THE QUALITY OF THE ZYGMUNT SPRING WATER (SOUTHERN POLAND) – PRELIMINARY RESULTS

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ABSTRACT: Natural springs are one of the potential sources of water supply, but due to negative anthropogenic impacts, the water quality can deteriorate. The Zygmunt Spring in Złoty Potok does not form the basis of the population's water supply, but it is constantly being exploited by residents and tourists. This study was carried out at Zygmunt Spring in two measurement series for 34 physicochemical and bacteriological parameters. The average electrolytic conductivity (EC) of the water in this spring is about $0.039 \text{ S} \cdot \text{m}^{-1}$, the pH is about 7.04 and the discharge is equal to 15 dm³ · s⁻¹. The test results were compared with the permissible limits for national drinking water, groundwater quality and WHO standards. The value of the Backman pollution index was calculated for these parameters. This index takes into account parameters that exceed the upper permissible concentrations of contaminants. The Backman Contamination Index value was about -13, but the results of bacteriological analyses indicate a very high number of microorganisms in the water (>300 cfu · mL⁻¹), indicating a high health risk.

KEYWORDS: spring, karst, water quality, microbiology, the Backman Contamination Index, risk, Złoty Potok

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Introduction

Society's demand for water of an appropriate quality suitable for drinking is constantly growing. Due to the increase in pollution, providing such resources has become extremely difficult (Stevanović 2010). This phenomenon affects not only developing countries but is a global problem. Globally, approximately 30% of freshwater is groundwater, which is at risk due to climate change and human activities such as industry, urbanisation, mining, and agriculture. Examples of drinking water sources include springs, streams, and dug and drilled wells (Owamah et al. 2013). It is important to remember that on a global scale, karst aquifers are one of the main sources of freshwater (Hamed et al. 2023). In Europe, approximately 5.1% of the surface area contains continuous exposures of carbonate rocks, which are particularly endangered due to the hydrogeological properties of these rocks. This applies not only to the physicochemical parameters but also to bacteriological threats. Springs connect surface and groundwater ecosystems and are therefore often vulnerable to pollution (Todd 2009, Pokładek et al. 2011, Sari et al. 2022) depending on geological, climatic conditions and land use (Ansari et al. 2015, Kayastha 2015, Meng et al. 2016, Kumar et al. 2017, Pinter et al. 2018). The same factors will influence the amount and type of contaminants



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that will be present in spring water. Moreover, the topography and development of the surrounding area may result in faster migration of contaminants (Gothwal, Shashidhar 2014).

Contaminated water may pose direct or indirect risks to human health (Guo et al. 2022). Typical water contaminants include compounds of organic and inorganic origin, including heavy metals, detergents, fertilisers, pesticides, pharmaceuticals, and biomaterials (Benson et al. 2010). Heavy metals occur naturally in water in trace amounts and are essential for human metabolism, but increased concentrations lead to the development of diseases of the skeletal, nervous and digestive systems (Muhammad et al. 2011). Faecal bacteria from domestic sewage, septic tanks and sewage treatment plants constitute the majority of threats to karst groundwater (Humphrey et al. 2018, Iverson et al. 2020). Springs can be subjected to various tests that help in assessing the quality and quantity of resources. These include primarily hydrological, hydrogeological and bacteriological research. The results of such studies can be interpreted using various methods, including indicator methods (Backman et al. 1998, Gogu, Dassargues 2000, Tałałaj 2014, Zhang et al. 2018).

The aim of this article is to present the current state of knowledge on the water quality of Zygmunt's Spring and to evaluate the hypothesis that water from a spring located in an area under anthropogenic pressure is characterised by an altered chemical composition, based on the examination of the water quality of a karst spring in two series of measurements. The choice of Zygmunt Spring as the subject of research is dictated by the fact that it is a very popular place among tourists in the Kraków-Częstochowa Upland, from which water is often drawn for drinking purposes. The research took into account the physicochemical parameters and selected bacteriological indicators. The Backman Pollution Index was used as an auxiliary method in water risk assessment.

