obecnie mniejsze znaczenie. Wody podziemne wydobywane na terenie Polski należą do różnych typów chemicznych i odgrywają ważną rolę w balneoterapii i przemyśle rozlewniczym. Szczególne znaczenie mają wody termalne, wodorowęglanowe, chlorkowe czy siarczanowe. Rosnące zainteresowanie budzą również wody humusowe występujące na terenie Wielkopolski.

Słowa kluczowe: *wody infiltracyjne, wody termalne, przewodność elektryczna wód, wody humusowe, typy chemiczne wód*

INTRODUCTION

Water is one of the most important substances that can be found in nature. It is necessary for hydration; thus, it is life-sustaining and constitutes a substantial and major constituent of a living cell in terms of weight [23,26]. Most physiological, chemical and physicochemical processes occurring in living organisms involve water. Waters present on the Earth can be divided into three basic groups, depending on their location (atmosphere, hydrosphere and lithosphere). These include atmospheric waters, surface waters and groundwaters [21,22].

Particular attention needs to be paid to groundwaters. According to the definition provided in the Water Law Act of 20 July 2017, groundwaters are understood as all the waters located under the Earth's surface within the saturation zone, including groundwaters that remain in direct contact with the ground and the substratum [17, 37]. In the previous definition set forth in the Water Law Act of 18 July 2001, groundwaters were waters occurring under the earth's surface in free cavities of the earth's crust's rocks, which create – depending on the water depth – near-surface or deeper usable aquifers [36].

A scientific field that is concerned with groundwaters is called hydrogeology (Greek: *hýdōr*

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– water, *ge* – ground, *logos* – science). It deals with studying their origin, physicochemical properties, distribution and movement within the earth's crust. The aim of hydrogeological studies is knowing the quality and quantity of groundwaters occurring in various geological formations, explaining the origin of those waters and determining the potential of their use for economic, industrial or health purposes [10].

Groundwaters are also studied by balneology, in order to determine their potential use in various forms of therapeutic treatments: drinking therapy, inhalation or bathing.

ORIGIN AND DIVISION OF GROUNDWATERS

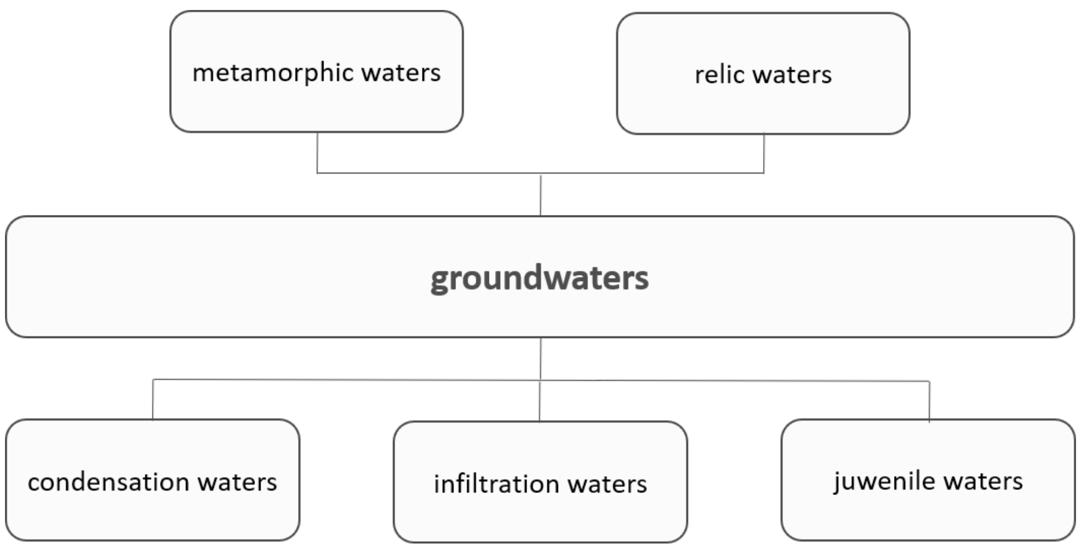
In terms of origin, groundwaters can be divided into infiltration, condensation, juvenile, metamorphic and relic waters (Scheme 1) [10,21,38].

