Hydrochemical Types of Spring Waters in West Carpathian Catchments (Poland) under Different Pressure of Acidic Deposition

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Abstract: Springs are natural outflows of groundwater to the surface and are often the only places to gain insights into underground processes, especially in protected areas. Contact with rocks changes the parameters of water, especially its chemical composition, which can be easily expressed via hydrochemical typing using the Szczukariew–Priklonski classification. Knowledge of the distribution and chemical compositions of springs is essential for a good hydrological and hydrogeological understanding of a given area. In previous decades, underground water remained mostly uncontaminated, and the ions used in the Szczukariew–Priklonski classification, namely, Na⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻ and HCO₃⁻, provided accurate descriptions of this water. However, due to anthropogenic activity in the last decades, NO₃⁻ and NH₄⁺ ions in shares greater than 20% have been frequently noted in underground and spring water. Research has been conducted in two forested regions: within the Skrzyczne range, which is under pressure from high air pollution coming from the Ostrava and Upper Silesia industrial districts, and in Gorce National Park, which is impacted by low-level air pollution. Water samples were collected three times per year in 2011 and 2012 at various water levels after a spring snow thaw, a period of heavy rain and a dry period. A search for the following ions was conducted: Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, HCO₃⁻, SO₄²⁻, Cl⁻ and NO₃⁻. Under the Szczukariew–Priklonski classification system, due to the continuous accumulation of nitrogen compounds from air pollution, the shares of nitrates and ammonium ions in underground water and spring water are likely to increase.

Keywords: spring waters; hydrochemistry; nitrates; West Carpathians; Szczukariew–Priklonski classification

1. Introduction

Springs are natural and often the only way to gain insights into the processes occurring underground between water and bedrock. Knowledge of the distribution, efficiency, physical properties and chemical compositions of springs is essential for a good hydrological and hydrogeological understanding of a given area [1]. Geological processes are the main influences on spring water chemistry [2–4]. As a result of infiltration and circulation in deeper layers, water changes its chemical composition while interacting with various geological formations [5,6]. In order to discuss the chemistry of spring water in Poland, a hydrochemical classification system, namely, the Szczukariew–Priklonski classification scheme, is often used [7–11]. It is based on the assumption that the hydrochemical typing of natural waters depends on ions occurring in amounts not less than 20% mval L⁻¹ in relation to the sum of the anions or the sum of the cations. This classification divides water into 49 classes according to the proportions of six main ions present. In previous decades, underground water remained mostly uncontaminated, and the ions considered in the Szczukariew–Priklonski classification, i.e., Ca²⁺, Mg²⁺,
Na\(^+\), HCO\(_3\)^\(-\), SO\(_4^{2-}\) and Cl\(^-\), were able to provide accurate structures for underground water. However, in recent years, due to anthropogenic activity, NO\(_3^\) and NH\(_4^+\) in shares greater than 20% have been noted frequently in underground and spring water [3,12], preventing the Szczukariew–Prikłonski classification system from providing accurate water structures. Another factor influencing ground and surface water chemistry is precipitation, especially when acidic compounds are present. Since the middle of the 20th century, due to rapid industrialization, nitrogen and sulfur deposition have increased, respectively, five- and seven-fold [13]. This acidic deposition has influenced the water chemistry in Europe [14–17] and North America [18,19]. Changes in water chemistry are visible not only close to the source of emission but also in the forest catchments in protected areas without any sources of emission [17]. Plant cover, and especially forests, can also influence water chemistry, but highly acidic compounds can affect forests and are the main contributors to spruce stand decay, which has been observed since the 1970s in Central Europe [14,15,20,21]. There is a growing concern about the proper functioning of ecosystems in Europe (including in the Western Carpathians) due to the increasing nitrogen deposition, and its effects in the future will be higher than sulphur deposition due to strong nitrogen retention in forests [22,23].

In this study, the following research hypothesis was tested: the hydrochemical nature of spring water was modified by high-pressure acidic compounds and the vegetation cover in an alimentation area when the geological structure was homogeneous (Carpathian flysch). The aim of this study was to analyze the hydrochemical diversity of spring water in the research area in relation to the changes occurring in the environment, especially high acidic deposition.