Study area

The research covered the main outflow in the discharge system of the Zygmunt Spring, which is located in the Janów commune (the Silesian Voivodeship), at a distance of 30 km from Częstochowa (southern Poland) with an altitude of 296 m above sea level (Fig. 1). In terms of physical and geographical regionalisation, according to Kondracki (2000), it is located in the Kraków-Częstochowa Upland macroregion and in the Częstochowa Upland mesoregion. The spring is located in the Jurassic plateau and gives rise to the Wiercica catchment. It is a perennial spring. A niche has developed on the slope, from which several springs flow. The spring is located within the Natura 2000 area Ostoja Złotopotocka PLH240020 (Wojtal et al. 2017). Moreover, the spring in Złoty Potok is located within the boundaries of the 'Parkowe' nature reserve, which was established in 1926. It should be noted that this is an area very poor in surface water - typical of karst areas, and has one of the rarest river networks in Poland. Water from the spring creates the Zygmunt Stream, which is 500 m long. Despite the fact that the main source of water supply for the population is groundwater, water from the spring in Złoty Potok is taken all the time by nearby residents and tourists. The close proximity of the road (about 150 m) makes the intake site easily accessible.

The Zygmunt Spring is located in a region with a distinct continental climate. Taking into account the available hourly archival meteorological data from the Institute of Meteorology and Water Management from the nearest observation station (Częstochowa) for the years 1971–1991, the average annual air temperature is 8.18°C, the maximum 31.4°C and the minimum −16.3°C (MIIR 2019). The annual rainfall is approximately 800 mm. The greatest amount of rainfall falls in April. The highest average monthly humidity occurs in January, whereas the lowest is observed in July.

The study site is located in a forested area, but at a distance of about 1 km to the northwest and 2 km to the southeast are agricultural fields, which may be a source of pollution. Hence, according to the hydrogeological map of Poland in scale 1:50,000 (Zembal et al. 2013), the first aquifer has a very high level of vulnerability to pollution in the area.

The Zygmunt Spring is geologically located in the northern part of the Silesian-Kraków Monocline. This area is composed of Jurassic, Cretaceous, Tertiary and Quaternary deposits (Heliasz et al. 1987). The Jurassic formations are represented by plate limestones, marly limestones,

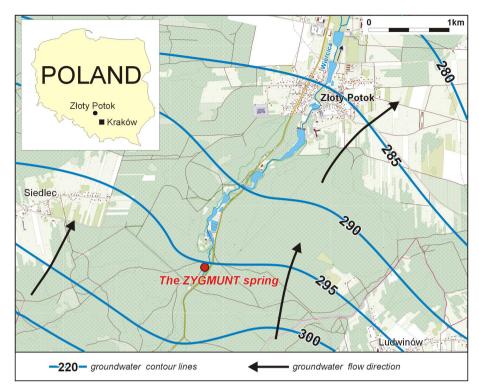


Fig. 1. Map of study area location (based on Pacholewski, Guzik 1997b).

marls, and rocky and fissured, plate limestones of a cream-beige colour, often with flints. The inselberg forms are made of rocky limestone, which is the most resistant to weathering processes. Tertiary formations are mainly represented by various-grained sands and weathered clays with clasts and fine- and medium-grained sands with an admixture of clay minerals. The thickness of the Jurassic formations in the area of the spring is approximately 120 m. The Quaternary formations are represented by sediments and marginal forms of the Central Polish glaciation (boulder clays, sands, end moraine gravels and gravels, sandy eluvia of boulder clays), loess covers, aeolian sands in dunes and boulder clays, river sediments, that is, bottom silts, sands and gravels of floodplain terraces. In the area of the described spring, these deposits are not >1 m thick.

From a hydrogeological point of view, usable groundwater in the commune area occurs in the Upper Jurassic level, including a series of Kelovian, Oxfordian and Kimmeridgian carbonate deposits. This is a fracture-karst level with a water table on the outcrops and a confined groundwater surface under the Quaternary formations. The thickness of this level is up to 350 m, its transmissivity is about 110 m² · 24 h⁻¹ and hydraulic conductivity ranges from 6.0×10^{-7} m · s⁻¹

to $9.7 \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$ (Pacholewski, Guzik 1997a). Well discharges are also varied, ranging from a few to over 250 m³ · h⁻¹. Discharge of springs in this area ranges from 6 dm³ · s⁻¹ to >1400 dm³ · s⁻¹ (Pacholewski, Guzik 1997a). The flow of groundwater in the main aquifer is in a north-eastern direction. Groundwater quality is good but may be unstable due to lack of isolation from the surface. This causes the waters to be exposed to pollution -high risk (Pacholewski, Guzik 1997b).

