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Assessment of the Vulnerability of Zygmunt Spring Water to Pollution (southern Poland)

Introduction

Population growth significantly impacts water quality while also increasing society's demand for drinking water. Ensuring the safety of drinking water is of paramount importance to human health (Thapa et al. 2020). It is important to note that water quality issues affect both developing and highly developed countries. Globally, approximately 30% of freshwater is sourced from groundwater, which is increasingly at risk due to climate change and human activities (Sitti et al. 2022). One example of a drinking water source is springs (Ansari et al. 2015).

Karst aquifers are among the most widely used drinking water resources worldwide (Kayastha et al. 2015; Meng et al. 2016), supplying over 9% of the global population (Kuniansky et al. 2022). While their accessibility makes them advantageous for drinking water distribution, their quality is under threat due to geological conditions, climate change,

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and land use (Adeyemo et al. 2008; Lahr et al. 2010; Vesković et al. 2024). Pollutant migration rates are influenced by both the area's topography and land development (Li et al. 2023). Additionally, the structure of rock faults and fractures plays a significant role in a water source's vulnerability to pollution (Han et al. 2015; Chen et al. 2017). Karst systems serve as crucial reservoirs of clean water, necessitating effective management to maintain water quality (Pu et al. 2013).

Water quality in karst systems is closely linked to the composition of the surrounding rock formations. The dissolution of carbonate rocks influences water chemistry and is connected to the cycles of carbon, water, and calcium. Carbonate rock components dissolve in the presence of carbonic acid, making it essential to assess the amount of dissolved carbon dioxide in groundwater.

Since springs are often fed by outcrops, their water quality is highly susceptible to pollution from atmospheric precipitation. Contaminants can migrate from nearby agricultural fields, industrial facilities, or faulty sewage systems. Such sources introduce pollutants like heavy metals, nitrates, chlorides, sulfates, antibiotics, organic pollutants, and bacteria into spring water (Geyer et al. 2007; Adesakin et al. 2020; Janik et al. 2024; Ruman and Dąbrowska 2024). Even if springs are not primary water sources, they are frequently used for recreational purposes by local residents and tourists. Although some belong to national water quality monitoring networks, these systems are often dominated by wells and piezometers, leading to limited monitoring of spring water. Consequently, contaminated springs can pose direct or indirect health risks (Paikaray and Mahajan 2023). People consuming untreated spring water may be exposed to diseases affecting the skeletal, nervous, and digestive systems due to contaminants such as heavy metals and fecal bacteria (Sari et al. 2022).

Spring water quality monitoring should be conducted not only at national monitoring sites but also in tourist and recreational areas. To facilitate the interpretation of physicochemical analysis results, various indices–such as the Nemerow Pollution Index, Metal Index, Backman Index, and Water Pollution Index–can be used (Backman et al. 1998; Beeckman et al. 2018; Juntunen et al. 2017; Katz et al. 2011; Tamasi and Cini 2004).

Most water quality indices are based on reference values derived from drinking water regulations, groundwater quality legislation, WHO guidelines, or the natural hydrochemical background of the study area (Kumar et al. 2017). These indices can incorporate various sets of parameters, including both physicochemical and bacteriological data. The latter is particularly useful for detecting issues such as leaks in sewage systems (Karkocha 2021; Zhu et al. 2023).

This study presents the results of three series of water quality tests conducted at Zygmunt's Spring, located in Złoty Potok (southern Poland). The Zygmunt Spring was selected due to its location in a tourist area, where spring water is frequently collected by visitors. Given this usage, assessing water quality in both physicochemical and bacteriological terms is crucial.

The evaluation included an analysis of physicochemical and selected bacteriological parameters, with results compared against drinking water guidelines. Additionally, geochemical modeling was conducted to determine the saturation state of minerals in various solutions. The Backman Pollution Index and Water Quality Index (WQI) were applied to assess potential threats to spring water quality. Since chemical reactions at the water-rock interface are reversible, understanding the processes of mineral dissolution and precipitation, as well as the conditions affecting carbon dioxide supply to the water, is essential. To address this, saturation indices and log pCO_2 values were calculated.

1. Study area

The water quality tests were conducted at Zygmunt Spring (50°41'13.42"N, 19°24'48.37"E), located in the Janów commune, approximately 90 km north of Kraków in southern Poland. The spring is situated at an altitude of 296 meters above sea level (Figure 1).

Zygmunt Spring lies within the Kraków–Częstochowa Upland macroregion and the Częstochowa Upland mesoregion (Kistowski et al. 2018). It is classified as a fissure-karst spring with both slope and flow characteristics (Figure 2). A niche has formed on the slope, from which several smaller springs emerge (Okoń et al. 2020).

The hydrographic network in this region is relatively underdeveloped. The spring is located within the catchment area of the Wiercica River, where surface water resources are limited. As a result, groundwater serves as the primary water source in this area.