2. Material and Methods

2.1. Research Area

The springs in this study were located in two forested regions: the first region was the Skrzyczne (1257 m a. s. l.) range (49°39′56″–49°42′01″ N, 18°59′59″–19°04′01″ E), and the second region was on the slope between Jaworzyna Kamienicka (1288 m a. s. l.) and Gorc (1228 m a. s. l.) in Gorce National Park (49°32′33″–49°33′39″ N, 20°10′13″–20°14′35″ E). Hence, both research areas were located in the Western Carpathians (Figure 1) in Poland. The Skrzyczne range is under high pressure from air pollution coming from the Ostrava and Upper Silesia industrial districts, and its forests are managed on a regular basis, which includes logging. Gorce National Park experiences lower pressure from air pollutants. The analyzed catchments is a build of rock composed of alternating layers of sandstone and shale, called the Carpathian flysch. Aquifer in the Carpathians is characterized by thick sediment complexes, where sandstones make up the largest share, and is limited essentially to the sur-face zone heavily cracked and weathered to a depth of 60–80 m [7]. The springs in these regions are part of the Carpathian flysch area, and they are supplied via shallow water circulation; their efficiency usually does not exceed 0.1 L·s\(^-1\). Their efficiency rates and their chemical compositions respond quickly to precipitation [24,25]. Both research areas have been affected by spruce stand dieback but at different intensities (Figure 2).

The springs were chosen so that the field work (sampling and measurements of physicochemical parameters in the field) could be performed in the shortest possible time (during stable meteorological conditions).
After a spring was located, it was assigned a number, its coordinates were recorded (MobileMapper 6 GPS receiver) and it was added to the digital map. A water sample was taken from each spring with a 120 mL polyethylene bottle. The number of springs from which samples were taken varied depending on the degree of hydration of the massif. Water sampling from the springs was carried out in six measurement sessions lasting 2–3 days in 2011 and 2012. Sessions I (after snowmelt 2011), II (after summer rainfall 2011) and IV (after snowmelt in 2012) were conducted in high water levels, and sessions III (after dry period in 2011), V and VI (both after dry period in 2012) were conducted in low water levels. The first measurement session in 2011 involved the maximum number of springs. After the snowmelt, 146 springs in the Gorce National Park catchment and 92 springs in the Skrzyczne range were sampled. In terms of minimum counts, in October 2011, only 68 samples were collected in the Skrzyczne range, and, in October 2012, in Gorce National Park, samples were taken from just 58 springs (Table 1).
### Table 1. Number of springs with particular hydrochemical types of water in the measurement sessions.