Methodology

The spring research included two series of measurements on 25 November 2023 and 18 February 2024. These two measurement series are the beginning of research on the water quality in this spring and will be continued. The average air temperature in October was 10.1°C and rainfall was 90 mm, while in January the average temperature was 4.8°C and rainfall was 73 mm. These are the monthly data before the spring water measurements. It should be noted that from October to February there was no snow cover in the analysed area, so a factor such as snow melt is not considered for the analysis of the measurements.

Field tests included measurements of temperature, electrolytic conductivity (EC), pH, dissolved oxygen and spring discharge using a CC-401 conductivity meter, pH using a CP-411 pH meter, and dissolved oxygen using a CO-401 oxygen meter, produced by Elmetron (accuracy 0.01). Water samples were collected for physicochemical and bacteriological analyses performed in GBA Polska accredited laboratory (laboratory accreditation number: AB 1095). The values of EC, pH, Ca²⁺, Na⁺, K⁺, Mg²⁺, Fe²⁺, Al³⁺, Mn²⁺, Ni²⁺, Cu²⁺, Sr²⁺, S²⁻, Cl⁻, SO₄²⁻, HCO₃²⁻, NO₃⁻, NO_{2}^{-} , NH_{4}^{+} , PO_{4}^{3-} , Kjeldahl nitrogen, TOC, Pb^{2+} , Cd²⁺, Cr⁶⁺, Hg²⁺, Zn²⁺, acidity and alkalinity were tested. In the bacteriological scope, coliforms Escherichia coli, Enterococci, Clostridium perfringens, microorganisms at 22 ± 2°C, Pseudomonas aeruginosa and microorganisms at 36 ± 2°C were examined. The following PN-EN ISO standards were taken into account in the laboratory tests: 11885:2009 (metals except mercury), 9297:1994 (chlorides), 9280:2002 (sulphates), 9963-1:2001 (bicarbonates), 13395:2001 (nitrogen compounds), 6878:2006 point 4 (phosphates), 1484:1999 (total organic carbon), 12846:2012 point 7 (mercury), 27888:1999 (EC), 9308-1:2014-12, 9308-1:2014-12/ A1:2017-04 (coli bacteria), 7899-2:2004 (number of Enterococci), 14189:2016-10 (Number of C. perfringens), 16266:2009 (Number of P. aeruginosa), 6222:2004 (total number of microorganisms at 22 ± 2°C and total number of microorganisms at $36 \pm 2^{\circ}C$).

The discharge was obtained by dividing the container volume by the filling time. Three different measurements were made and the average value was used. To improve the reliability of the measurement, the bucket method was used to measure discharge.

The concentration of chemical components in groundwater depends on many processes and conditions, including mineral availability and solubility (Gascoyne 2004), the geochemical environment and exchange processes. Several hydrochemical indicators were used to assess vertical hydrochemical zonation. In order to check whether groundwater is in contact with atmospheric water, the following indicators were used:

$$r\frac{Na^{+} + K^{+}}{Cl^{-}}$$
 and $r\frac{Na^{+} + K^{+} + Mg^{2^{+}}}{Cl^{-}}$

If these values are >1, this condition is confirmed. In the case of dynamic stagnation, these values decrease. The origin of spring waters was also determined based on the index $\frac{Ca^{2+}}{Sr^{2+}}$ which >200 for waters enriched by leaching of carbonate rocks (Macioszczyk 1987).

The analytical results from the laboratory were compared with the permissible values contained in the following regulations:

- Regulation of the Minister of Health of 07 December 2017 on the quality of water intended for human consumption (Journal of Laws of 2017, item 2294);
- Regulation of the Minister of Maritime Economy and Inland Navigation of 11 October 2019 on the criteria and method of assessing the status of groundwater bodies (Journal of Laws of 2019, item 2148);
- WHO standards in terms of exceedances of the established limits.

