SYLWAN 165 (12): 824-840, December 2021
https://doi.org/10.26202/sylwan.2021093
Journal homepage: https://sylwan.lasy.gov.pl

ORIGINAL PAPER

Hydrochemical characteristics of spring water from selected catchments of the Forest Experimental Station in Krynica-Zdrój (Poland)

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ABSTRACT

The study investigated the differentiation of hydrochemical spring water types in the forest catchments located in the buffer zone of the Krynica-Zdrój health resort, and the influence of environmental factors such as soil, precipitation, and tree species composition on this diversity. The research was carried out from 2014-2016 in the Beskid Sądecki mountains within the Jaworzyna Krynicka range (1114 m a.s.l.) and covered the catchments of the right-bank tributaries of the Kryniczanka stream. Twenty-eight permanent springs located in the lower mountain areas (548-1003 m a.s.l.) were selected for the study. In monthly samples taken, the pH, electrical conductivity, and the content of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Li^{+}, NH_4^{+}) and anions (F^{-}, Cl^{-}, NO_2^{-}, Br^{-}, NO_3^{-}, PO_4^{3-}, SO_4^{2-}, HCO_3^{-}) were obtained via ion chromatography (Dionex-5000 chromatograph). Water from each investigated spring was classified to be a specific type according to the Altowski-Szwiec classification, and the appropriate hydrochemical class was assigned according to the Szczukariew-Prikłoński classification. The mean ion concentrations in the spring water samples indicated the presence of 4 main hydrochemical types: class 39 (HCO_3^{-}-SO_4^{2-}-Ca^{2+}-Mg^{2+} and Ca^{2+}-Mg^{2+}-HCO_3^{-}-SO_4^{2-}), class 18 (HCO_3^{-}-Ca^{2+}-Mg^{2+} and Ca^{2+}-Mg^{2+}-HCO_3^{-}), class 27 (Ca^{2+}-HCO_3^{-}-SO_4^{2-} and Ca^{2+}-SO_4^{2-}-HCO_3^{-}) and class 9 (Ca^{2+}-HCO_3^{-}), which are typical for the Carpathian flysch geological substrate. It was also found that the springs located in the Kryniczanka stream catchment area, covered with forest in which forest management is carried out, are characterized by a stable chemical composition. These springs very rarely showed a higher concentration of pollutants in the form of nitrates.

KEY WORDS

Beskids Mts., forest catchments, spring waters, water chemistry, environmental features.

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Received: 1 October 2021; Revised: 16 January 2022; Accepted: 20 January 2022; Available online: 22 March 2022

Introduction

Water plays an important role in environmental processes. As it falls in the form of precipitation, it penetrates vegetation, soil layers and rocks. As a result of water-plant-rock interactions, it becomes enriched with chemical components before supplying groundwater reservoirs (Ciężkowski, 2007). Flowing out in the form of springs, it fills surface watercourses. Knowledge of the distribution and nature of springs is one of the most important factors in the study of the hydrological and hydrogeological conditions of a given area (Jokiel, 1997), because these springs form a 'keyhole' for the groundwater. When conducting research on forest ecosystems, the quantity and quality of water circulating in them is a very important consideration (Humnicki, 2007).

The physicochemical properties of springs are a measure of the quality of the groundwater supplying them in a specific area. The quality of normal groundwater has a direct impact on the chemistry of mineral and healing waters (Ciężkowski, 2007; Józefko *et al.*, 2013; Nowicki and Felter, 2013; Gągulski, 2014). This fact is of great importance in spa buffer zones, where balneology is based on local resources.

The main factor influencing the chemistry of spring water is geological structure (Paczyński and Sadurski, 2007; Żelazny *et al.*, 2013), although the amount (Buczyński *et al.*, 2007; Astel *et al.*, 2009; Małek and Krakowian, 2009; Wójcik, 2012) and chemical composition of water supplied to the environment, along with rainfall, are also important (Kosmowska *et al.*, 2015; Malata and Motyka, 2015; Jasik *et al.* 2020). In many areas, rainfall is polluted with nitrogen and sulfur compounds due to human activity, which then penetrate into the groundwater, causing changes in its composition. This effect, among others, was investigated in the Silesian Beskids and the Świętokrzyski National Park (Małek and Krakowian, 2009; Małek *et al.*, 2010; Kosmowska, 2016; Jasik *et al.*, 2017) which are subjected to industrial emissions, as well as in Gorczański, Tatrzański and Babiogórski National Parks (Malata, 2015; Żelazny, 2017; Siwek and Żelazny, 2019; Jasik *et al.*, 2020).

Another factor influencing the hydrochemical parameters of spring water is the vegetation cover of the supply area (Kosmowska *et al.*, 2015; Malata, 2015). Forest cover reduces fluctuations in water chemistry and improves its quality, although the species composition of the forest does influence the physicochemical properties of spring water (Małek *et al.*, 2010; Jasik *et al.*, 2017). To date, research undertaken in the Polish mountains has concerned mainly in protected areas such as national parks and nature reserves. A question thus arises, as to how the physicochemical characteristics of springs are shaped in managed forests. The following research hypothesis was adopted in this study: environmental factors such as the amount of precipitation, soil type, species composition of stands covering the alimentation reservoir, and man-made forest management, influence the differentiation of hydrochemical spring water types. The aim of the study was to characterize the hydrochemical characteristics of the spring water in a catchment area covered with good condition lower montane forests, managed in a manner typical of mountain areas, in the buffer zone of a health resort (SPA) on the Carpathian flysch substrate.

Material and methods

STUDY SITE. The research was carried out from 2013-2016 in the Beskid Sądecki and Jaworzyna Krynicka mountain ranges, 1114 meters above sea levels (m a.s.l.). This area included the following catchments of the right-bank tributaries of the Kryniczanka stream: Czarny Potok, with an area of 14.37 km^2; Pastewnik stream, with an area of 1.84 km^2; Halny stream, with an area of

1.17 km^2; and the north-eastern slopes of the Smreczyna mountain, with an area of 0.56 km^2. (Oszczypko *et al.*, 1999). The research area is owned by the University of Agriculture in Krakow and is in the Krynica Wieś and Jaworzyna forests – part of the Forest Experimental Station at Krynica-Zdrój (Fig. 1). The catchments belong to the 3rd sanitary protection zone for the Krynica--Zdrój Health Resort.

Since 1856, the Krynica-Zdrój Health Resort has been conducting sanatorium activities based on the underground water deposits. The unique composition of this water is used for drinking therapy, inhalation therapy, treatments in the form of mineral and carbonic acid baths, and the production of bottled water (Porwisz, 2013).