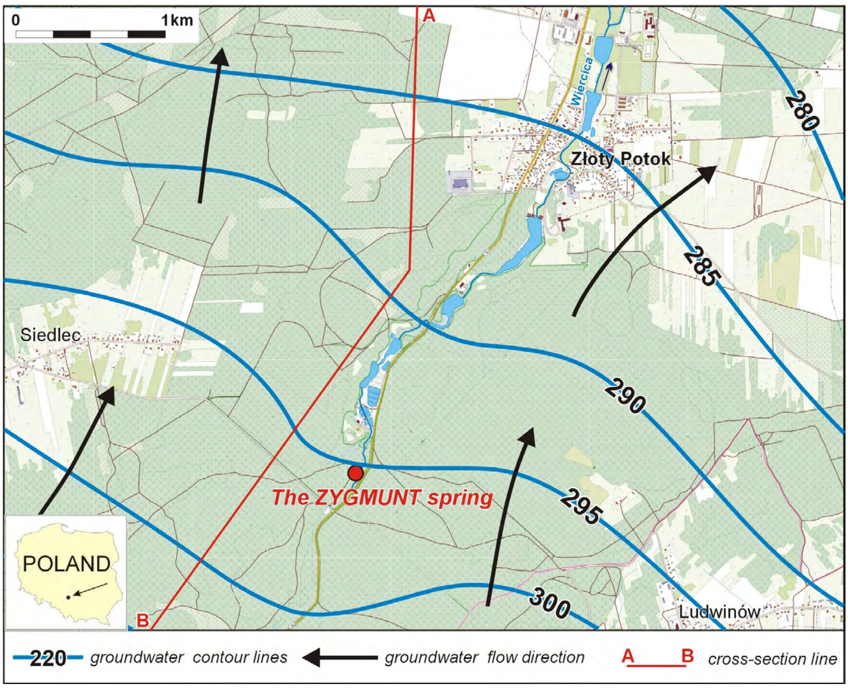

Fig. 1. Hydrogeological map of the study area (based on Pacholewski and Guzik 1997)

Rys. 1. Mapa hydrogeologiczna obszaru badań

Fig. 2. Zygmunt's spring (Fot. A. Witkowski)

Rys. 2. Źródło Zygmunta

Climatically, the Zygmunt Spring is situated in a region with a distinct continental climate. The average annual air temperature ranges from approximately 6 to 7°C. Precipitation is highest in April, while average monthly air humidity peaks in January and reaches its lowest levels in July.

Geologically, Zygmunt Spring is situated in the northern part of the Silesian-Kraków Monocline. This area consists of Jurassic, Cretaceous, Tertiary, and Quaternary sediments (Heliasz et al. 1986; Pacholewski and Guzik 1997). The geological conditions are illustrated in a fragment of the geological map (Figure 3).

The Jurassic formations in this region primarily comprise plate limestones, marly limestones, and marls, along with cream-beige rocky and plate limestones, often containing flints and exhibiting fractures. The Tertiary deposits mainly consist of various-grained sands and weathered clays with clay fragments and flints, as well as fine- and medium-grained sands mixed with clay minerals.

Quaternary sediments in the area include deposits and marginal formations from the Central Polish glaciation, such as boulder clays, sands, terminal moraine gravels, fluvioglacial sands and gravels, and sandy eluvia of boulder clays. Additionally, loess covers, aeolian sands on dunes and boulder clays, and river sediments–such as bottom silts, sands, and gravels of flood terraces–are present, with thicknesses ranging from 0 to 42 meters.

The usable aquifer is a Jurassic-level fractured-karst aquifer with a free surface on outcrops and a compact surface under the Quaternary formations (Figure 4). It is at an Upper Jurassic level.

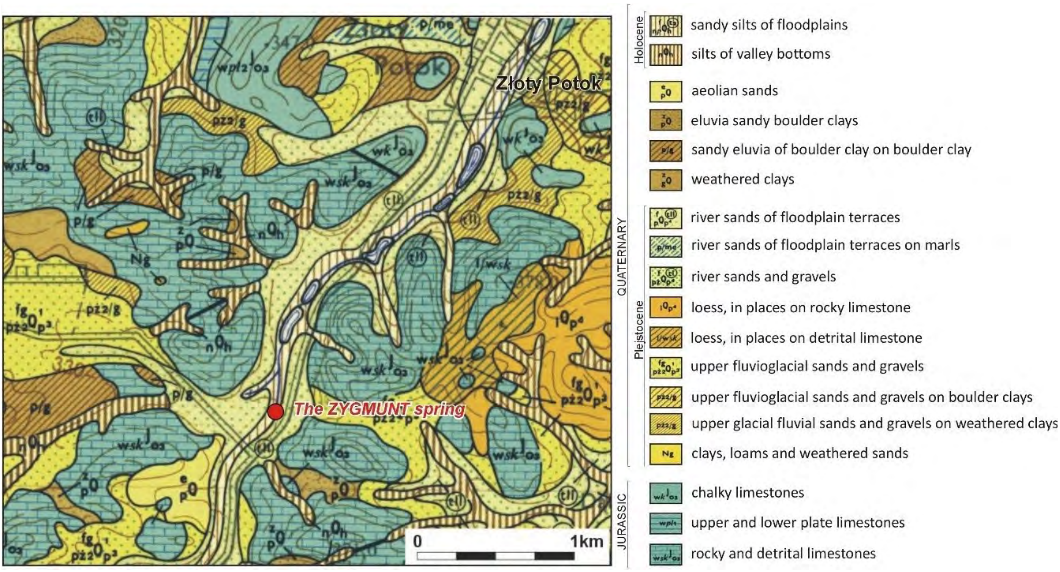

Fig. 3. Geological map of the study area (based on Heliasz et al. 1986)