| Class No. | Hydrochemical Type (Szczukariew–Priklonski Classification) | Gorce National Park | Skrzyczne Range |
|-----------|---------------------------------------------------------------|--------------------|-----------------|
|           |                                                               | Session            | Session         |
|           |                                                               | Number of Samples  | Number of Samples |
|           |                                                               | (H) (L) (L) (H)   | (H) (L) (L) (H) |
| 6         | \( \text{SO}_4^{2-} \cdot \text{Ca}^{2+} \)                  | 146               | 82              |
| 9         | \( \text{HCO}_3^- \cdot \text{Ca}^{2+} \)                    | 131               | 79              |
| 14        | \( \text{SO}_4^{2-} \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 101               | 68              |
| 15        | \( \text{SO}_4^{2-} \cdot \text{Mg}^{2+} \cdot \text{Ca}^{2+} \) | 115               | 67              |
| 17        | \( \text{HCO}_3^- \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \)   | 71                | 45              |
| 18        | \( \text{HCO}_3^- \cdot \text{Mg}^{2+} \cdot \text{Ca}^{2+} \) | 58                | 26              |
| 21        | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot \text{Ca}^{2+} \)   | 92                | 36              |
| 27        | \( \text{SO}_4^{2-} \cdot \text{HCO}_3^- \cdot \text{Ca}^{2+} \) | 146               | 102             |
| 30        | \( \text{HCO}_3^- \cdot \text{Mg}^{2+} \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 131               | 101             |
| 38        | \( \text{SO}_4^{2-} \cdot \text{HCO}_3^- \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 101               | 71              |
| 39        | \( \text{SO}_4^{2-} \cdot \text{HCO}_3^- \cdot \text{Mg}^{2+} \cdot \text{Ca}^{2+} \) | 115               | 82              |
| 43        | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot \text{Na}^+ \cdot \text{Mg}^{2+} \cdot \text{Ca}^{2+} \) | 71                | 45              |
| 48        | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot \text{HCO}_3^- \cdot \text{Mg}^{2+} \cdot \text{Ca}^{2+} \) | 45                | 26              |
|           | \( \text{HCO}_3^- \cdot (\text{NO}_3^-) \cdot \text{Ca}^{2+} \) | 36                | 18              |
|           | \( \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{Mg}^{2+} \cdot \text{Ca}^{2+} \) | 22                | 17              |
|           | \( \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 19                | 17              |
|           | \( \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{Mg}^{2+} \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 10                | 8               |
|           | \( \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{NH}_4^+ \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 9                 | 8               |
|           | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{Na}^+ \cdot \text{Mg}^{2+} \cdot \text{Ca}^{2+} \) | 4                 | 2               |
|           | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{Mg}^{2+} \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 3                 | 2               |
|           | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{NH}_4^+ \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 2                 | 1               |
|           | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{NH}_4^+ \cdot \text{Mg}^{2+} \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 1                 | 1               |
|           | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{NH}_4^+ \cdot \text{Mg}^{2+} \cdot \text{Na}^+ \cdot \text{Ca}^{2+} \) | 1                 | 1               |
|           | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{NH}_4^+ \cdot \text{Mg}^{2+} \cdot \text{Ca}^{2+} \) | 1                 | 1               |
|           | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{NH}_4^+ \cdot \text{Ca}^{2+} \) | 1                 | 1               |
|           | \( \text{Cl} \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{Ca}^{2+} \) | 1                 | 1               |

Roman numbers refer to the sampling session and the arabic numbers to the number of springs sampled (H)-high water level, (L)-low water level.

### 2.3. Analysis

The water samples were then placed in a refrigerator and transported to the Laboratory for Geochemistry of Forest Environment and Areas Intended for Reclamation. In the laboratory, the water samples were filtered through a membrane (0.45 μm), and their chemical compositions (\( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{NH}_4^+ \), \( \text{HCO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{Cl}^- \) and \( \text{NO}_3^- \)) were determined by ion chromatography using a Dionex-5000 chromatograph. The analysis of samples were started within 24 h of being brought to the laboratory. The chromatographic system was calibrated using the Dionex series of multicomponent standards (Dionex Seven Anion Standard II, and Dionex Six Cation Standard II). The results of the analyses were verified by comparing the obtained values with a Canadian water standard (LETHBRIDG-03) of known ionic composition [26]. The basic hydrochemical typing of the outflows in both catchment areas was conducted based on the concentrations of their main cations and anions. Next, all samples were assigned a Szczukariew–Priklonski classification [7]. Ions with shares of more than 20% mval·L\(^{-1}\) not included in the Szczukariew–Priklonski classification were recorded in brackets. For example, the classification \( \text{HCO}_3^- \cdot \text{SO}_4^{2-} \cdot (\text{NO}_3^-) \cdot \text{Ca}^{2+} \) indicates that the water was enriched with nitrate. A graphical presentation of the results was created using QGIS 2.8.2 software.
3. Results and Discussion

In the Gorce, according to their Szczukariew–Priklonski classifications, most of the springs belonged to classes 9 and 18 (Table 1), i.e., they had above 20% shares of $\text{HCO}_3^-$ within the anions and $\text{Ca}^{2+}$ or $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ within the cations. The next most common component in these springs was $\text{SO}_4^{2-}$, which was observed during measurement sessions I and II, in particular. There were also 35 samples in total that contained nitrate ions in shares above 20%. These samples were collected during the high-water sessions (sessions I, II and IV) (Table 1). Fourteen springs with shares of nitrate ions above 20% in the anions were found in each of sessions I and II, while, in session IV, seven springs had the same composition trait. In the Gorce Mountains, the percentage of $\text{NO}_3^-$ found in the samples increased markedly after the snowmelt and precipitation periods: the mean value of the $\text{NO}_3^-$ share rose from about 1% to about 3% (Figure 3).