The Carpathian flysch is the geological basis of Beskid Sądecki; this heterogeneous sedimentary rock is composed of alternating layers of sandstone and clay shale. The study area is in the south-eastern part of the Magura Nappe, the Krynica facies and the Zarzecka and Magura formations (Oszczypko *et al.*, 1999).

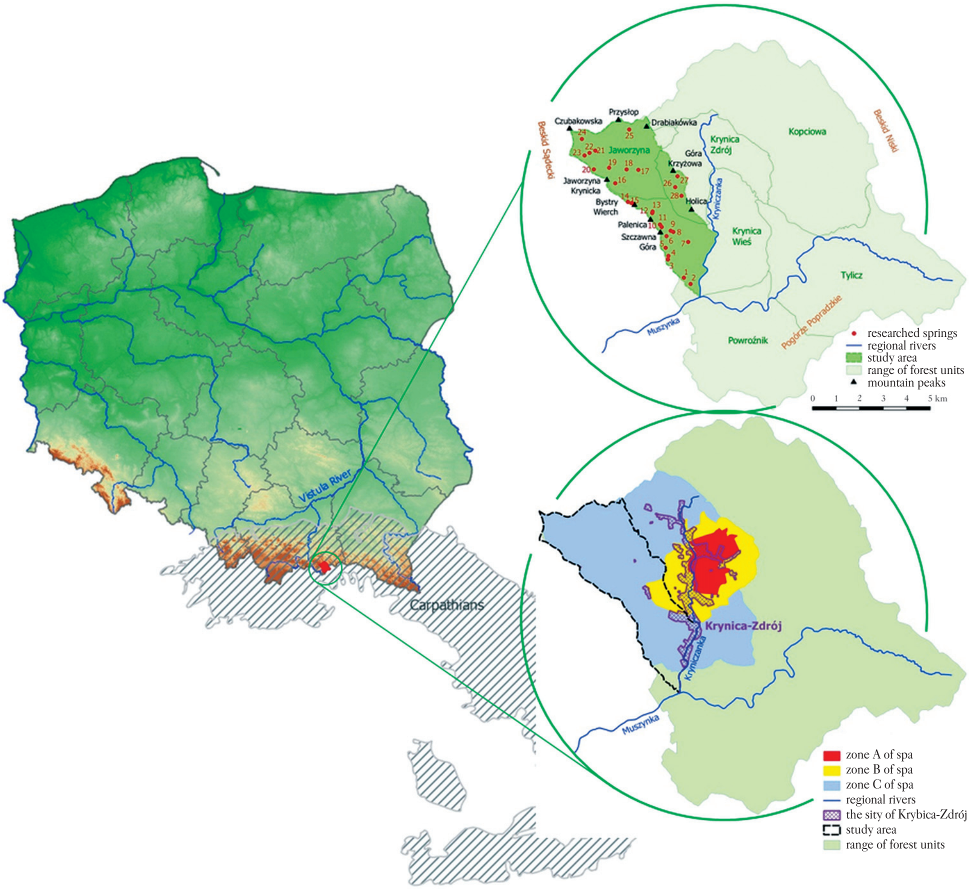

Fig. 1.

Location of the research area

Zone A – the area where spa treatment facilities are located or planned; zone B – the area of non-burdensome service and tourist facilities for people staying in the spa; zone C – the area influencing the preservation of landscape and climate values and the protection of natural healing resources

The formations bearing the most water are the thick-layered, porous and fractured Magura sandstones and Krynica sandstones, which cover the entire Czarny Potok catchment (Oszczypko *et al*., 1981; Gągulski, 2014). Groundwater reservoirs in the Magura sandstones consist of a complex network of fissures and cracks; therefore, they are characterized by a large underground outflow with a low filtration coefficient value (Buczyński *et al*., 2007). The area is within reach of the main groundwater reservoir (Magura-Nowy Sącz GZWP 438). This pore-fracture reservoir is associated with the Tertiary formations (BULiGL w Krakowie, 2017). The crenological coefficient for the Kryniczanka stream catchment area in the valley of Krynica-Zdrój is 10.1 springs/km^2 (Porwisz, 2013).

All researched springs are located in the lower mountain areas at altitudes ranging from 548 m a.s.l. (spring no. 2) up to 1003 m a.s.l. (spring no. 20). The plant communities covering the study area consist of almost 100% Carpathian beech *Dentario glandulosae-Fagetum*, with a dominance of beech at higher altitudes and fir in the lower areas. The peaks are covered by spruce forest, and

Table 1.

Characteristics of the supply area of the studied springs

Spring no.	Location altitude [m a.s.l.]	Tree stand composition	Stand age	Geology	Soil texture	Soil unit
1	637	7Fs3Ps	60	T3	SL	DC
2	548	5Ps2PaLdAiFe	65	T3	SL	DC
3	623	10Fs	55	T3	LS	DC
4	629	10Fs	55	T3	LS	DC
5	659	8Ps2Pa	80	T3	SL	DC
6	701	8Pa2Ps	85	T3	SL	DC
7	593	5Ps3FsLdPa	70	T3	SL	DC
8	659	7Aa2PaFs	105	T4	SL	DC
9	670	6Aa2Pa2Fs	110	T4	SL	DC
10	688	6Aa3LdPaFs	100	T4	SL	DC
11	682	5Aa3Pa2Fs	100	T4	SL	DC
12	728	7Fs2PaAa	100	T4	SL	DC
13	701	6Pa2FsPsAa	80	T4	SL/LS	DC/EC
14	802	7Fs3Ps	70	T4	SL/LS	DC/EC
15	763	9FsPa	100	T4	SL/LS	DC/EC
16	958	7Pa3Fs	60	T4	SL/L	DC/DEL
17	834	5Fs4LdPa	60	T4	SL	DC
18	890	7Fs2AaPa	110	T4	LS	DC
19	881	6Fs3PaAa	80	T4	SL	DC
20	1003	6Pa3FsLd	55	T4	SL	DC
21	951	5Fs4AaPa	65	T4	SL	DC
22	957	5Fs5Pa	80	T4	SL	DC
23	991	7Pa3Fs	65	T4	SL	DC
24	982	10Fs	60	T4	LS	DBC/AP
25	825	5Fs4AaPa	75	T4	LS	DC
26	670	6Pa3FsPs	70	T4	LS	DC
27	757	8Ps2Pa	65	T4	SL	DC
28	700	7PsLdPaFs	65	T4	LS	DC

Fs – *Fagus sylvatica* L., Ps – *Pinus sylvestris* L., Pa – *Picea abies* (L.) H. Karst., Aa – *Abies alba* Mill., Ld – *Larix decidua* Mill., Ai – *Alnus incana* (L.) Moench, Fe – *Fraxinus excelsior* L., T3 – thin-bedded sandstones and Zarzecka slate, T4 – thick-bedded sandstones and shales from Piwniczna, SL – sandy loam, LS – loamy sand, SC – sandy clay loam, L – loam, DC – Dystric Cambisol, EC – Eutric/Epidystric Cambisol, DBA – Dystric Brunic Arenosols, AP – Albic Podzol, DEL – Dystric Eutric Leptosols (27) the lowest parts feature pine and larch stands (BULiGL w Krakowie, 2017) (Table 2, Fig. 2).