The Backman Contamination Index was used to assess the risk for water in the spring for all parameters mentioned in the regulation (EC, Na⁺, Mg²⁺, Fe²⁺, Al³⁺, Mn²⁺, Ni²⁺, chlorides, sulphates, nitrogen compounds, Pb²⁺, Cd²⁺, Cr⁶⁺ and Hg²⁺). This index has been calculated using the following formula (Backman et al.1998):

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

where:

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

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

The total value of the index is reduced by 1. With an increase in the concentration of a given component in relation to the drinking water limit, the value of the contamination index grows. This index classifies water based on three classes: the threat to groundwater is high in an area wherein the index value is >3, moderate pollution with a value in the range of 1–3 and the low threat when the index value is <1 (Knopek, Dąbrowska 2021).

Results and discussion

The discharge spring measurement results were 15 dm 3 \cdot s⁻¹ in November 2023 and 14 dm³ · s⁻¹ in February 2024. All physiochemical parameters were within the standard permissible limit. The value of specific EC was $0.0359 \text{ S} \cdot \text{m}^{-1}$ in the first measurement series, and 0.0421 S \cdot m⁻¹ in the second series. The water falls into the medium saline category (Kadhem 2013). The pH values measured during the field tests were 6.95 and 7.13, respectively, which classifies the water from slightly acidic to slightly alkaline (Pazdro, Kozerski 1990). The water temperature in the spring was 8.7°C in November and 9°C in February, while the air temperature on the day of measurement was 0°C and 8°C, respectively. Taking into account the water temperature, the spring is classified as cold (Stevens et al. 2021).

Among the macroelements, the highest concentrations were recorded in the case of bicarbonates (approximately 200 mg \cdot dm⁻³), the concentration of chlorides was on average 20 mg \cdot dm⁻³ and sulphates – $20 \text{ mg} \cdot \text{dm}^{-3}$. Among the cations, the highest concentrations were observed for calcium – about 80 mg \cdot dm⁻³, followed by sodium – about 11 mg \cdot dm⁻³. The concentration of magnesium was about 1.6 mg \cdot dm⁻³ and potassium about 0.5 mg · dm⁻³. Concerning inorganic nitrogen compounds, the highest concentration was observed for nitrates (about 13.5 mg \cdot dm⁻³), while for ammonium ions and nitrites the concentration was at the limit of quantification in both series of measurements. Half of these values were taken into account, that is, 0.065 mg \cdot dm⁻³ and 0.033 mg \cdot dm⁻³, respectively. The average iron concentration was 0.02 mg · dm⁻³. Among the microelements, only the concentrations of zinc and mercury differed from the limit of quantification. In the first case, the average of two series of measurements was 0.009 mg \cdot dm⁻³ and in the second case it was 0.00009 mg \cdot dm⁻³.

In the case of bacteria, no *Enterococci*, *C. per-fringens* or *P. aeruginosa* were observed. *E. coli* was equal to 9 cfu \cdot 100 mL⁻¹ in the second series of measurements. Increased values were recorded for two indicators: the total number of microorganisms at 22 ± 2°C and the total number of microorganisms at 36 ± 2°C. The results of the laboratory tests are shown in Table 1.

The results of chemical analyses confirm that the water is of good quality. The waters of this spring are of the bicarbonate-calcium type based on the Shchukaryev-Priklonski classification (Macioszczyk 1987). The percentage composition of dominant ions in the first measurement series was as follows: HCO₃⁻ (84.34%), Cl⁻ (8.41%), Ca^{2+} (89.03%), and in the second series $HCO_{2^{-}}$ (81.49%), Cl⁻ (9.89%), Ca²⁺ (83.73%), Na⁺ (11.56%). The values of sodium-potassium-chloride, sodium-potassium-magnesium-chloride and calcium-strontium hydrochemical indicators were, respectively, 0.70, 0.89 and 1408. This proves that the spring waters are not in contact with atmospheric waters. Additionally, the high value of the last weight index for calcium and strontium ions confirms the significant role of carbonate rocks in forming the chemical composition of the spring waters.

All physicochemical parameters meet the standards for drinking water in the case of national standards. However, if the EC values were related to WHO recommendations, in the case of the second measurement series the value exceeds the norm $(0.0400 \,\mathrm{S} \cdot \mathrm{m}^{-1})$. Some of the parameters such as aluminium, manganese, nickel, cadmium, copper, lead, chromium, Kjeldahl nitrogen, nitrites, ammonium ion and total organic carbon had contents below the limit of quantification. In Table 1, the values of these parameters are marked in italic font. Half of the quantification limit value was to be used for further analysis. Such good results of the quality of water contained in the spring in relation to the standards for drinking water and WHO standards mean that the Contamination Backman Index results were -13.80 and -13.43. For comparison, in the area of pollution sources, the values of this index may be >1000 (Karkocha 2021, Knopek, Dąbrowska 2021).