Rys. 3. Mapa geologiczna obszaru badań

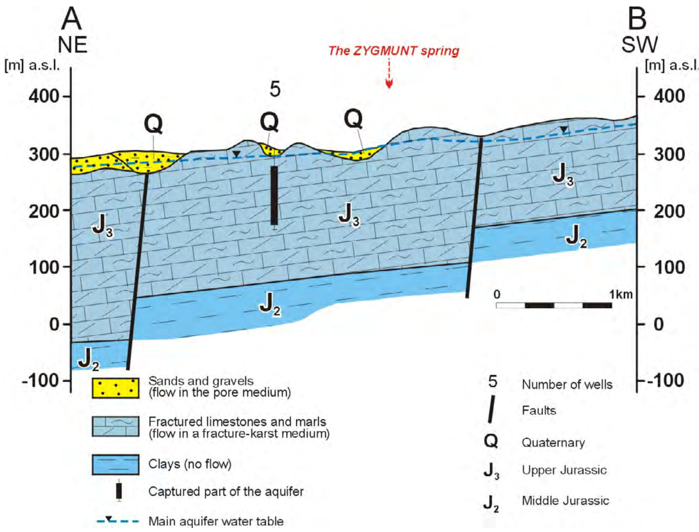

Fig. 4. Hydrogeological cross section

Rys. 4. Przekrój hydrogeologiczny

The thickness of this level is up to 350 m. This is a fracture-karst level with a free surface on the outcrops and strained under impermeable Quaternary and Cretaceous formations. The level is made up of Jurassic (Malmian) sediments, represented by plate limestones, marly limestones, marls (Kimmeridian), and rocky and plate limestones, often with flints and fissured (Oxfordian). The permeability of aquifers varies, and the hydraulic conductivity ranges from $6.0 \cdot 10^{-7}$ to $9.7 \cdot 10^{-4}$ m/s (Pacholewski and Guzik 1997). The flow of groundwater in the aquifer is in a north-easterly direction (Figure 1). Groundwater quality is good but maybe unstable due to lack of isolation from the surface. This area is classified as a high-risk area for water.

Groundwater in this area was tested as part of diagnostic monitoring by the State Environmental Monitoring system. This system operates based on the provisions of the Regulation of the Minister of Maritime Economy and Inland Navigation of October 11, 2019, on the criteria and method of assessing the status of groundwater bodies (Journal of Laws of 2019, item 2148) and the Regulation of the Minister of Maritime Economy and Inland Navigation of October 9, 2019, on the forms and methods of monitoring surface water bodies and groundwater bodies (Journal of Laws of 2019, item 2147). The scope of the research includes the following parameters: reaction, total organic carbon, electrical conductivity, temperature, dissolved oxygen, ammonium ions, antimony, arsenic, nitrates, nitrites, barium, beryllium, boron, chlorides, chromium, free cyanides, tin, zinc, fluorides, phosphates, aluminum, cadmium, cobalt, magnesium, manganese, copper, molybdenum, nickel, lead, potassium, mercury, selenium, sulfates, sodium, silver, thallium, titanium, uranium, vanadium, calcium, bicarbonates, iron. The nearest groundwater quality measurement point in this region is the piezometer located in Złoty Potok, about 3 km from the spring. This measurement point belongs to the national observation network. The latest data from 2022 shows that the electrical conductivity here was 808 μS/cm, the pH was 7.58, dissolved oxygen was 11.75, nitrates 11.90 mg/l, chlorides 183 mg/l, zinc 1.71 mg/l, magnesium 1.6 mg/l, sulfates 17.6 mg/l, sodium 59.3 mg/l, potassium 1.8 mg/l, calcium 107.7 mg/l, and bicarbonates 185 mg/l. The remaining components occurred in concentrations lower than the limit of quantification. In terms of quality, the waters are classified as class four due to their high zinc content. Such results indicate that water quality is shaped by three factors: evaporation, precipitation, and water-rock interaction.

Archived data for the spring show that the mineralization of this aquifer reaches 400 mg/l. The average results of water quality measurements indicate that the content of sulfates is 14 mg/l, chlorides 10 mg/l, nitrates 24 mg/l, and iron 1 mg/l.

Research on a minimal number of parameters is carried out at a measurement point on the Wiercica River. Data from 2022 show that the conductivity in this river was 371 μS/cm, dissolved oxygen was 9 mg/l, and total organic carbon was 4.58 mg/l.

So far, research on the quality of spring waters in this region has not shown the impact of human activity on the flow and quality of surface and groundwater. Municipal and industrial intakes intensively exploit the Upper Jurassic groundwater level. The inferior degree of natural isolation of the aquifer and the fissure-karst conditions of water and pollutant migration (high filtration speeds) make this reservoir vulnerable to rapid contamination. The level is recharged by infiltration of atmospheric waters through well-permeable Quaternary sediments or directly in the outcrop zone of Upper Jurassic formations. The waters of this level constitute the basis of the water supply for local residents. The water intake is located in Złoty Potok in a deep well with an operational capacity of 72.0 m^3/h. A direct protection zone has been established for this intake, which limits the inflow of pollutants.

2. Methodology

The first element of research on the quality of water in the Zygmunt Spring was filling out a form – the so-called standardized Howard's method (Omara et al. 2019) – which aims to determine the risks for a spring. This test consists of ten questions that can be answered yes or no. If a given risk occurs and the answer to the question is "yes," one point is entered. For each negative answer, zero points remain. The total risk score was manipulated into a percentage, and the aggregate risk score was graded as very high (81% to 100%), high (51% to 80%), medium (31% to 50%), low (1% to 30%) or nil (0%). Due to the fact that question no. 3 from the basic version of the form (i.e., 'Is the backfill area behind the retaining wall or spring box eroded?') does not apply to the examined object; it was replaced by a question regarding the geological conditions. The list of questions is below.

1. Is the spring unprotected?
2. Is the masonry protecting the spring defective?
3. Does the geological structure of the area favor the migration of pollutants?
4. Does spilled water flood the collection point?
5. Is the fence missing or damaged?
6. Are animals allowed within 10 m of the spring?
7. Are there septic tanks within 30 m and uphill from the source?
8. Does surface water collect upstream?
9. Is there no diversion ditch, or is it inoperable?
10. Are there other sources of pollution in the spring area (e.g., solid waste)?