The whole area is located far away from urban agglomerations and major industrial pollution emission centers.

Field work. Twenty-eight natural outflows (springs) were selected for the study, according to the following criteria:

– each spring represented the outflow of groundwater to the ground surface at the beginning of a permanent watercourse,
– the outflows were evenly spread out throughout the study area, making it is possible to take samples or measurements over a one-day period (Fig. 2).

Samples were collected at monthly intervals on the last or penultimate day of the month from March 2014 to March 2016. The sampling sites were marked with Arabic numbers in the field, and the geographical coordinates were measured with a GARMIN Montana 600 device. The temperature of the water flowing from the springs was measured with an electronic thermometer across 8 measurement sessions during the collection of samples for physicochemical tests. The water was drawn into 120 ml polyethylene bottles and refrigerated immediately after collection.

Laboratory analysis. The collected water samples were delivered to the Laboratory of Forest Environment Geochemistry and Areas Intended for Reclamation, Department of Ecology and

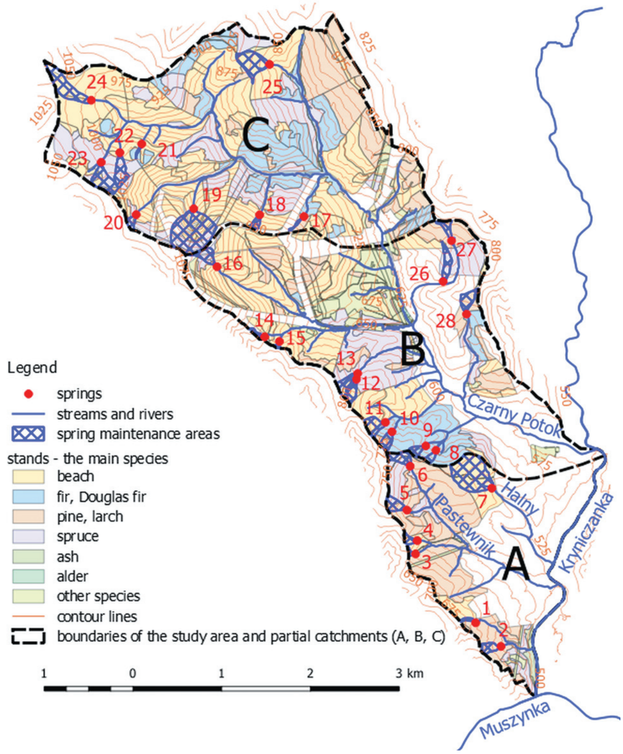

Fig. 2.

The location of the springs and the range of their alimentation areas against the forest stand map of the Experimental Plant in Krynica-Zdrój

Silviculture, Faculty of Forestry, University of Agriculture in Krakow. In the laboratory, water samples were filtered through a membrane (0.45 µm) and their pH, electrical conductivity (EC) (multifunction meter – Elmetron CX-705) and concentrations of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Li^{+}, NH_4^{+}) and anions (F^{-}, Cl^{-}, NO_2^{-}, Br^{-}, NO_3^{-}, PO_4^{3-}, SO_4^{2-}, HCO_3^{-}) were obtained via ion chromatography (Dionex-5000 chromatograph). The chemical analyses were validated in accordance with the PN-89 C-04638/02 standard.

The percentage composition (mEq L^{-1}) of the basic anions and cations in relation to the sums of the anions and cations, respectively, were calculated. Then the water from each investigated spring was classified according to type via the Altowski-Szwiec classification method (Kleczkowski, 1979) and placed in the appropriate hydrochemical class based on the Szczukariew-Prikłoński classification scheme (Macioszczyk, 1987). In accordance with the above-mentioned classifications, it was assumed that the ions present in proportions of not less than 20% mEq · L^{-1} in relation to the sum of the cations or the sum of the anions, had a decisive influence on the chemical nature of water. The class names assigned to the water samples began with the ion with the highest content, regardless of whether it was a cation or an anion (see Altowski-Szwiec classification). For example, if three- and four-ion water samples had an anion as the main ion, then the anions were listed sequentially in the name, followed by the cations.

The maintenance reservoirs for the springs were drawn based on a numerical terrain model (1 m pixels – from the database of the Central Geodetic and Cartographic Documentation Center) and surface runoff. The SAGA 7.0.0 and QGIS 3.9.0-Zanzibar programs were used in their development.

Based on the numerical maps (Forest Numerical Map of LZD Krynica) of the Forest Management Plan for the Experimental Plant in Krynica-Zdrój, the following information was determined for these maintenance reservoirs: m a.s.l., soil type as well as the species and type, forest habitat type, species composition, and the age of the stands covering them (Table 1).

Considering the geological basis (soil type), m a.s.l. and the depths of the spring supply, the study area was divided into three sub-catchments: A, B and C, which resulted in three groups of springs under similar conditions (Table 2).

Sub-catchment A (the Pastewnik stream) contained springs no. 1-7, which all had shallow feeds and were located in the lower part of the study area at 548-701 m a.s.l. These springs were on the northeastern slopes of Szczawna Góra (781 m a.s.l.) in thin-bedded sandstones and Zarzecka slate. Until the 1950s, the area was used for agriculture. Currently, the area is covered with pre-crop stands of spruce and pine with many beech and fir saplings, or beech forests representing the second-generation forest on this post-agricultural land (Table 2) (BULiGL w Krakowie, 2017).

Sub-catchment B (the lower part of the Czarny Potok) contained springs no. 8-16 and 26-28, which were situated at altitudes of 659-958 m a.s.l. and found on the northeastern slopes of the Palenica (807 m a.s.l.) and Bystry Wierch (827 m a.s.l.) mountains. These springs have shallow supply. The supply areas consist of thick-bedded sandstone and slate from Piwniczna and are covered with mature fir and beech stands, as well as maturing spruce and pine stands (Table 2) (BULiGL w Krakowie, 2017).