Infiltration waters are groundwaters that owe their existence to penetration (infiltration) of atmospheric precipitation deep into the earth's crust. The amount of water penetrating the rocks mainly depends on the amount of precipitation and the size of chasms and pores in the rocks. The more cracks, pores and other cavities in rocks, the greater is the permeability of grounds and rocks, i.e. their ability to conduct water. The amount of precipitation waters penetrating the rocks depends on the lay of the land – the more diverse the land, the greater is the surface runoff and the less waters infiltrate the rocks. Negative factors influencing the volume of infiltration waters are evaporation and related temperature and humidity. The evaporation rate in the air is rising along with rising temperature. Humid air lowers or stops water evaporation and then it is conducive to infiltration [21]. Vegetation present on a given land as well as the geographical position of the area where the water occurs also have a significant impact on the amount of precipitation water. Dense vegetation inhibits surface runoff of the water and stores it in-between the roots, creating better conditions for infiltration. Infiltration waters flowing through the rocks become mineralised, although usually these are low-mineralised waters. Infiltration waters are used to supply people with drinking water. They are usually treated with aeration and filtration processes in order to give them acceptable organoleptic properties (lack of sedimentation, colour, smell). In certain regions of Poland, e.g. Opole, Busko or Nowy Korczyn, infiltration waters are very high in iron compounds, while in the region of Tarnobrzeg, they are characterised by unstable physicochemical composition. This might necessitate more advanced processing to make them suitable for consumption by people [16].

The infiltration waters can be contaminated by pollution from the ground environment, which should be controlled and removed before using this type of water to supply the population.

Condensation waters are groundwaters formed through condensation of water vapour present in the air filling the pores and cavities in the soil, grounds and rocks. Probably, there are more condensation waters in those areas where there are strong temperature fluctuations in the near-surface layers as well as on deserts, where at night the ground cools down faster than the air. In oceanic climates, the role of condensation in groundwater formation is probably small.

Juvenile (magmatic) waters are groundwaters formed at the last stage of magma solidification as it travels towards Earth's surface. In the light of contemporary opinions, only a small amount of groundwater is of magma origin [10]. Relic waters are



Scheme 1. Division of groundwaters in terms of their origin

defined as waters occurring in the zone of impeded exchange, with a very long residence time in the rock medium [1]. Metamorphic waters are formed during thermal rebuilding of perishable minerals [38].

PHYSICAL, PHYSICOCHEMICAL AND ORGANOLEPTIC PROPERTIES OF GROUNDWATERS

Correct determination of groundwater physical, physicochemical and organoleptic properties allows a preliminary identification of the water type and its potential impurities. Water physical and physicochemical properties include temperature, pH, radon level and electrical conductivity. Organoleptic properties, on the other hand, are colour, turbidity, taste and odour. These properties depend on numerous factors, including geological environment of the water and its depth. Discussed below are selected physical, physicochemical and organoleptic parameters of groundwaters.

Temperature of groundwaters

In the latitude of Poland, shallow waters are 5-12°C. From larger depths, waters are obtained the temperature of which can be even up to several dozen Celsjus degrees .

Groundwater temperature is influenced by such factors as geothermic level (depth expressed in metres where temperature rises by 1°C), the depth of occurrence of the water resources, mean annual air temperatures, period air temperature fluctuations within a given area, water flow rate and rock thermal conductivity. Groundwater temperature determines the course of hydrogeochemical processes [21,22].

Temperature-based groundwater division can use the hydrogeological or balneological criterion.

