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Original Research

Hypsometric Factors for Differences in Chemical Composition of Tatra National Park Spring Waters

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Abstract

The aim of this study was to verify a hypothesis about the differences in chemical composition of spring waters as determined by hypsometric factors (relief) in the Tatra Mountains. During our research, 1,505 hydrological objects were inventoried, but this research was conducted on 872 selected outflows (swamps and springs). Temperature, conductivity, and pH were measured together with discharge in the field. A 0.5 dm^3 water sample was taken from each hydrological object. The chemical composition was determined by ion chromatography. The role of hypsometric factors in the formation of chemical composition of spring waters is reflected throughout the TNP as a systematic reduction of the importance of two major hydrochemical classes of spring waters (HCO_3-Ca, HCO_3-Ca-Mg) in favor of waters containing a large share of SO_4^{2-}. The lower and ridge parts of the mountains are characterized by low hydrochemical diversity for the entire Tatra range.

Keywords: chemistry, spring, the Tatra Mountains

Introduction

High mountain relief depends on the geological and tectonic structure and the commonly occurring process of denudation, in which chemical weathering is an important part. The existing strong relationships between various elements of the natural environment in mountain areas are visible in the form of distinct vertical zonation, belt-like structure and morphological sequence [1]. Vertical zonation of environmental elements, determined by a.s.l. elevation, is still the most characteristic element of mountain areas [2]. Therefore, in the Tatra Mountains, with typical high mountain relief, a number of climatic [3], plant [4], morphogenetic [5], geoecological [6], and soil [7] zones can be distinguished. According to Kotarba [6], the range of denudation in each geoecological zone depends on the amount of circulating water, rock-dissolving conditions, and environmental elements typical of a given zone, particularly temperature and precipitation regime. The denudation rate in the highest parts of the Tatra Mountains is slow [8]. According to Małecka [9, 10], the chemical composition of waters is modified, apart from the determinants of geological structure, by the chemical composition of precipitation, particularly in the ridge zone. Therefore, the zonal and belt-like system of factors affecting chemical composition of water may impact the formation of zonal variation of physical and chemical groundwater properties. Despite numerous papers on water hydrochemistry at Tatra National Park (TNP), there are relatively few comprehensive studies. Oleksynowa and Komornicki [8, 11-22] analyzed the chemical composition of over 800 water samples at TNP in the 1950s. Based on these studies they found that water mineralization clearly decreases from the lowest to the highest parts of the mountains. Moreover, Małecka [23],

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based on many years of research on spring waters in the 1980s-90s, after analyzing ~1000 springs, presented the hydrochemical water zonation of the Tatras. The separated hydrochemical regions have a parallel layout and refer to the major tectonic units [10, 23-25], while the water mineralization constantly increases from mountain peaks to their foothills. Also, Kostrakiewicz [26], based on his own research and the literature, separated three regions in the Tatras, but apart from the already known hydrochemical zones he observed waters with slightly different chemical composition in the Quaternary moraine and residual clay deposits.

The aim of this study was to verify the hypothesis about the differences in chemical composition of spring waters determined by the hypsometric factors (relief) in the Tatras.

The Study Area

The research was conducted in the Polish part of the Tatra Mountains in Tatra National Park (TNP) within an area of ~212 km^2 (Fig. 1). The Tatras are the highest and northernmost high-mountain massif of the Carpathians. The highest peaks of the Tatra Mountains exceed 2,600 m a.s.l. and rise to nearly 2 km above the bottom of the surrounding valleys: Podhale (N), Popradzka (SE), and Liptowska (SW). The average width of the Tatra Mountains is ~15 km, while the maximum width is ~18 km [27, 28].

Two fundamentally different tectonic units occur within the Tatras. In the southern part there is a crystalline core built mainly of igneous rocks (granitoids) and metamorphic rocks (gneiss, schists). On the other hand, the northern part is built of sedimentary rocks, mainly limestones, dolomites, and marls [28, 29].