Sub-catchment C (the upper part of the Czarny Potok) contained springs no. 17-25, which were located at altitudes of 825-1003 m a.s.l. on the northern and northeastern slopes of Jaworzyna Krynicka (1114 m a.s.l.), Bukowa (1077 m a.s.l.) and the Czubakowska (1082 m a.s.l.) mountains, in thick-bedded sandstones and shales from Piwniczna (T4). They have deep supply and the fluctuations in water temperature across all seasons do not exceed 2-3°C. This sub-

Table 2.
Characteristics of the sub-catchment areas designated in the study area

Spring no.	Sub-catchment	Water type according to Altowski-Szwiec	Water class according to Szczukariew-Prikłoński	EC (spring)	pH (spring)	pH (sub-catchment)	Spring altitude [m]	Sub-catchment altitude [m]	Water temp. amplitude [°C]	Average water temp. amplitude [°C]
1		HCO_3-Ca-Mg	18	284	7.79		637		7.4	
2		HCO_3-SO_4-Ca-Mg	39	279	7.71		548		10.3	
3		HCO_3-Ca-Mg	18	309	7.86		623		9.6	
4	A	HCO_3-Ca-Mg	18	315	7.86	7.76	629	627	8.9	9.4
5		HCO_3-SO_4-Ca-Mg	39	296	7.83		659		11.9	
6		HCO_3-SO_4-Ca-Mg	39	209	7.57		701		10	
7		HCO_3-SO_4-Ca-Mg	39	325	7.82		593		7.4	
8		HCO_3-SO_4-Ca-Mg	39	215	7.57		659		13	
9		HCO_3-Ca-Mg	18	277	7.83		670		12.8	
10		HCO_3-SO_4-Ca-Mg	39	183	7.70		688		12	
11		Ca-Mg-HCO_3-SO_4	39	182	7.10		682		9.4	
12		HCO_3-SO_4-Ca-Mg	39	175	7.56		728		7.6	
13	B	HCO_3-SO_4-Ca-Mg	39	187	7.64	7.40	701	732	6.2	8.9
14		HCO_3-SO_4-Ca-Mg	39	202	6.96		802		9.3	
15		HCO_3-Ca-Mg	18	215	7.65		763		5.8	
16		Ca-HCO_3	9	154	7.76		958		8.4	
26		Ca-Mg-HCO_3-SO_4	39	189	7.67		670		7.4	
27		Ca-Mg-HCO_3-SO_4	39	148	7.06		757		7.1	
28		HCO_3-SO_4-Ca-Mg	39	259	7.48		700		7.8	
17		HCO_3-Ca-Mg	18	287	7.87		834		3.1	
18		Ca-Mg-HCO_3	18	205	7.59		890		0.7	
19		Ca-HCO_3	9	158	7.63		881		1.4	
20		Ca-HCO_3-SO_4	27	125	7.31		1003		1.4	
21	C	Ca-HCO_3-SO_4	27	133	7.41	6.99	951	924	1.8	1.5
22		Ca-Mg-HCO_3	18	170	7.63		957		1.2	
23		Ca-SO4-HCO_3	27	80	7.04		991		1.7	
24		HCO_3-SO_4-Ca-Mg	39	94	7.05		982		1.4	
25		Ca-Mg-HCO_3-SO_4	39	113	6.90		825		0.8	

catchment is covered with beech forests, although the upper part (springs no. 20 and 23) is former pasture land converted to spruce forests in the 1950s (Table 2) (BULiGL w Krakowie, 2017).

Data on the amount of precipitation was obtained from the Kopciowa Meteorological Station of the University of Agriculture in Krakow, located in Mochnaczka Wyżna. The station is situated at an altitude of 730 m a.s.l. and located 3.5 km from the research area.

In 2014-2015, both the annual precipitation and the monthly sums differed greatly. In 2014, the sum of precipitation was 1229 mm and in 2015 it was 926 mm. The heaviest precipitation in 2014 occurred in May and July, and amounted to 240 mm and 233 mm, respectively. In 2015, the heaviest rainfall occurred in May and September, and amounted to 140 mm and 119 mm, respectively (Fig. 3). Therefore, based on the monthly rainfall amounts, the following periods were distinguished for analysis: drought (November 2014 and August 2015), strong hydration (May, July and August of 2014, and May and September of 2015), thaw (March 2014 and April 2015) and winter (December 2014 and January, February and December of 2015).

Results and discussion

The water temperature changes ranged from 0.7°C (spring no. 17) to 12.9°C (spring no. 10). It was assumed that springs with temperature fluctuations limited to 2.0°C or less have a deep supply, whereas the springs with fluctuations above 2.0°C have a shallow supply (Rzonca *et al.*, 2008; Kisiel *et al.*, 2015). Springs no. 17 to 25 (sub-catchment C) had temperature fluctuations of 0.7 to 1.9°C and were considered to have deep supply. The other springs had temperature fluctuations of more than 2.0°C, therefore it was assumed that their water supplies were shallow (Table 2).

The average concentrations for the entire period indicated the dominance of HCO_3^- and Ca^{2+} in the chemical compositions of the analyzed springs. The overall mineralization of the springs was 35-248 mg/l. Neither spring has reached the level of mineral water mineralization (Table 3).

According to the Altowski-Szwiec classification (Kleczkowski, 1979), there were seven hydrochemical types of springs. However, most springs were of hydrochemical types HCO_3^--

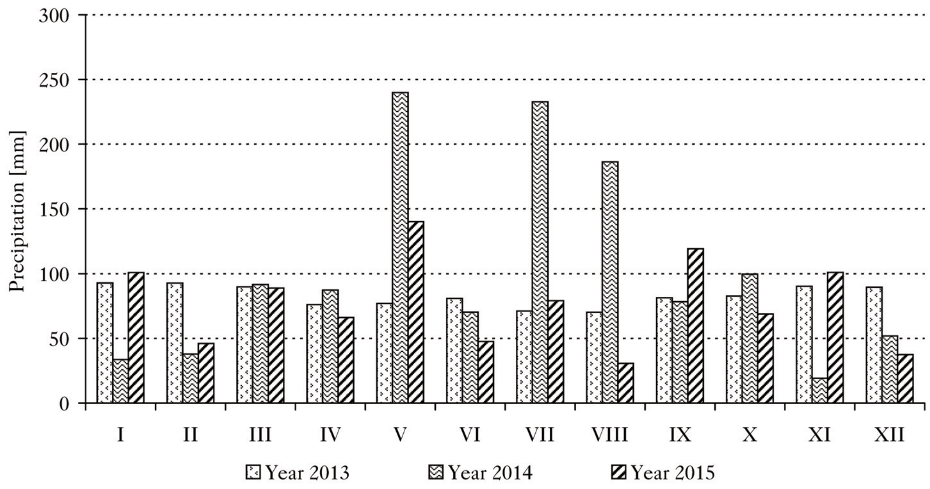

Fig. 3.