The research at the Zygmunt Spring included three measurement series collected in November 2023, February, and May 2024. Parameters were measured in the field, and water samples were taken for physicochemical and bacteriological analyses in an accredited laboratory. The scope of physicochemical tests was as follows: electrical conductivity (EC), pH, Ca, Na, K, Mg, Fe, Al, Mn, Ni, Cu, Sr, S, Cl, SO_4, HCO_3, NO_3, NO_2, NH_4, PO_4, N, K, TOC, Pb, Cd, Cr, Hg, Zn and acidity and alkalinity. In bacteriological terms, the number of coliforms, Escherichia coli, Enterococci, Clostridium perfringens, the total number of microorganisms at a temperature of 22 ± 2°C, Pseudomonas aeruginosa and the total number of microorganisms at a temperature of 36 ± 2°C were examined. The flow rate was also measured. The scope of physicochemical and bacteriological analyses included the most popular parameters used to assess water quality. They are among the parameters used in legal acts and can also be compared with state environmental monitoring studies. The analyses also included parameters indicating pollution caused by anthropogenic factors, such as nitrates, ammonium ions, and arsenic. The scope of microbiological parameters included the most popular indicators of contamination with bacteria of fecal origin as well as two additional indicators, i.e., the total number of microorganisms growing at 36 ± 2°C (suggesting the presence of pathogenic bacteria) and the total number of microorganisms growing at 22 ± 2° C (assessing the effectiveness of treatment systems).

The water samples from the Zygmunt spring were collected in November, February, and May in accordance with sampling guidelines based on ISO 5667-3:2024 and PN-EN ISO 19458: 2007. Clean, sterile bottles with a volume sufficient to perform the planned analyses were used to collect samples. The bottles were prepared by an accredited laboratory. Samples were stored in a refrigerator during transport. They were collected by the same people each time, and the analysis took place in the same laboratory (laboratory accreditation number AB 1095). The following standards were taken into account in the laboratory tests: PN-EN ISO 11885:2009 (metals except mercury), PN-ISO 9297:1994 (chlorides), PN-ISO 9280:2002 (sulfates), PN-EN ISO 9963-1:2001 (bicarbonates), PN-EN ISO 13395:2001 (nitrogen compounds), PN-EN ISO 6878:2006 point 4 (phosphates), PN-EN 1484:1999 (total organic carbon), PN-EN ISO 12846:2012 point 7 (mercury), PN-EN 27888:1999 (conductivity), PN-EN ISO 9308-1:2014-12, PN-EN ISO 9308-1:2014-12/A1:2017-04 (coli bacteria), PN-EN ISO 7899-2:2004 (number of Enterococci), PN-EN ISO 14189:2016-10 (number of Clostridium perfringens), PN-EN ISO 16266:2009 (number of Pseudomonas aeruginosa), PN-EN ISO 6222:2004 (total number of microorganisms at 22 ± 2°C and total number of microorganisms at 36 ± 2°C).

Because the chemical composition of water depends on many factors and processes (Gascoyne 2004), the relationship between the physicochemical composition of water and the characteristics of the aquifer is presented in a Gibbs diagram (Gibbs 1970). The diagram presents three distinct areas, such as precipitation dominance, evaporation dominance, and rock-water interaction dominance areas, which indicate which factor has the greatest influence on the chemical composition.

The test results were compared with the reference values contained in the Regulation of the Minister of Health of December 7, 2017, on the quality of water intended for human consumption (Journal of Laws of 2017, item 2294) and first-class water quality standards based on the Regulation of the Minister Maritime Economy and Inland Navigation of October 11, 2019, on the criteria and method of assessing the status of groundwater bodies (Journal of Laws of 2017, item 2294).

The Backman Contamination Index (Cd) was used to assess the risks associated with water in the spring for all parameters mentioned in the regulation on the quality of water intended for human consumption (conductivity, Na, Mg, Fe, Al, Mn, Ni, chlorides, sulfates, nitrogen compounds, Pb, Cd, Cr, and Hg). The following formula was used (Backman et al. 1998):

$$C_d = \sum_{i=1}^{n} C_{fi} \tag{1}$$

where:

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \tag{2}$$

↳ C_{fi} – contamination factor for the *i*-th component,
C_{Ai} – analytical value of the *i*-th component,
C_{Ni} – upper range of natural hydrogeochemical background.

The total value of the index is reduced by 1. The index value increases with any increase in the content of individual components in the water being analyzed. This indicator assigns water to one of three classes: the threat to groundwater is high in areas where the index value is greater than 3, moderate for a value in the range of 1–3, and low when the index value is less than 1 (Harichandan et al. 2017).

The Water Quality Index was a second measure used to determine the risk to water. The WQI was calculated in relation to selected values stated in the same regulation as for the Cd index. This index was used as one of the most representative indices for water risk assessment (Knopek and Dabrowska 2021). Calculating this index involves the following stages:

- assigning weights to physicochemical parameters,
- developing a rating scale and
- calculating the WQI.

The parameters used for the WQI included the most characteristic indicators for water. They were selected based on other research. However, one change consisted of using the total number of microorganisms at 22 ± 2°C instead of a specific group of bacteria due to the inability to use an index when the measured value is 0. This index was calculated for dissolved oxygen (0.22), total number of microorganisms at 22 ± 2°C (0.21), pH (0.15), total phosphate (0.13), nitrates (0.13), and EC (0.16), taking into account weights from (Kumar et al. 2017; Ruman and Dąbrowska 2024). Weights for individual parameters can also be determined using statistical analyses where a large number of samples have been taken. Attention should also be paid to the fact that higher weights should be assigned to parameters for which water quality will deteriorate more as their value increases. Weights may also be assigned based on knowledge of the natural hydrochemical background or other national standards.