Hydrogeological division distinguishing cool waters ($t < t_{mean}$), ordinary waters ($t = t_{mean}$) and warm waters ($t > t_{mean}$) is based on the criterion of mean annual air temperature of this area where the given groundwaters are present [21].

Balneological division is based on the ratio of water temperature to human body temperature and the impact of different water temperatures on human body. Cool waters (t < 20°C) and thermal waters (t > 20°C) are distinguished. What is more, thermal waters are divided into:

- hypothermal, t = 20°C - 35°C
- homeothermal, t = 35°C - 40°C
- hyperthermal, t > 40°C [21]

Waters of natural origin – i.e. underground origin – with a noticeable higher temperature at their outflow point are referred to as a thermal spring or geothermal waters [12]. In the recent years, many new sources of this type of waters have been found in Poland. They are very diverse in terms of temperature and chemical composition [11,14]. Their mineralisation ranges from 0.15 g/dm^3 to 135 g/dm^3 and temperature from 20°C to 86°C. Dominating components of geothermal waters in Poland are usually chloride and sodium ions, but also sulphate carbonate, calcium and magnesium ions. Besides them, there are also various levels of components with specific biochemical properties, including ferrous, iodide and fluoride ions, radon, as well as sulphate compounds (II) [14,28]. Geothermal waters have been recognised as the first natural spa resources [9,12].

In Poland, thermal waters are commonly found in the three major regions: Polish Lowland, Sudetes and Carpathians. Based on observations conducted by *Chowaniec* et al., it can be concluded that the best conditions for sourcing thermal waters in the Carpathian Mountains are within the Podhale Basin due to: favourable geological structure, high temperature (up to 86°C at the outflow), low mineralisation (up to 3 g/dm^3), high efficiency (even more than 200 m^3/h from a single spring), renewability and easy land access [4].

Geothermal energy and be used directly for heating, leisure and balneology purposes, as well as agriculture, fishkeeping or thermophilous animal species. It is currently used in 78 countries of the world, although China, USA, Sweden, Turkey and Japan account for 55% of the total annual global use of geothermal heat [28]. Polish thermal waters are diverse in terms of temperature, therefore their use should especially be restricted to heating, preparation of hot utility water, as well as leisure and balneology. However, it is rather improbable that they will constitute an electrical energy source in the near future [20].

Electrical conductivity of groundwaters

Water is a solution of electrolytes that conduct electricity. Electrical conductivity is one of the characteristic features of groundwaters and depends on the valence of all the free ions. Divalent ions can carry twice as much a charge than the same number of univalent ions. The determination of conductivity is of practical importance as it is one of the methods of detecting changes in the physicochemical state of water [27]. Therefore, it can be a simple indicator of stability or variability of water chemical composition in control testing of groundwaters [11]. Water electrolytic conductivity expressed in μS/cm roughly corresponds to water mineralisation expressed in mg/dm^3 [27]. It must be remembered, though, that the presence of surface-active substances in water, and another compounds like oils, greases, tars, might falsify the results due to contaminating the electrode of the testing equipment.

Oxidation-reduction potential of groundwaters

It is one of the factors that is largely determined by the chemical composition of groundwaters. It measures the ability to transfer (return or accept) electrons by ions, molecules, and solid phases participating in a reaction. It is an index parameter based on the presence of specific concentrations (activities) of all the components involved in the oxidation-reduction reactions in the solution [8]. Both water pH and oxidation-reduction potential (also known as redox potential, Eh) are values that change when the water comes in contact with the external environment. Hence, determining a water's redox potential should happen right after it flows to the surface or in as short a time after sampling as possible before iron hydroxide (III) forms. Redox potential depends on pH and temperature and is also influenced by the oxidation number of polyvalent elements, as well as the content of some organic compounds that, by oxidation, constitute a source of CO_2 [34]. The presence of CO_2 in groundwaters allows them to keep a low redox potential. In waters with a low redox potential, ions such as iron and manganese, remain at a low oxidation number, which makes them better absorbed by the body [5].