The distribution of monthly precipitation in 2013-2015 at the meteorological station 'Kopciowa' of the University of Agriculture in Krakow

Table 3.
Concentrations of ions in water of tested springs

Spring no.	Sum of ions	Ca^{2+}	Mg^{2+}	Li^{+}	Na^{+}	NH_4^{+}	K^{+}	F^{-}	Cl^{-}	NO_2^{-}	Br^{-}	NO_3^{-}	SO_4^{--}	HCO_3^{-}
		mg*l-1												
1	203	31.5112	9.3538	0.0070	4.3192	0.0376	0.7729	0.0621	1.8833	0.0033	0.0458	8.7387	24.1920	121.7371
2	201	34.4721	8.3322	0.0012	3.7413	0.0069	0.6988	0.0830	2.1083	0.0074	0.1079	10.0582	25.0469	116.6901
3	246	36.8106	13.8704	0.0025	4.5939	0.0194	0.5716	0.0889	2.6766	0.0038	0.0999	5.1730	23.7742	158.5925
4	245	40.5202	11.7460	0.0028	4.0435	0.0048	0.7780	0.0626	1.9232	0.0051	0.1074	4.0022	27.1853	154.3986
5	224	33.7597	12.1122	0.0068	4.1457	0.0054	0.7813	0.0773	1.8598	0.0038	0.0993	5.6997	32.3745	132.6629
6	139	21.9278	5.7756	0.0009	3.6273	0.0114	0.0000	0.0711	1.7864	0.0041	0.1006	3.9941	24.5133	77.0125
7	248	41.1198	11.1308	0.0031	4.3199	0.0162	0.8105	0.0666	2.1088	0.0041	0.1032	9.8138	34.4375	144.0165
8	146	22.1644	7.0134	0.0008	3.2874	0.0066	0.5783	0.0614	1.8003	0.0032	0.0820	2.9748	23.2591	85.1690
9	208	33.5886	9.4371	0.0014	3.5498	0.0105	0.7267	0.0490	2.0393	0.0033	0.0949	5.0148	24.5448	128.4899
10	120	17.3190	5.6031	0.0009	2.9525	0.0146	0.6415	0.0497	1.8376	0.0033	0.1024	6.1906	18.0465	66.9663
11	134	25.0163	6.0820	0.0006	2.6532	0.0065	0.4842	0.0625	1.8018	0.0033	0.0825	7.9042	20.8144	69.0788
12	107	15.3300	5.3806	0.0010	3.2787	0.0044	0.5286	0.0675	1.6126	0.0033	0.1014	4.5385	16.7588	59.6162
13	124	18.6804	5.7880	0.0009	3.3282	0.0067	0.5653	0.0556	1.5476	0.0033	0.1070	6.8304	16.0424	71.0935
14	140	22.9269	5.3738	0.0009	2.7167	0.0101	0.5799	0.0747	1.8682	0.0047	0.1075	7.2981	19.4496	79.8640
15	161	28.2594	5.3484	0.0013	2.2647	0.0157	0.5833	0.0460	1.5689	0.0044	0.0877	3.6785	14.6236	104.2377
16	102	17.9858	2.2666	0.0005	1.7912	0.0084	0.4616	0.0562	1.4905	0.0033	0.0909	13.4449	11.2357	52.7537
17	213	32.3926	10.2673	0.0045	3.1270	0.0088	0.7770	0.0371	2.0037	0.0045	0.1235	8.3516	26.8626	129.1283
18	132	21.9385	4.9722	0.0016	2.1711	0.0127	0.5525	0.0469	1.5472	0.0033	0.1224	14.7781	14.5013	71.0538
19	97	17.1879	2.5051	0.0006	1.7632	0.0092	0.4129	0.0652	1.5810	0.0052	0.1100	8.9679	9.2608	55.5609
20	72	11.9816	1.9080	0.0005	1.6162	0.0160	0.2877	0.0767	1.2650	0.0033	0.0823	8.6887	9.7995	36.4750
21	70	12.1794	1.4983	0.0005	1.8351	0.0069	0.3282	0.0670	1.0915	0.0033	0.1245	8.9960	10.9335	32.7833
22	102	16.9861	2.9391	0.0013	1.8868	0.0139	0.4068	0.0797	1.2942	0.0033	0.1128	8.3377	11.4605	58.5738
23	35	5.5038	0.7642	0.0005	1.9315	0.0099	0.6149	0.0484	0.8920	0.0039	0.0869	4.9416	11.0408	9.5342
24	51	6.8962	1.6753	0.0011	2.5182	0.0080	0.5098	0.0684	0.9558	0.0062	0.1132	3.0907	10.6522	24.4215
25	62	8.8446	2.6292	0.0005	2.3216	0.0101	0.3745	0.0499	1.3925	0.0039	0.1019	3.4504	13.8846	28.9999
26	131	22.2165	4.0413	0.0005	2.7370	0.0051	0.5477	0.0476	1.8414	0.0033	0.0981	2.6713	26.3320	70.6878
27	90	14.8207	3.3419	0.0008	2.5224	0.0071	0.5430	0.0675	1.7290	0.0033	0.1131	2.8706	18.4022	45.5115
28	184	30.9665	8.1022	0.0022	2.9969	0.0063	0.7271	0.0629	1.9933	0.0033	0.0968	4.0623	25.1254	109.3569

$-SO_4^{2-}$-Ca^{2+}-Mg^{2+} (11 springs) and HCO_3^--Ca^{2+}-Mg^{2+} (six springs), which covered 39% and 21% of the measurement points. respectively. Using the Szczukariew-Prikłoński classification (Macioszczyk, 1987), only four hydrochemical classes could be distinguished: water class 39 (HCO^--SO_4^{2-}-Ca^{2+}-Mg^{2+} and Ca^{2+}-Mg^{2+}-HCO_3^--SO_4^{2-}). which covered 15 springs (54% of the springs); class 18 (HCO_3^--Ca^{2+}-Mg^{2+} and Ca^{2+}-Mg^{2+}-HCO_3^-), which covered eight springs (29%); class 27 (Ca^{2+}-HCO_3^--SO_4^{2-} and Ca^{2+}-SO_4^{2-}-HCO_3^-), which covered three springs and, class 9 (Ca^{2+}-HCO_3^-), which covered the remaining two springs (Table 2).