Following this, the quality rating scale (q_i) is calculated using Equation 3:

$$q_i = \frac{c_i}{s_i} \cdot 100 \tag{3}$$

↳ C_i – the concentration of parameters,
S_i – the standard value of parameters.

Finally, WQI is calculated using the Equation (4):

$$WQI = \sum_{N=1}^{N} SI \tag{4}$$

SI is the subindex calculated from the Equation (5):

$$SI = W_i \cdot q_i \tag{5}$$

The interpretation of this index is as follows:
- *WQI* < 50 indicates excellent water,
- 50–100 *WQI* good water,
- *WQI* > 100 poor water.

Geochemical modeling was also performed to determine the saturation status of minerals in various solutions and mixtures. Phreeqc software was used for this purpose. The saturation index (*SI*) is defined as log (*IAP*/*K*), where *IAP* is the ion activity product of the chemical species in the fluids, and K is their solubility product. Depending on the index value, it can assess whether the solution is oversaturated or undersaturated. In the first case (*SI* > 0), there is precipitation of secondary minerals, and in the second case (*SI* < 0), it suggests the dissolution of minerals. Calculating the partial pressure of carbon dioxide in water helps determine the CO_2 influencing the dissolution process in the aquifer. For example, calcite dissolution can also influence pCO_2 because the process consumes CO_2. The carbon dioxide content in water is influenced by biological, chemical, and physical processes, including carbonate dissolution and precipitation processes (Cole et al. 1994; Raymond et al. 1997; Frankignoulle et al. 1998).

3. Results and discussion

3.1. Howard's form results

In Howard's form, the answer was yes to questions 1, 3, 4, 5, 6 and 9. Affirmative answers to 60% of all questions indicate a high risk for the water from the spring. This risk is primarily related to the lack of security in the area. Despite the fact that the source is located in the forest, the issue of distance from the road and accessibility for animals remains. The form was also used in studies (Adimalla and Qian 2019), in which results of 70–90% were obtained for urban areas. In the case of sources exposed to strong anthropogenic influences, the least likely answer was an affirmative answer, as in the case of question no. 8. In the case of urban areas, however, it is more likely that the source is protected, e.g., through the use of concrete housing and the existence of other sources of pollution in the vicinity.

3.2. Field research and results of laboratory analyses

The highest values of most parameters were measured in the winter series, during which the lowest water temperature was observed. Based on t-tests for dependent samples, it should be concluded that there is no statistically significant relationship between individual measurement series. Determining the trend of changes in individual parameters, the downward trend could be attributed to sodium, calcium, iron, sulfur, nitrates, mercury, pH, and dissolved oxygen.

The discharge spring measurement results were 15 l/s in November 2023, 14 l/s in February 2024, and 22 l/s in May 2024. All physiochemical parameters were within the standard permissible limits. The temperature (°C) values change between 8.7 and 9.1 in the three series. The value of EC was 359 µS/cm in the first measurement series, 421 µS/cm in the second series, and 329 in the third series. The pH values measured during field tests were 7.13 in November and 6.95 in February and May. In terms of conductivity, the tested source falls within the range of typical karst sources of the Kraków-Częstochowa Upland. Previous studies conducted in the Jura (Okoń et al. 2020) indicate that the conductivity in the springs ranged from about 150 to about 600 µS/cm. The pH values were also similar to those of other springs in the area. The results of the measurements are presented in Table 1.

Dissolved oxygen was also measured during the field trips. In subsequent series, the following results were obtained: 10.3, 9.4 and 8.5. This is one of the parameters that affects, among other things, the taste of water. It is assumed that the correct value of this parameter for drinking water ranges from 6.5 to 8.5. High dissolved oxygen values indicate a constant flow of water and are associated with an improvement in taste.

The results of the three series of chemical analyses confirm that the water is of good quality. The waters of this spring are of the bicarbonate-calcium type (Table 2).

All parameters comply with national drinking water standards. However, the EC value in the second series of measurements exceeds the norm recommended by the WHO (400 µS/cm). Some parameters, such as aluminum, manganese, nickel, cadmium, copper, lead, chromium, nitrogen, and TOC, were below the limit of determination.

Comparing the results of the chemical analyses to first-class quality standards, exceedances can be observed in the case of calcium and bicarbonates. In the case of calcium, a deficiency in the body is much more dangerous than an excess. The concentration of nitrates also seems interesting. Although it does not exceed the permissible value for drinking water, its level may suggest contamination. An increased concentration of nitrates in water poses a much more significant threat. High levels of nitrates in water pose a threat to human health and are classified as a probable carcinogen (Darvishmotevalli et al. 2019).