Colour of groundwaters

Groundwaters are usually colourless. Groundwater colour can be caused by the content of certain organic or mineral compounds, or mechanical suspensions. The most frequent cause of natural water colour (yellow or brownish) is the scouring of humic substance and other products of plant material decomposition from the substrate. The greatest role in this process is attributed to humic and fulvic acids, which are high-molecular-weight substance with numerous function groups. Bluish-green colour of water might indicate the presence of acidic iron salts (such as sulphates), while rust colour might indicate the content of trivalent iron compounds [2,21,22].

Water colour is determined using platinum-cobalt or dichromate-cobalt standard solutions by comparing water samples with the standards. Colour determination should be performed immediately after a sample is taken.

Turbidity of groundwaters

Turbidity is an optical property of water, which involves scattering and adsorbing some of visible spectrum by particles dispersed in water. The most common causes of water turbidity are the presence of sand, insoluble carbonates, iron hydroxide, organic substances or microorganisms. Clear groundwater might become significantly turbid after flowing out to the surface and being exposed to air. This is caused by the release of natural carbon dioxide and then precipitation of iron hydroxide or calcium carbonate. Turbidity determination should be performed immediately after sampling water from a spring [2, 10].

Odour of groundwaters

Groundwaters are usually odourless. Waters having a less or more intensive odour are frequently those sourced from shallow layers that come in contact with swamps, marshes and moors, as well as waters contaminated with municipal or industrial sewage. There are five degrees of odour intensity – just like taste intensity. Water at three degrees is not suitable for consumptions, while at higher degrees it cannot be used even for household purposes.

Due to the origin, several types can be distinguished:

1. Odours of natural origin, which are divided into three groups:
   a) Plant odours caused by organic compounds, which are not subject to decomposition (smell of earth, peat, moss, tree bark, etc.),
   b) Decay odours caused by organic substances subject to decomposition (stale, decayed, etc.),
   c) Odours associated with the presence of natural inorganic water components (e.g. hydrogen sulphide)
2. Specific odours of unnatural origin caused by the contamination of groundwaters mainly by sewage, e.g.: chloric, phenolic [10].

Taste of groundwaters

Groundwater taste frequently depends on their mineralisation. Highly mineralised waters (containing >1500 mg/dm^3 of dissolved substances) often has a distinctive taste, e.g. salty taste can be caused by the content of sodium chloride. Bitter taste, on the other hand, can come from sodium and/or magnesium sulphates, while alkaline taste can come from the dominant amount of sodium, calcium, and magnesium bicarbonate [13]. Excessive content of carbon dioxide gives water sour and stinging taste, which is why waters containing more than 250 mg CO_2/dm^3 are referred to as carbonic acid waters.

CHEMICAL TYPES OF GROUNDWATERS

Chemical composition of waters largely depends on the composition of the earth's crust layers in which they form and through which they are flowing. Mineral components, such as calcium, magnesium, sodium, potassium, iron, manganese, ammonium ion, chlorides, bicarbonates, fluorides, iodides, sulphates, sulphides are accompanied by non-ionic components: orthoboric and metasilicate acids. Groundwaters also contain gases, such as carbon dioxide, hydrogen sulphide or radon. Waters naturally saturated with carbon dioxide in a larger concentration usually contain a certain amount of carbon dioxide bound in the form of bicarbonates. Waters containing carbon dioxide in concentrations higher than 250 mg CO_2/dm^3 are referred to as carbonic acid waters, while those containing more than 1000 mg/l – acidulous waters. Waters containing hydrogen sulphide are also characterised by the presence of hydrosulphides. Nitrogen and noble gases are present in waters come from considerable depths [19,21].