Two hydrochemical classes were distinguished in sub-catchment A: class no. 39 (of water type HCO_3^--SO_4^{2-}-Ca^{2+}-Mg^{2+}) and class no. 18 (of type HCO_3^--Ca^{2+}-Mg^{2+}). In sub- catchment B, three hydrogeochemical classes were distinguished. Nine springs fell in class 39, two fell in class 18, and one fell in class no. 9. Sub-catchment C received four water class designations: class no. 39 (2 springs), class no. 27 (3 springs), class no. 18 (3 springs), and class no. 9 (1 spring) (Table 2).

The classes and hydrochemical types of the spring water obtained in this study are characteristic of Carpathian flysch geology. Similar results were obtained in studies on the Bieszczady mountains in Połonina Wetlińska (Kisiel *et al*., 2018) and the Kryniczanka catchment, where the dominant type was HCO_3^--Ca^{2+}-Mg^{2+}, followed by type HCO_3^--SO_4^{2-}-Ca^{2+}-Mg^{2+} (Ciężkowski and Kozłowski, 1999; Rzonca *et al*., 2008). In the Satora flysch, types Ca^{2+}–HCO_3^-–SO_4^{2-} and HCO_3^--Ca^{2+}-Mg^{2+} were dominant (Satora, 2009). Water of the bicarbonate-calcium-magnesium type (HCO_3^--Ca^{2+}-Mg^{2+}) was described by Gągulski (2014) as typical of an aquifer composed of thick-bedded Magura series sandstones with a carbonate-silica-clay binder. The water of the Markowy Potok catchment (Babiogórski National Park) had similar features, where bicarbonates dominated among anions and calcium dominated among cations (Malata, 2015).

In sub-catchments A and B, the springs with feed areas covered by beech stands had a higher pH and contained the three-component water type HCO_3^--Ca^{2+}-Mg^{2+} (class no. 18), with shares of SO_4^{2-} in the 16-18% mval $\cdot$ L^{-1}1 range. On the other hand, the springs covered with a pine or spruce stand, or a mixed stand with an admixture of spruce, exhibited a lower pH and higher proportions of SO_4^{2-} ions – often exceeding 20% mval $\cdot$ L^{-1}. The water in these springs was of type HCO_3^--SO_4^{2-}-Ca^{2+}-Mg^{2+} (class no. 39) (Table 2). This type can be explained by the shallow water supply systems, where environmental factors have a greater influence on the chemical composition of the water, and sulphates in the air enter the groundwater through rainfall (Małek and Gawęda, 2006; Malata, 2015; Jasik *et al*., 2020). In the study area, there is a lot of horizontal precipitation (frost and rime), which is deposited more heavily on the needles than on the branches of deciduous trees.

The springs of sub-catchment C had more diversified chemical compositions, while the species composition of the stands covering them did not affect the type of water. These findings are related to deep feeding, i.e., long stays in flysch and its main influence on the ionic composition (Malata, 2015).

In sub-catchments A and B, regardless of the degree of watering, there were two main classes of water (classes no. 39 and 18), with some exceptions:

a) in spring 2 (sub-catchment A) in the dry period, the amount of Mg^{2+} decreased below 20% mval $\cdot$ L^{-1} and it was reclassified as being from class no. 27 (hydrochemical type Ca^{2+}-HCO_3^--SO_4^{2-}) (Fig. 4).

b) spring 16, located at an altitude of 958 m a.s.l. and in a deep ravine with accumulated beech litter, was placed in hydrochemical class no. 9 (type Ca^{2+}-HCO_3^-) and remained there during all spring measurement sessions. Low concentrations of the remaining ions are most likely due to the high altitude and severe weather conditions limiting the decomposition of organic matter, plus having the bedrock most resistant to weathering (thick-bedded Magura sandstones) (Siwek and Żelazny, 2019). In winter, the amount of SO42- ions increased and exceeded 20% mval · L^{-1}, moving this spring to class no. 27 (type Ca^{2+}-HCO_3^--SO_4^{2-} – perhaps due to the proximity of a ski slope featuring artificial snow.

The hydrochemical types of water found in springs in sub-catchment C were more diverse than those in sub-catchments A and B (Figs. 4, 5). Due to their deep supply, their physicochemical