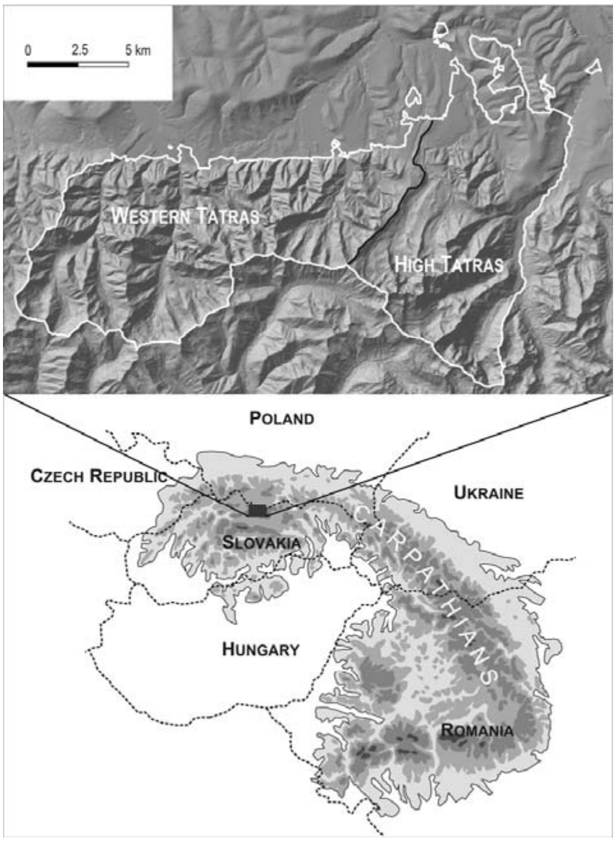

Fig. 1. The study area.

The homogenous groundwater body within the TNP (JCWPd No. 156) is a part of the subregion of the Interior Carpathians region of the upper Vistula [10, 30]. Aquifers (limestones, dolomites, granites) are slotted and have poor permeability and their filtration coefficient is $1·10^{-6}$-$3·10^{-4}$ [10, 30]. Carbonate rocks, in which water occurs up to a depth of about 500 m, are the main water-bearing deposits in the Tatras. On the other hand, the crystalline core of the Tatras is characterized by poor water permeability. The circulation of water within these rocks is limited to the network of cracks that occur up to a depth of ~ 20-30 m [30]. The rock layers with various water-bearing properties are intersected by transverse faults. A denser network of fractures and rock disintegration occurs in the dislocation zones, which facilitates the water flow [10].

The Tatra slopes are covered with debris-clay-sand residual material with thickness usually not exceeding 2 m [30]. However, in places transformed by glaciers, thickness of moraine cover may reach even up to 40 m [31]. Residual clay deposits conduct water only locally. Sand-gravel fluvial and fluvio-glacial deposits are the main aquifers among Quaternary sediments, while the moraine cover constitutes small water-bearing systems [30].

The impermeable bedrock and large slope gradients favor low water retention. These conditions cause low discharge springs (up to 0.5 dm^3·s^{-1}), supplied with water from a shallow circulation, that are typical of the Tatras. There also are a few karst springs, typical of karst limestone, with discharge of several hundred liters per second [32, 33].

The small thickness of the aquifer within the Tatra crystalline core causes the chemical composition of groundwater in this part of the mountains to be formed mainly by infiltration of precipitation water. However, karst processes and deep penetration of the massif are common in the sedimentary part of the Tatras, especially the limestone fragment. According to the classification of Szczukariew-Prikłoński, Tatra groundwaters are sweet and ultra-sweet. These are mostly waters containing two or three ion types dominated by the following ions: HCO_3^-, Ca^{2+}, and Mg^{2+} [23].

Five climatic and four vegetation zones may be distinguished in the Tatras [3, 4]. The average amount of precipitation in the Tatras in the period 1966-2006 varied from 1,120 mm in the foothills of the Tatras to 1,800 mm at their tops (Kasprowy Wierch) [34].

Material and Methods

Fieldwork

Hydrochemical analyses of groundwater were performed twice in 2007-09 within the project financed by the Ministry of Science and Higher Education, called "Factors determining the spatial variation and dynamics of chemical composition of water in Tatra National Park."