Table 1. Results of measurements

Tabela 1. Wyniki pomiarów

Parameter	Unit	November 2023	February 2024	May 2024	Limits for drinking water[1]	Limits for the first class of quality[2]	WHO standards[3]	Limit of quantification
EC	µS/cm	359	421	329	2,500	700	400	<10–12,000>
Ca	mg/l	81	82	44	–	50		<1–100,000>
Na	mg/l	9.7	13	8.6	200	60		<1–10,000>
K	mg/l	0.5	0.5	0.5	–	10		<0.1–10,000>
Mg	mg/l	0.73	2.6	2.1	125	30		<0.1–5,000>
Fe	mg/l	0.002	0.041	0.002	0.2	0.2		<0.01–500>
Al	mg/l	0.005	0.005	0.005	0.2	0.1		<0.05–50>
Mn	mg/l	0.0005	0.0005	0.004	0.05	0.05	0.4	<0.005–100>
Ni	mg/l	0.002	0.002	0.002	0.002	0.005	0.07	<0.01
Cu	mg/l	0.002	0.002	0.002	–	0.01	2	<0.005–100>
Sr	mg/l	0.044	0.071	0.062	–			<0.02–500>
S	mg/l	4.3	5	3.7	–			<0.1–150>
Cl	mg/l	23	28	25	250	60	200	<1–10,000>
SO_4	mg/l	16	23	16	250	60		<1–10,000>
HCO_3	mg/l	198	201	181	–	200		<6.1–6100>
NO_3	mg/l	14	13	9.4	50	10	50	<0.44–443>
NO_2	mg/l	0.033	0.033	0.033	0.5	0.03	3	<0.033–33>
NH_4	mg/l	0.065	0.065	0.065	0.5	0.5		<0.04–2576>
PO_4	mg/l	0.081	0.068	0.094	–	0.5		<0.15–100>

Parameter	Unit	November 2023	February 2024	May 2024	Limits for drinking water[1]	Limits for the first class of quality[2]	WHO standards[3]	Limit of quantification
N_K	mg/l	2.5	2.5	2.5	–		1.5	<1–1,000>
TOC	mg/l	1	1	1	–	5		<1–1,000>
Pb	mg/l	0.002	0.002	0.002	0.01	0.01	0.01	<0.01–100>
Cd	mg/l	0.00025	0.00025	0.00025	0.005	0.001	0.003	<0.0002–1>
Cr	mg/l	0.0015	0.0015	0.0015	0.05	0.01	0.05	
Hg	mg/l	0.00005	0.00013	0.00005	0.001	0.001	0.006	<0.0001–0.01>
Zn	mg/l	0.0025	0.016	0.015	–	0.05		<0.02–500>
Acidity	mmol/l	0.1	0.32	2	–			<0.1–100>
Alkalinity	mg/l $CaCO_3$	162	164	148	–			<5–5,000>
Number of coliform bacteria	cfu/100 ml	0	0	0	8			–
Number of Escherichia coli	cfu/100 ml	0	9	0	6.5–8.5	6.5–9.5	6.5–8.5	<2–12>
Number of Enterococci	cfu/100 ml	0	0	14	0		0	≥ 0
Number of Clostridium perfringens	cfu/100 ml	0	0	0	0		0	≥ 0
Total number of microorganisms at 22 ± 2°C	cfu/ml	>300	70	>300	100		100	≥ 0
Number of Pseudomonas aeruginosa	cfu/100 ml	0	9	0	0		0	≥ 0
Total number of microorganisms at 36 ± 2°C	cfu/ml	13	12	12	20		20	≥ 0

[1] Regulation of the Minister of Health of December 7, 2017 on the quality of water intended for human consumption.
[2] Regulation of the Minister of Maritime Economy and Inland Navigation of October 11, 2019 on the criteria and method of assessing the status of groundwater bodies.
[3] The guidelines for drinking–water quality (GDWQ) proposed by WHO.

Table 2. Hydrochemical types of water

Tabela 2. Typy hydrochemiczne wód

Sample	% mval of dominant ions			
Sample 1	HCO_3 (84.34%),	Cl (8.41%),	Ca (89.03%),	Na (9.29%)
Sample 2	HCO_3 (81.49%),	Cl (9.89%),	Ca (83.73%),	Na (11.56%)
Sample 3	HCO_3 (84.54%),	Cl (9.16%),	Ca (79.53%),	Na (13.55%)

Although the limit for nitrates in drinking water is set at 50 mg/l, it should be noted that in various countries, such as Japan, this is often lowered to 10 mg/l. High levels of nitrates in water may result from runoff or leakage from fertilized soil, as well as damage to septic tanks, sewage, or landfill leachate.

Compared to other karst sources of the Kraków-Częstochowa Upland, the Zygmunt Spring has a low potassium, magnesium, and calcium content but a relatively high sodium content (Okoń et al. 2020).

However, the bacteriological condition of the tested waters indicates contamination. In the first and third series of measurements, the total number of microorganisms at a temperature of 22 ± 2°C was over 300 cfu/ml. This is an indicator of the total number of bacteria cultured at 22°C for 72 hours. These are psychrophilic organisms that die at temperatures below 0°C and above 30°C and develop best at 15°C. They are not considered to pose a threat if their number does not exceed 100. The total number of microorganisms in water at 36°C was also non-zero. In all series, these values were in the range of 12–13 cfu/ml. This is an indicator of the total number of bacteria cultured at 36°C for 48 hours. These are mesophilic organisms for which the optimal temperature for growth and development is between 30°C and 40°C. They may include pathogenic bacteria because the optimal temperature is the same as the human body temperature. It is believed that there is no danger of getting sick if the number of these bacteria does not exceed 50 in 1 ml of water.

3.3. Backman Pollution Index and Water Quality Index results

The good results on the quality of water contained in the source in relation to national standards for drinking water meant that the results of the Backman Pollution Index amounted to –13.78 in the autumn series, –13.33 in the winter series, and –14.26 in the spring series. The reduced value of this indicator in the spring series was mainly caused by a decrease in the content of calcium and nitrates. This index was also calculated by taking the limits for water quality class I as reference values. In this case, the values of the Backman index increased to –11.86, –12.14, and –11.39, respectively. With these parameters and reference values, it can be concluded that the waters of the spring in Złoty Potok are not under any anthropogenic influence. For comparison, near pollution sources, the values of this indicator may be approximately 600 (Knopek and Dąbrowska 2021) or even exceed 1400 (Karkocha 2021).