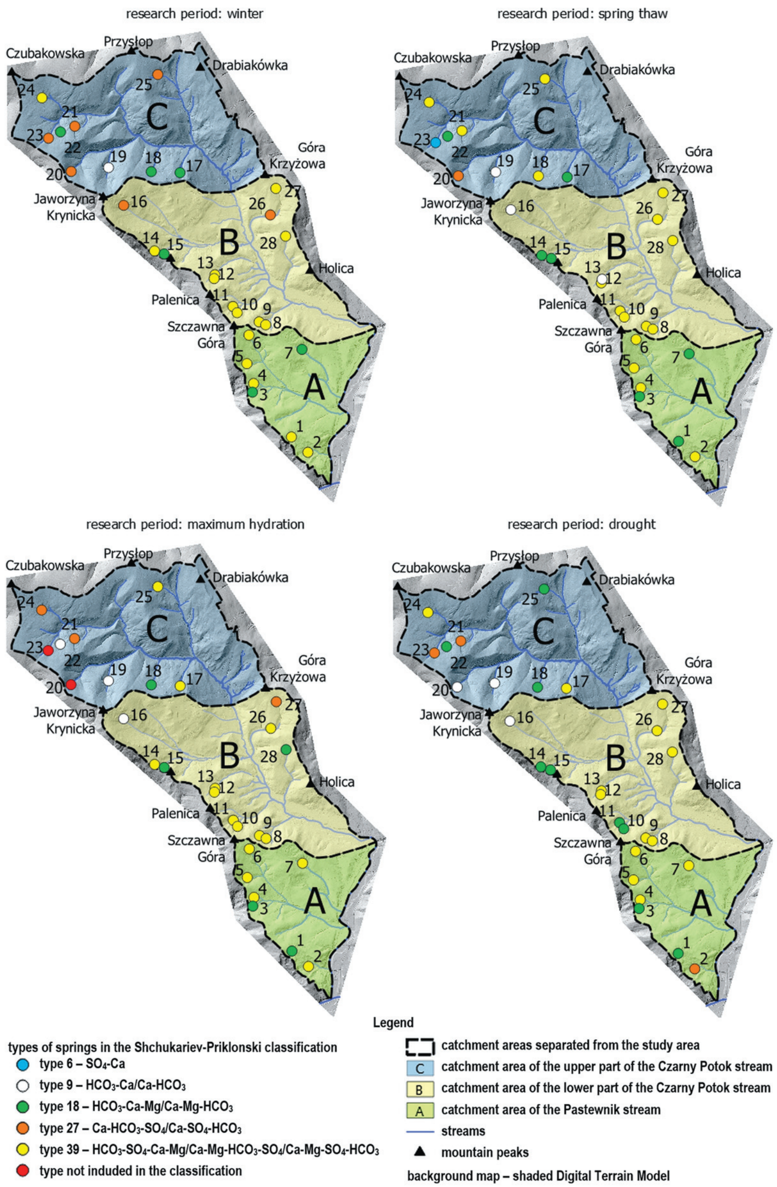

Fig. 4.
Hydrochemical types of water in springs under various water conditions

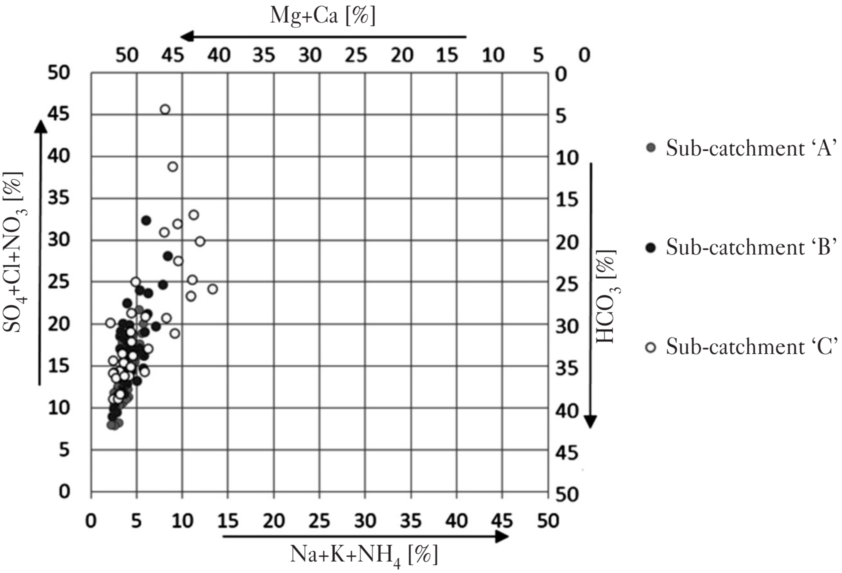

Fig. 5.
Hydrochemical structure of water from springs in sub-catchments (Modified Ludwig-Langerier diagram)

compositions depend mainly on the geological base (Ciężkowski *et al.*, 1999; Siwek *et al.*, 2010; Wójcik, 2012). The influence of deep supply may also cause the lack of correlation between hydrochemical classes and the species composition of the stands covering the alimentation reservoirs (Table 1).

The most stable water chemistry composition was found for spring 19 (water class no. 9; type Ca^{2+}-HCO_3^-). This composition did not change, regardless of the degree of water supply or the season. This spring is located in the middle of the slope and its area is covered with old beech stands.

Spring 18 was quite stable (water class no. 18; type HCO_3^--Ca^{2+}-Mg^{2+}); however, during the thaw period, the proportion of SO_4^{2-} ions increased and moved the spring to class no. 39 (type Ca^{2+}-Mg^{2+}-HCO_3^--SO_4^{2-}). The maintenance area of this spring includes a ski slope, which may result in higher amounts of anthropogenic sulphates.

It is worth noting that spring 23 (water class no. 27; type Ca^{2+}-SO_4^{2-}-HCO_3^-) was the only case where SO_4^{2-} (at 46% mval · L^{-1}) clearly exceeded the share of HCO_3^- (32% mval · L^{-1}). The absolute value of the sulphates was not high at 11.04 mg · L^{-1} because the overall mineralization is very low (30 mg L^{-1}). This spring was also characterized by a high concentration (16% mval · L^{-1}) of NO_3^- ions. During the thaw period it belonged to type SO_4^{2-}-Ca^{2+}, and in the period of the highest rainfall it belonged to type Ca^{2+}-SO_4^{2-}-HCO_3^--NO_3^-.

Spring 20 had a similar type of water (class no. 27; type Ca^{2+}-HCO_3^--SO_4^{2-}), which lost SO_4^{2-} ions during drought and became type Ca^{2+}–HCO_3^-. At the highest water level, the spring had type Ca^{2+}-HCO_3^--SO_4^{2-}-NO_3^- water. Stands with a dominant share of spruce were present.

Water types with nitrate levels above 20% mval · L^{-1} do not have appropriate classes in the Szczukariew-Prikłoński classification. Recently, researchers have often found NO_3^- ion proportions above 20% mval · L^{-1} because of anthropogenic activity promoting the acidification of precipitation and increasing nitrogen and sulfur depositions. These are recorded both in the vicinity of pollution and at great distances from these sources (Żelazny *et al.*, 2011; Jasik and Małek, 2013; Jasik *et al.*, 2020).

The alimentation area of springs 20 and 23 is covered with spruce stands. In the case of spring 23, the stand is largely damaged by wind and the spruce bark beetle. In places of decay, the area is covered with spruce-fir saplings. The effect of the leaching of elements from spruce thickets, especially sulphates, was observed here, as young stands have a limited ability to absorb substances flowing into the ecosystem (Żelazny *et al*., 2017; Sajdak *et al*., 2019). A similar washout effect of NO_3^- ions accumulated in decaying spruce stands during the strongest rainfalls and spring thaws was confirmed in the Beskid Śląski, Gorce and Świętokrzyskie mountains (Małek and Krakowian, 2009; Jasik and Małek, 2013; Jasik, 2015; Jasik *et al*., 2020).

Despite the remoteness of the studied area from the sources of air pollution, NO_3^- ions determined the water type of two springs. Pollutants that accumulated in the 1960-70s can be the trigger (Rzychoń *et al*., 2009; Małek *et al*., 2010; Kosmowska *et al*., 2015).

Springs 18, 20 and 23 are located on flats, and the outflow is in a large depression. According to some researchers, in periods of thaw and heavy rainfall, such springs tend to have a lower pH and release sulphates and nitrates (Małek and Gawęda, 2006). The increased shares of nitrate ions in periods of maximum rainfall (springs 20 and 23) or sulphate ions (springs 18 and 20) during the thaws, seem to be the result of surface water run-off from the precipitation feeding the springs (Ciężkowski *et al*., 1999; Małek *et al*., 2010; Wolanin, 2014) (Fig. 5).