Apart from health-benefiting elements and compounds, groundwaters contain some trace amounts of heavy metals, including natural radioactive elements, which can have a negative impact on human body [18]. It is especially important when it comes to groundwaters used for bottled water manufacture. Natural, potentially toxic compounds that might occur in natural mineral waters include arsenic, barium, boron, lead, antimony, cadmium, mercury, chromium, copper, manganese, nickel, selenium, cyanides, fluoridesand radioactive compounds [6,15,24]. In waters made available for human consumption, including natural mineral and spring waters, maximum acceptable concentrations are determined for these components, the exceeding of which may constitute a health risk. Groundwaters in some regions of Poland, including the south-west region, are characterised by a considerable concentration of arsenic and radon from the toxicological point of view. However, appropriate procedures for preparing the water to be sold in unit packaging, including degassing and ozone aeration, allows reducing the content of these elements below the maximum acceptable limits. Some of the Polish groundwaters also contain barium and boron in concentrations higher than the maximum acceptable limits established by the Regulation of the Ministry of Health [30].

In the case of waters made available in unit packages (natural mineral and spring waters), it is permissible to remove or reduce the concentration of only some components, including arsenic, radon, fluoride, manganese, using methods proven and allowed in the applicable regulations cited above, provided that the method used does not change the concentration of other components, especially specific to a given water.

Natural components of groundwaters also include organic compounds, especially humus acids, i.e. humic, hymatomelanic and fulvic acids. A specific type of groundwaters are humic waters. Humic compounds they contain are formed in biochemical processes – condensation and polymerisation of decomposition products of plant- and animal-derived material. The aforementioned humic acids are macromolecular compounds with a poorly identified chemical structure, which can be divided depending on their solubility into:

- fulvic acids – soluble in water within the entire pH range
- humic acids – insoluble in water at pH < 2
- hymatomelanic acids – soluble in alcohol, insoluble in aqueous solutions with a pH < 2 [13].

Literature available so far shows that the structure of humic acids contains an aromatic core (indole, pyrimidine) and peripheral functional groups of aliphatic structure. Furthermore, fulvic, humic and hymatomelanic acids display significant differences in terms of molecular weight and molecular shape. Humic acids are compounds with a large molecular weight ranging from 50,000 Da to 100,000 Da and an extensive structure – a diameter of 60-100 Å. Fulvic acids, on the other hand, have a molecular weight ranging from 500 Da to 2000 Da and a diameter of 20-30 Å. Acid molecules with a larger weight show a higher affinity to bind metal ions. With a higher molecular weight and polymerisation degree, the colour intensity of humic waters also rises – from yellow (fulvic acid) to dark brown (humic and hymatomelanic acids) [15,32]. An example of intensely coloured waters in Poland are humic waters from the Miocene level within the Wielkopolska region [13].

Waters sourced from deep earth layers are generally characterised by stable chemical properties. Stable chemical composition does not mean absolutely the same concentration of particular water components, but their stable quantitative proportions [19,23]. Concentration fluctuations often depend on the size of the water intake from a given well.

Results of the determination of ions contained in tested water can be expressed in weight and equivalent concentrations. In hydrochemical practice, weight concentrations are expressed in mg/l, while equivalent concentrations in miligram equivalent in one litre of water (mval/l) [10]. One of the most frequently used qualification of mineralised and specific waters is Altowski-Szwiec qualification based on anionic-cationic composition and specific component concentration. According to the qualification, water type is determined based on concentration that is no less than 20% of milligram equivalents (mval%) of aggregate content of main ions – hydrogen carbonate, sulphate, chloride, calcium, magnesium, and sodium ions.

In the characterization of medicinal waters, in addition to the components that are quantitatively dominant (> 20 mval%), the names of components with specific biochemical properties are listed - if their content is equal to or higher than the established limits - also in descending order of concentration.

When determining the chemical type of water, the name of the water begins with anions and then the cations with the highest content in the water are listed in terms of milligram equivalents. Below, three main chemical types of waters in Poland are discussed (based on their quantitatively dominating anionic component).