Referring the obtained results of chemical analyses to the standards for the first quality class, exceedances can be observed for calcium, bicarbonates and nitrates. In the case of the first ingredient, its deficiency in the body is much less beneficial than its excess. The increased concentration of nitrates in water poses a much greater danger. High levels of nitrate in water are a human health concern in the context that nitrate is classified as a probable human carcinogen (Darvishmotevalli et al. 2019). Despite the fact that the limit of nitrates in drinking water is set at 50 mg \cdot dm⁻³ (in the Polish regulation and by WHO standards), it should be noted that in various countries it is often lowered to 10 mg \cdot dm⁻³, as for first-class water quality. The situation is slightly different in the case of the bacteriological condition. Based on WHOrecommended and national standards, exceedances include the total number of microorganisms at 22 \pm 2°C, *E. coli* and the total number of

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Parameter	Unit	Nov 2023	Feb 2024	Relative difference RD [%]	Standard deviation SD	Standard error SE [%]	Limit ¹	Limit ²	Limit ³
Electrolytic conductivity EC	$S \cdot m^{-1}$	0.0359	0.0221	15.89	0.0043.84	31.00	2500	700	400
pH	[-]	7.13	6.95	2.56	0.13	0.09	6.5-8.5	6.5-8.5	6.5-8.5
Ca ²⁺	mg ⋅ dm ⁻³	81	82	0	2.33	1.65	80	50	
Mg ²⁺	mg ⋅ dm ⁻³	0.73	2.6	112.31	1.32	0.94	125	30	
Na ⁺	mg ⋅ dm ⁻³	9.7	13	29.07	0.00	0.00	200	60	
K+	mg ⋅ dm ⁻³	0.5	0.5	0	0.00	0.00		10	
HCO ₃ -	mg ⋅ dm ⁻³	198	201	1.50	2.12	1.50		200	
SO4 2-	mg ⋅ dm ⁻³	16	23	35.90	4.95	3.50	250	60	
Cl-	mg ⋅ dm ⁻³	23	28	19.61	3.54	2.50	250	60	200
NO ₃ -	mg ⋅ dm ⁻³	14	13	7.41	0.71	0.50	50	10	50
NO ₂ -	mg · dm⁻³	0.033	0.033	0	0.00	0.00	0.5	0.03	3
NH4 ⁺	mg ⋅ dm ⁻³	0.065	0.065	0	0.00	0.00	0.5	0.5	
PO, 3-	mg ⋅ dm ⁻³	0.081	0.068	17.45	0.01	0.01		0.5	
Fe ²⁺	mg ⋅ dm ⁻³	0.002	0.041	181.40	0.03	0.02	0.2	0.2	
Al ³⁺	mg · dm⁻³	0.005	0.005	0	0.00	0.00	0.2	0.1	
Mn ²⁺	mg ⋅ dm ⁻³	0.0005	0.0005	163.64	0.00	0.00	0.05	0.05	0.4
Ni ²⁺	mg · dm⁻³	0.002	0.002	0	0.00	0.00	0.002	0.005	0.07
Cu ²⁺	mg ⋅ dm ⁻³	0.002	0.002	0	0.00	0.00		0.01	2
Sr ²⁺	mg · dm⁻³	0.044	0.071	46.96	0.02	0.01			
Pb ²⁺	mg ⋅ dm ⁻³	0.002	0.002	0	0.00	0.00	0.01	0.01	0.01
Cd ²⁺	mg · dm⁻³	0.00025	0.00025	0	0.00	0.00	0.005	0.001	0.003
Cr ⁶⁺	mg ⋅ dm ⁻³	0.0015	0.0015	0	0.00	0.00	0.05	0.01	0.05
Hg ²⁺	mg ⋅ dm ⁻³	0.00005	0.00013	88.89	0.00	0.00	0.001	0.001	0.006
Zn ²⁺	mg ⋅ dm ⁻³	0.0025	0.016	145.95	0.01	0.01		0.05	
S ²⁻	mg ⋅ dm ⁻³	4.3	5	15.05	0.49	0.35			
Kjeldahl nitrogen	mg ⋅ dm ⁻³	2.5	2.5	0	0.00	0.00			1.5
TOC	mg ⋅ dm ⁻³	1	1	0	0.00	0.00		5	
Alkalinity	mg · dm ⁻³ CaCO ₃	162	164	1.23	1.41	1.00		-	
Coliform bacteria	cfu · 100 mL ⁻¹	0	0	0	0.00	0.00	0	-	0
Escherichia coli	cfu · 100 mL ⁻¹	0	9	200	6.36	4.50	0	-	0
Enterococci	cfu · 100 mL ⁻¹	0	0	0	0.00	0.00	0	-	0
Clostridium perfringens	cfu · 100 mL ⁻¹	0	0	0	0.00	0.00	0	-	0
Microorganisms at 22 ± 2 °C	cfu ∙ mL ⁻¹	>300	70	124.32	162.63	115.00	100	-	100
Pseudomonas aeruginosa	cfu \cdot 100 mL ⁻¹	0	0	0	0.00	0.00	0	-	0
Microorganisms at 36 ± 2 °C	cfu ∙ mL ⁻¹	13	12	8	0.71	0.50	20	-	20