The Water Quality Index values suggest very high contamination and risk for water. The values of WQI were equal to 113.37, 62.71, and 106.65, respectively, in the three series. As can be seen, the index values in the first and third measurement series are similar, which results from the high value of the bacteriological parameter (the total number of microorganisms at a temperature of 22 ± 2°C). The index value increased by approximately 80% between the second and third series. In the second measurement series, in which the value of this parameter was equal to 0, the index value decreased significantly. The results of the second series of measurements suggest that the waters in the Zygmunt Spring are of good quality. In this situation, convergence with the values obtained for the Backman index can be seen.

Water contamination with feces resulting from the discharge of raw sewage is a serious health and environmental problem (Arvizu and Murray 2021). Escherichia coli and Enterococci bacteria are indicators that can confirm contamination. In the second series of measurements, Escherichia coli was detected at nine cfu/100 ml. An increased number of bacteria in water (even if it is recorded at a medium risk level) may lead to numerous diseases of the digestive system and, in some cases, even to urosepsis or meningitis (Biran and Ron 2018; Hernandez-Pastor et al. 2023). In the last measurement series, Enterococci were detected. Their number was 14 cfu/100 ml. Enterococci in drinking water most often occur in the form of splits or short chains and indicate that the water is contaminated with human fecal bacteria. It is worth emphasizing that Enterococci, unlike bacteria from the Coli group, are characterized by a slightly longer lifespan and survival in water. Moreover, these bacteria are resistant to chlorine and can cause kidney and bladder diseases (Lundberg et al. 2018).

3.4. Geochemical aspects

The Gibbs diagram for cations in the analyzed spring water samples shows that the water samples fall within the rock dominance area (Figure 5) due to the fact that the water from the spring in the study region is characterized by low ratios of chlorides/chlorides + + bicarbonates and sodium + potassium/sodium + potassium + calcium and a moderate value of EC.

Karst systems are among the most heterogeneous and anisotropic due to the system of karst channels and cracks resulting from the uneven flow of groundwater, which creates complex hydrogeological conditions. Therefore, the chemistry of spring waters may reflect various processes occurring at the water-rock contact (Aquilina et al. 2003; Zheng et al. 2018; Guo et al. 2019). Springwater geochemistry was analyzed based on saturation with respect to calcite, dolomite, aragonite, anhydrite, gypsum, goethite, and hematite (Table 3).

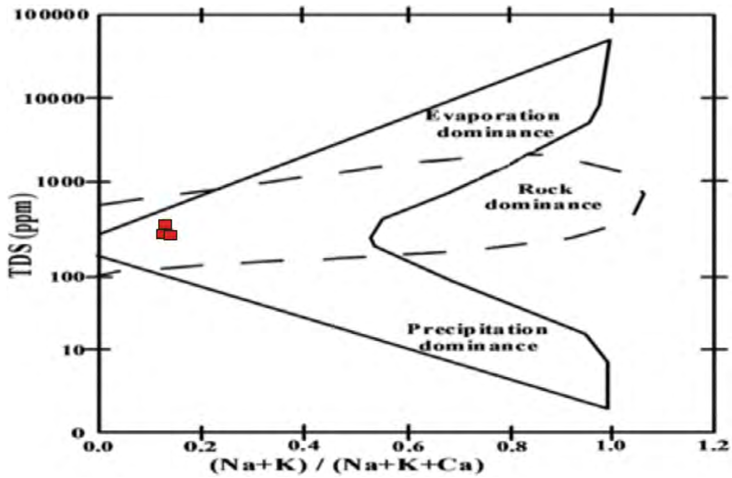

Fig. 5. Gibbs diagram for water samples of Zygmunt spring (based on Gibbs 1970)

Rys. 5. Diagram Gibbsa dla próbek wód ze źródła Zygmunta

Table 3. Calculation of saturation indices resulting from Phreeqc simulation

Tabela 3. Wyniki obliczeń wskaźników nasycenia w programie Phreeqc

Sample	Calcite	Aragonite	Dolomite	Gypsum	Anhydrite	Goethite	Hematite
Sample 1	–0.34	–0.51	–2.49	–2.28	–2.52	4.80	11.59
Sample 2	–0.18	–0.33	–1.58	–2.13	–2.37	6.59	15.16
Sample 3	–0.61	–0.79	–2.32	–2.48	–2.72	4.82	11.63

The springs in this area are recharged mainly by limestone aquifers, the mineral composition of which is not very diverse (Okoń et al. 2020). The saturation indices of the carbonate and sulfate minerals are pessimistic over the two measurement series, indicating undersaturation, which means these minerals could dissolve. Lower saturation indices were observed for dolomite in the case of carbonate minerals and for anhydrite in the case of sulfate minerals so that they will be more soluble. The dissolution processes of sedimentary rocks in the sample are consistent with the geochemistry of water found in fractured aquifers.

Positive saturation index values were observed in the cases of goethite and hematite, which suggests precipitation of these minerals. Iron minerals also precipitate within the typical pH range of groundwater.

One of the factors causing changes in CO_2 solubility is a change in temperature. Theoretically, the solubility of CO_2 is inversely proportional to the water temperature (Drysdale et al. 2003; Pu et al. 2013), but in this case, there is no consensus on this principle. The pCO_2 values were 10–1.69, 10–1.87, and 10–1.73 for the series in November, February, and May, respectively. Based on the analysis of the correlation of this parameter with saturation indices for individual minerals, it can be seen that there is a statistically significant correlation with *SI* for dolomite (Table 4). In other cases, the correlation coefficient is at the level of (–0.98 to – 0.63).