Bicarbonate waters

Bicarbonate waters constitute a dominating type of shallow groundwaters of infiltration origin. They are used mainly for drinking water supply. Bicarbonate waters are characterised by renewability. The presence of bicarbonates is mainly caused by the dissolution of carbonate minerals and atmospheric carbon dioxide 11].

Due to the quantitative dominance of various cations, groundwaters in Poland belong to the following chemical types:

- bicarbonate-calcium-magnesium HCO_3-Ca-Mg
- bicarbonate-calcium-sodium HCO_3-Ca-Na
- bicarbonate-calcium-sodium-magnesium HCO_3-Ca-(Na)-(Mg)
- bicarbonate-sodium HCO_3-Na
- bicarbonate-sodium-calcium-magnesium HCO_3-Na-(Ca)-(Mg) [11].

For example, in the town of Krynica, there are numerous groundwater intakes characterised by diverse chemical type, with HCO_3^- always dominating among anions and Ca^{2+} i Mg^{2+} dominating among cations [6]. Bicarbonate waters are also found in other areas of Poland, for example in Świeradów-Zdrój, Szczawnica, Polanica-Zdrój, Kudowa-Zdrój, Duszniki-Zdrój, Piwniczna and Muszyna [12].

Bicarbonate waters that are most frequently used for health and spa treatments are carbonic acid waters and acidulous waters. Carbon dioxide present in the waters intensifies the process of mineral component dissolution [9].

Sulphate waters

This chemical type of waters is relatively rare within the territory of Poland. Dominating concentration of sulphates compared to other anions is usually associated with the presence of easily soluble minerals containing sulphur (e.g. gypsums and anhydrites) in the geological environment [11]. They also form in the weathering of sulphide minerals, oxidising gradually through sulphur to the sulphate form [27].

Sulphate waters containing hydrogen sulphide or sulphides in concentrations higher than 1 mg/dm^3 belong medicinal waters and are used in balneotherapy. Sulphates in combination with other components create various types: SO_4-Cl-Ca-Na,S, SO_4-(HCO_3)-Ca-(Mg)-(Na),S, SO_4-Cl-Na-Ca-Mg,S [11].

Sulphate waters with a dominating content of sodium, i.e. SO_4-Na, are referred to as Glauber's water, calcium SO_4-Ca – gypsum waters, magnesium SO_4-Mg – bitter waters, iron SO_4-Fe – vitriol waters [27].

Sulphate and sulphide waters occur, among others in Busko Zdrój, Solec Zdrój, Lądek-Zdrój, Tarnów or Horyniec Zdrój [12].

Chloride waters

Chloride waters constitute a dominating type of deep groundwaters in the territory of Poland. According to observations, their mineralisation level rises along with their rising depth [11].

Chloride-sodium waters Cl-Na – brines, form as a result of lixiviation of rock salt deposits or marine-origin sedimentary rocks. These waters also contain bromides and iodides. Apart from simple brines containing mainly chloride and sodium ions, there are also brines containing significant amounts of bicarbonate (Cl-HCO_3-Na), calcium (Cl-Na-Ca) and magnesium (Cl-Na-Mg) ions.

In geology, brine is defined as water containing > 35g/dm^3 of dissolved components, mainly sodium chloride, useful for industrial purposes. In balneology, brine is water containing more than 15 g/dm^3 of dissolved components with a predominance of sodium chloride. For medicinal baths it is recommended (depending on medical indications) concentration from 3 to 6 g/dm^3; for inhalation concentration in the range 0.9-1.5 g/dm^3.

An example of chloride waters are groundwaters of Rabka Zdrój. These are chloride-sodium waters with total mineralisation ranging from 17.1 to 27.8 g/dm^3, containing a specific component — iodides, at concentrations from 12 to 20 mg/dm^3 [29]. Chloride-sodium waters are also present, among others in Ciechocinek, Kołobrzeg, Międzyzdroje, Bochnia, Goczałkowice-Zdrój or Konstancin Jeziorna [12].

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Conflict of interest

The authors declare no conflict of interest.

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