![Figure 3](image)

**Figure 3.** Distribution of the hydrochemical types of water in the Jaszcze and Jamne catchments in Gorce National Park at high (May 2011) and low water levels (October 2012).

In the Skrzyczne range, there were 12 traditional Szczukariwe–Priklonski classes distinguished and 14 classes with shares of $\text{NO}_3^-$ or $\text{NH}_4^+$ ions above 20%. The most common ions deciding about hydrochemical type of a sample were $\text{SO}_4^{2-}$, $\text{HCO}_3^-$, $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$. These four ions were enough to classify 406 samples. In nine springs, the $\text{Cl}^-$ and $\text{Na}^+$ concentrations were significant (above the 20% threshold). $\text{NO}_3^-$ or $\text{NH}_4^+$ ions making up shares greater than 20% were found in 90 samples in total, with the lowest number found in session III, when many springs characterized by high nitrate or ammonium ions concentrations had dried up. The rest of the sessions did not exhibit any clear tendencies (Table 1, Figure 4).
The chemical structure of spring water in Gorce is much more consistent than in the Skrzyczne range (Figure 5), with prevailing ratio of HCO$_3^-$, Ca$^{2+}$ and Mg$^{2+}$ ions. In comparison, the chemical structure of spring water in the Skrzyczne range is characterized by greater ratio of ions such as SO$_4^{2-}$, Cl$^-$, NO$_3^-$, Na$^+$, K$^+$ and NH$_4^+$. Additionally, in Gorce about one third of the samples remained almost uncontaminated (NO$_3^-$ ions in share lower than 0.5% of all ions), while in the Skrzyczne range there were only several such samples.

![Figure 4](image1.png)  
**Figure 4.** Distribution of the hydrochemical types of water in the Skrzyczne range at high (May 2011) and low water levels (October 2012).

![Figure 5](image2.png)  
**Figure 5.** Chemical structure of spring waters in the Gorce National Park and Skrzyczne range with the distinguished samples of close to 0 nitrates concentration (modified Ludwig-Langerier diagram).
The hydrogeochemical type that dominated on the Skrzyczne range, i.e., \( \text{SO}_4^{2-}\text{-HCO}_3^-\text{-Ca}^{2+} \), is described by Kostrakiewicz [27] as appropriate for sandstone, shales and conglomerates of godula layers. Underground waters of this type have also been found in Bystra [27], the Potok Dupniański catchment [28], the Nydek-Strelma spring [29], the Pieniny [1] and the Bieszczady Mountains [30]. The other hydrochemical types of spring waters in the Skrzyczne range, namely, \( \text{SO}_4^{2-}\text{-HCO}_3^-\text{-Mg}^{2+}\text{-Ca}^{2+} \), \( \text{SO}_4^{2-}\text{-Ca}^{2+} \) and \( \text{HCO}_3^-\text{-Ca}^{2+} \), are typical representatives of the upper hydrogeochemical zone of the Polish Carpathians [31]. Due to their strictly local occurrences, the high shares of \( \text{Na}^+ \) and \( \text{Cl}^- \) in several springs are probably connected to the presence of geological inserts containing easily weathering \( \text{Na}^+ \) and \( \text{Cl}^- \) components. Two samples with share of \( \text{Ca}^{2+} \) lower than 20% were noted, resulting in presence of hydrochemical types \( \text{SO}_4^{2-}\text{-Mg}^{2+}\text{-}\text{(NH}_4^+\text{)} \) and \( \text{SO}_4^{2-}\text{-HCO}_3^-\text{-Mg}^{2+}\text{-}\text{(NH}_4^+\text{)} \). Both of them were collected from the same spring, which was located in the Malinowska Skala conglomerates. The number of samples containing significant amounts of nitrogen, as well as their constant presence throughout the measuring sessions and Skrzyczne research site, reveals that alarming amounts of air pollutants have already accumulated in the ecosystem [18,32].