Table 4. Correlation between SI and pCO_2 values

Tabela 4. Korelacja pomiędzy wartościami SI oraz pCO_2

Variable	Calcite	Aragonite	Dolomite	Gypsum	Anhydrite	Goethite	Hematite	CO_2
Calcite	1.00	1.00	0.66	1.00	1.00	0.78	0.78	–0.63
Aragonite	1.00	1.00	0.68	1.00	1.00	0.79	0.79	–0.65
Dolomite	0.66	0.68	1.00	0.71	0.71	0.99	0.99	–1.00
Gypsum	1.00	1.00	0.71	1.00	1.00	0.82	0.82	–0.68
Anhydrite	1.00	1.00	0.71	1.00	1.00	0.82	0.82	–0.68
Goethite	0.78	0.79	0.99	0.82	0.82	1.00	1.00	–0.98
Hematite	0.78	0.79	0.99	0.82	0.82	1.00	1.00	–0.98
CO_2	–0.63	–0.65	–1.00	–0.68	–0.68	–0.98	–0.98	1.00

If samples from February and May were analyzed, a greater negative correlation could be observed between pCO_2 values and saturation indices for dolomite or calcite. Low carbon dioxide values suggest a closed system where the voids are not directly connected to the surface. This also suggests that the dissolution of carbonate minerals and atmospheric precipitation have a smaller impact on the flux of carbon dioxide in water.

Conclusions

Springs in karst layers are highly vulnerable to pollution due to the system of cracks and fissures in the rock. This vulnerability increases for sites located in areas under anthropogenic pressure. Proximity to transportation routes, agricultural fields, or unsanitized areas can pose a threat to inorganic substances or bacteria. In this context, it is essential to conduct reliable monitoring of water quality and make the inspection results available.

The results of three measurement series in the waters of the Złoty Potok spring did not confirm elevated concentrations of the measured parameters, which is due to the extremely low value of the Pollution Index, but indicated the possibility of migration of bacteria into the water. This, in turn, was confirmed by the Water Quality Index. Based on the results of this index, low vulnerability to pollution can be concluded. However, bacteriological tests for this type of water should be performed more frequently due to the possibility of ingestion of spring water, which in turn can lead to diseases and health risks. This is especially important because the spring is located in a Natura 2000 area, which is supposed to be non-endangered. Geochemical modeling indicates the solubility of minerals such as calcite and dolomite and the precipitation of goethite and hematite.

Future studies should determine the seasonality of changes in the various parameters and examine the possibility of determining the hydrodynamics of these waters in karst formations.

The Authors have no conflict of interest to declare.

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ASSESSMENT OF THE VULNERABILITY OF ZYGMUNT SPRING WATER TO POLLUTION (SOUTHERN POLAND)

Keywords

spring, contamination index, water quality index, Złoty Potok

Abstract

Karst aquifers are among the most widely used drinking water resources worldwide. However, their water quality can deteriorate due to negative anthropogenic impacts. Monitoring the quality of spring water is crucial, both in terms of physicochemical and bacteriological parameters. In this study, 34 parameters of the Zygmunt Spring in Złoty Potok (southern Poland) were analyzed across three measurement series. The average water conductivity was 370 μS/cm, with a pH of approximately 7 and a flow rate of about 17 L/s. The Backman Pollution Index (average value: –13) and the Water Quality Index (average value: 94) were calculated, indicating that bacterial contamination poses the greatest risk to water quality. Additionally, geochemical modeling was conducted to identify minerals undergoing dissolution and precipitation. The results confirmed the dissolution of calcite and dolomite, as well as the precipitation of goethite and hematite.

OCENA PODATNOŚCI WÓD NA ZANIECZYSZCZENIA W ŹRÓDLE ZYGMUNTA (POŁUDNIOWA POLSKA)

Słowa kluczowe

źródło, wskaźnik zanieczyszczenia, wskaźnik jakości wody, Złoty Potok

Streszczenie

Systemy krasowe należą do najbardziej niejednorodnych i anizotropowych ze względu na system kanałów krasowych i szczelin powstałych w wyniku nierównomiernego przepływu wód podziemnych, co tworzy złożone warunki hydrogeologiczne. Należą również do najczęściej wykorzystywanych zasobów wody pitnej na świecie. Jednak ze względu na negatywne oddziaływanie antropogeniczne jakość ich wody może się pogorszyć. Monitorowanie jakości wody w źródłach jest niezwykle ważne, zarówno pod względem parametrów fizykochemicznych, jak i bakteriologicznych. W trzech seriach pomiarowych zbadano 34 parametry w źródle Zygmunta w Złotym Potoku (południowa Polska). Średnia przewodność wody w tym źródle wynosi 370 µS/cm, pH wynosi około 7, a natężenie przepływu około 17 l/s. Pierwszym elementem badań nad jakością wody w źródle Zygmunta było wypełnienie formularza – tzw. znormalizowanej metody Howarda, która ma na celu określenie ryzyka dla źródła. W ramach badań obliczono *Backman Pollution Index* (średnia wartość –13) i *Water Quality Index* (średnia wartość 94). Wyniki obliczeń wskazują, że bakterie stanowią największe zagrożenie dla wody. Bliskie sąsiedztwo szlaków transportowych, pól uprawnych lub obszarów niesanitarnych może stanowić zagrożenie dla substancji nieorganicznych lub bakterii. Przeprowadzono również modelowanie geochemiczne w celu zidentyfikowania minerałów rozpuszczonych i wytrąconych w wodzie. W wyniku modelowania potwierdzono rozpuszczenie kalcytu i dolomitu oraz wytrącanie się getytu i hematytu.