Summary and conclusions

Average ion concentrations in the spring water of the Czarny Potok and Pastewnik catchment areas indicate the presence of four hydrochemical classes (according to the Szczukariew--Prikłoński classification): class no. 39 with hydrochemical types HCO_3^--SO_4^{2-}-Ca^{2+}-Mg^{2+} and Ca^{2+}-Mg^{2+}-HCO_3^--SO_4^{2-}, representing 54% of the springs; class no. 18 with types HCO_3^- -Ca^{2+}-Mg^{2+} and Ca^{2+}-Mg^{2+}-HCO_3^-, representing 29% of the springs; class no. 27 with types Ca^{2+}– HCO_3^-–SO_4^{2-} and Ca^{2+}-SO_4^{2-}-HCO_3^-, representing 3 springs; and class no. 9 with type Ca^{2+}-HCO_3^-, representing 2 springs. All classes are typical for their geological basis – the Carpathian flysch.

Springs with shallow supplies (sub-catchments A and B) located within the Carpathian flysch show a correlation between the change in hydrochemical type and the species composition of the forest stands covering them. In the maintenance areas covered with beech stands, type HCO_3^--Ca^{2+}-Mg^{2+} is prevalent. However, when the cover consists of spruce or pine stands, the share of sulphate ions (SO_4^{2-}) increases and water type HCO_3^--SO_4^{2-}-Ca^{2+}-Mg^{2-} is created.

In the springs located on the thin-bedded sandstones and shales of the Zarzecze layer, the ionic composition is stable; season and amount of rainfall do not affect the hydrochemical type.

The springs of sub-catchment C (the upper part of the Czarny Potok catchment), with deep water supplies on the Carpathian flysch, are characterized by a more diverse ionic composition than those with shallow supplies. The geological structure of these springs has a major influence on their hydrochemical type.

Water containing NO_3^- ions (types Ca^{2+}-HCO_3^--SO_4^{2-}-NO_3^- and Ca^{2+}-SO_4^{2-}-HCO_3^--NO_3^-) appeared in two springs located in the immediate vicinity of stands with dying spruce, but only during high hydration after a period of heavy rainfall.

The springs located in the Kryniczanka stream catchment area, which is covered with forest, were characterized by a stable chemical composition and very rarely exhibited higher concentrations of pollutants in the form of nitrates.

Authors' contributions

K.U. – sampling, study investigation, writing manuscript; S.M. – supervising, methodology, writing manuscript; M.J. – data preparation and analysis, writing, J.G. – visualization, writing.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding source

This work was supported by the ministry of Science and Higher Education of the Republic of Poland (SUB/040012/D019)

Acknowledgements

Special thanks to Iwona Skowrońska for providing chemical analysis.

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STRESZCZENIE

Charakterystyka hydrochemiczna wód źródeł wybranych zlewni na terenie Leśnego Zakładu Doświadczalnego w Krynicy-Zdroju

Przy prowadzeniu badań ekosystemów leśnych ilość i jakość krążącej w nich wody jest istotnym czynnikiem. Podejmowane dotychczas badania źródeł w polskich górach dotyczyły głównie terenów chronionych (parki narodowe). Nasuwa się pytanie, jak kształtują się cechy fizykochemiczne źródeł w zagospodarowanych lasach górskich, zwłaszcza tam, gdzie jakość zwykłych wód podziemnych wpływa na chemizm wód mineralnych i leczniczych. Fakt ten ma wyjątkowe znaczenie w otulinie uzdrowiska, gdzie balneologia oparta jest na miejscowych zasobach.

W pracy badano zróżnicowanie typów hydrochemicznych wód źródeł występujących w zlewniach leśnych otuliny uzdrowiska Krynica-Zdrój oraz wpływ na to zróżnicowanie takich czynników środowiska, jak: opady (ryc. 3), gleby i skład gatunkowy drzewostanu.

Badania przeprowadzono w latach 2013-2016 w Beskidzie Sądeckim, paśmie Jaworzyny Krynickiej (1114 m n.p.m.) i obejmowały one zlewnie prawobrzeżnych dopływów potoku Kryniczanka (ryc. 1). Do badań wytypowano 28 stałych źródeł zlokalizowanych w piętrze regla dolnego, między 548 a 1003 m n.p.m. (tab. 1, ryc. 2). W pobranych comiesięcznie próbkach oznaczano pH, przewodność elektryczną właściwą oraz zawartość podstawowych kationów (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Li^{+}, NH_4^{+}) i anionów (F^{-}, Cl^{-}, NO_2^{-}, Br^{-}, NO_3^{-}, PO_4^{2-}, SO_4^{2-}, HCO_3^{-}) metodą chro-

matografii jonowej z wykorzystaniem chromatografu Dionex-5000. Następnie zakwalifikowano wodę z każdego badanego źródła do określonego typu wg klasyfikacji Altowskiego-Szwieca oraz odpowiedniej klasy hydrochemicznej wg klasyfikacji Szczukariewa-Prikłońskiego.

Średnie wartości stężenia jonów w wodach źródeł wskazały na występowanie 4 głównych typów hydrochemicznych: HCO_3^--SO_4^{2-}-Ca^{2+}-Mg^{2+}, Ca^{2+}-Mg^{2+}-HCO_3^--SO_4^{2-}, HCO_3^--Ca^{2+}-Mg^{2+} i Ca^{2+}-Mg^{2+}-HCO_3^-, które są typowe dla tego podłoża geologicznego – fliszu karpackiego (tab. 3).

Źródła z płytkim zasilaniem (zlewni A i B) wykazują zależność między zmianami typu hydrochemicznego a składem gatunkowym pokrywających je drzewostanów. Przy pokryciu obszarów alimentacyjnych drzewostanami bukowymi posiadają klasę hydrochemiczną wód 18 (z typem HCO_3^--Ca^{2+}-Mg^{2+}), a przy pokryciu drzewostanami świerkowymi lub sosnowymi wzrasta udział jonów siarczanowych (SO_4^{2-}), tworząc klasę 39 (typ wody HCO_3^--SO_4^{2-}-Ca^{2+}-Mg^{2-}) (tab. 2).

Wszystkie badane źródła nie wykazywały w składzie jonowym azotynów, a sporadycznie zawierały azotany. Wody z typem hydrochemicznym zawierającym jon NO_3^- (Ca^{2+}-HCO_3^--SO_4^{2-}-NO_3^- oraz Ca^{2+}-SO_4^{2-}-HCO_3^--NO_3^-) pojawiły się tylko w dwóch źródłach znajdujących się w zamierających drzewostanach świerkowych, tylko w okresie maksymalnego zawodnienia – po obfitych opadach (ryc. 4). Stwierdzono również, że badane źródła położone w zlewni potoku Kryniczanka, pokryte lasem z prowadzoną w nim gospodarką leśną, charakteryzują się stabilnym składem chemicznym (ryc. 5).