¹Regulation of the Minister of Health of 07 December 2017 on the quality of water intended for human consumption. ²Regulation of the Minister of Maritime Economy and Inland Navigation of 11 October 2019 on the criteria and method of assessing the status of groundwater bodies.

³The Guidelines for drinking-water quality (GDWQ) proposed by WHO (2022), Harichandan et al. (2017).

* Italic font suggests half the value of the limit of quantification of a given parameter.

microorganisms at 36 ± 2°C. In the first measurement series, the total number of microorganisms at 22 \pm 2°C was over 300 cfu \cdot mL⁻¹. This is an indicator of the total number of bacteria cultured at 22°C for 72 h. These are psychrophilic organisms that die <0°C and >30°C, and develop best at 15°C. They are considered not to be a threat if their number does not >100. The total number of microorganisms in water at 36°C was also different from zero. This is an indicator of the total number of bacteria cultured at 36°C for 48 h. 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. It is considered that there is no danger of disease if the number of these bacteria does not >50 in 1 mL of water. Although the amounts of bacteria measured in the samples did not exceed the permissible standard, attention should be paid to this parameter in further measurements.

Faecal contamination of waters resulting from the discharge of raw sewage is a serious problem for human health and the environment (Arvizu, Murray 2021). Such contamination is evidenced by the presence of *E. coli* in water. In the second measurement series, the content of this indicator was 9 cfu · 100 mL⁻¹. An increased number of bacteria in water (even if it is recorded at a medium risk level) can lead to numerous diseases. E. coli most often leads to digestive system problems, but in people with weakened immunity it can lead to urosepsis, bacteraemia, meningitis and peritonitis (among others), with potentially severe outcomes including sepsis and death (Biran, Ron 2018, Hernandez-Pastor et al. 2023). Observations of this indicator are particularly important for springs from which water is collected, because E. coli can acquire resistance features through chromosomal mutations and mobile genetic elements (Petty et al. 2014).

Summary and conclusions

Springs located in close proximity to buildings or communication networks may be vulnerable to anthropogenic pressures due to inorganic contaminants or bacteriological threats. The results of physicochemical tests for the spring in Złoty Potok did not confirm an increased concentration of the measured parameters, which results from the exceptionally low value of the Contamination Index, but indicated the possibility of bacterial migration into the water. Bacteriological tests should be conducted for this type of water more often due to the possibility of drinking spring water, which in turn may lead to diseases and health hazards. This is especially important in the area of such a spring, which is located in a Natura 2000 area and should additionally be located in a non-threatened area.

The next step in the research will be periodic monitoring observation of selected water quality indicators, and trend analysis of changes in the quality of these waters.

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Author's contribution

D.D., M.R. – conceptualisation, D.D. – methodology, D.D. – software, D.D., M.R. – formal analysis, D.D. – investigation, D.D. – data curation, D.D., M.R., J.W. – writing – original draft preparation, D.D. – writing – review and editing, D.D., J.W. – visualisation. The authors declare no conflict of interest in this study. All authors have read and agreed to the published version of the manuscript.

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