In the Jaszcze and Jamne catchments in Gorce National Park, water with a high concentration of nitrate ions was found in the north-western part of the Jaszcze catchment. This part of the catchment is dominated by decayed spruce stands in a subalpine forest zone (Figure 2). In the Jaszcze catchment, all measurement sessions (Table 1) were dominated by water containing \( \text{HCO}_3^-\text{-Ca}^{2+} \), \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) (numbers 9 and 18 in the Szczukariew-Priklonski classification system). These same ions were noted in the Bieszczady Mountains, and are often considered as the hydrogeochemical background for the flysch Carpathians [7,30,31]. The lowest diversity in the water samples was recorded in the V measurement session (Figure 3—low water level). Only three hydrochemical types of water were distinguished (numbers 9, 17 and 18, according to the Szczukariew-Priklonski classification), although type 17 (\( \text{HCO}_3^-\text{-Ca}^{2+}\text{-Na}^+ \)) was found in one spring only (Figure 3, Table 1). The hydrochemical types occurring after snowmelt and precipitation (sessions I, II and IV) containing nitrates, i.e., \( \text{HCO}_3^-\text{-}(\text{NO}_3^-\text{-}\text{Ca}^{2+}) \), \( \text{HCO}_3^-\text{-SO}_4^{2-}\text{-}(\text{NO}_3^-\text{-}\text{Ca}^{2+}) \), \( \text{HCO}_3^-\text{-SO}_4^{2-}\text{-}\text{Ca}^{2+}\text{-Mg}^{2+} \) and \( \text{SO}_4^{2-}\text{-}(\text{NO}_3^-\text{-}\text{Ca}^{2+}) \), were mainly located in the north-western part of the Jaszcze catchment, where the decomposition of organic matter due to spruce stands dieback was observed. The fluxes of nitrate, ammonium and sulfate ions in the forested catchments where spruce dominated were about twice as high as those found when beech dominated [33,34]. The shares of nitrate ions in the chemical compositions in the Gorce National Park catchments were so high that they formed as many as five “new hydrochemical types” not included in the Szczukariew-Priklonski classification. The share of nitrates increased significantly after snow melted and precipitation, which indicates that they were leaching from vegetation and soil as well as part of the inflow from the snow and precipitation [35]. The phenomena of nitrogen uptake by vegetation and its increased outflow after intense precipitation was explained by Weiner [36]. A similar situation was observed in the Silesian Beskids Mountains, where the entry of nitrate ions into the hydrochemical types of water was explained by the constant high nitrogen deposition in the second half of the 20th century and its systematic leaching from forest ecosystems [32,37]. Major changes in the hydrochemical types of water occurred in the upper part of Gorce National Park where spruce stands had decayed, and they were most visible in periods of precipitation and snowmelt. A similar effect has been observed in agricultural catchments [38,39]. Due to the continuous accumulation of nitrogen compounds from air pollution in ecosystems [19], the share of nitrates and ammonium ions in underground and spring water is likely to continue to increase in the future.
4. Summary and Conclusions

1. Both research areas had hydrochemical backgrounds typical for their geological structures, with prevailing HCO$_3^-$, Mg$^{2+}$ and Ca$^{2+}$ ions in Gorce National Park (497 samples belonged to types 9 and 18 from the Szczukariew–Priklonski classification) and SO$_4^{2-}$, HCO$_3^-$, Mg$^{2+}$ and Ca$^{2+}$ in the Skrzyczne range area (359 samples belonging to types 27 and 39). The concentration of SO$_4^{2-}$ ions in the Gorce National Park area increased after precipitation, which indicated its external origin.

2. The hydrochemical types were more diverse in the Skrzyczne range area (26 types), which is the result of collecting samples from different slopes, while in the Gorce National Park catchments, samples were collected from just one slope, making the results more homogenous (11 types).

3. Both in the Skrzyczne range and in Gorce National Park, hydrochemical types with a Na$^+$ component were noted for several springs and were considered to be the result of inserts in the geological structure. A similar explanation was provided for the Cl$^-$ components found in several springs in the Skrzyczne range.

4. The Gorce National Park studied catchment area seems to be more resistant to the eutrophication caused by air pollutants, as the NO$_3^-$ ions affected the spring water chemistry only after precipitation periods and in the proximity of the spruce stands dieback area, while springs on the Skrzyczne range contained noticeable NO$_3^-$ ion concentrations regardless of the precipitation inflow, even beyond the spruce dieback area, where the nitrates could be washed out of spruce remains.

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