During the research, 1,505 hydrological objects were inventoried, including: 1,018 groundwater outflows (springs, swamps, karst springs, and seepage spring areas), 49 ponds, and 469 watercourses. Generally, the temperature (T), conductivity in relation to 25ºC (EC_{25}ºC), and pH were measured together with discharge (sometimes estimated) and noted in the field. In the case of karst springs, water level was recorded, and afterwards, based on the flow curve, the discharge was determined. A 0.5 dm^3 water sample was taken to a disposable polyethylene bottle from each hydrological object. Due to the diversity of water mineralization falling within the range from 0.5 $\mu S\cdot cm^{-1}$ to 515 $\mu S\cdot cm^{-1}$, handheld meters (WTW Multi350i, Elmetron CX 401, CPC 401) were used with appropriate pH electrodes and conductometric sensors with low k constant adjusted to conductivity (i.e. k=0.1, conductometric sensor LR205).

The field studies were conducted over the summer-autumn low flow at low hydration of the Tatra massif, beginning from the last week of August to mid-September 2007, 2008, and 2009.

The research was conducted on 872 selected outflows (swamps and springs), hereinafter referred to as springs, which represent relatively shallow water circulations in mountain slopes. The interpretation did not include karst springs, i.e. springs with very high discharges, which are characterized by a complex, geologically conditioned, water supply system [35-38]. Furthermore, so-called seepage spring areas were not considered in this research, because reaching the outflow itself was technically impossible, therefore it was impossible to exactly determine height.

Laboratory Analyses

EC and pH were measured again in the Hydrochemical Laboratory of the Institute of Geography and Spatial Management, and water samples were filtered through a 0.45 mm syringe filter (Sartorius). The chemical composition was determined by ion chromatography. The applied gradient chromatographic system (DIONEX ICS 2000) consists of anionic and cationic chromatographic modules, which during about twenty minutes allows us to simultaneously separate and determine the concentrations of 14 ions in water: main ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, Cl^-), biogenic compounds - mineral forms of nitrogen and phosphorus (NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}), and microelements (Li^+, Br^-, F^-). Mineralization was calculated as the sum of determined ions, and the average concentration of H^+ was calculated based on pH: $H^+=10^{-pH}$. The hydrochemical characteristics were presented according to the Szczukariew-Prikłoński Classification commonly used in Poland [39]. A hydrochemical class was separated when the share (% mval) of ions, expressed in gram equivalent in water in relation to a group of determined anions or cations, was 20% mval. If the class included ion not considered in the classification (e.g. NO_3^-), then this water would be indicated as "off classification," at the same time including the ion into the name of the class. Commonly used and interpreted statistical characteristics were calculated in STATISTICA 10, while to determine the variability (dispersion) of the chemical composition parameters a Ψ indicator was used, understood as the quotient (upper quartile-lower quartile)/(2*median). The presented index is more representative for the average dispersion of water chemical composition parameters, as it is based on positional measures and is not sensitive to extreme values that are typical of areas with complex geological structures. The hydrochemical analysis was related to the contour lines every 100 m, in three variants: for the whole TNP, the High and the Western Tatras. In the performed calculations, the springs of Sucha Woda Valley were included within the High Tatras.

Results

In general, great variability of mineralization, pH, and chemical composition was observed in TNP waters. The highest concentration (mg/dm^3) and share (% mval) of Ca^{2+} cations and HCO_3^- anions is a characteristic feature of these waters (Table 1). The concentrations of the remaining main ions and nitrates is a few to several times lower. There is a very low concentration of NH_4^+ and F^-, and concentrations of NO_2^-, PO_4^{3-}, and Br^- are hardly ever above the detection limit. It needs to be noted that the greatest diversity in the concentration of main ions, expressed as the Ψ index, was observed for cations Ca^{2+} (Ψ =1.94), and anions HCO_3^- (Ψ = 1.62).

The mineralization and ion concentration in spring waters decreases with the increase in absolute height, from the foot to the peak part of TNP (Fig. 2), except for Na^+, which increases to a height of 1,500-1,600 m a.s.l. Normally, ion concentrations in the High Tatras significantly decrease with increasing absolute height, which is similar to the Western Tatras, except that in the highest parts (1,800-1,900 m a.s.l.) there is an increase in concentration, particularly of HCO_3^-, Ca^{2+} and to a lower extent of Mg^{2+} (Fig. 3). In the case of Na^+ the uneven increase in its concentration may be observed toward the foothills in the springs draining the High Tatras, while in the case of the Western Tatras such a relationship does not exist. Springs located in the highest parts of the Western Tatras are characterized by significantly higher concentrations of Mg^{2+}, Na^+, K^+, and SO_4^{2-} than springs in the High Tatras (Fig. 3), except for NO_3^-, whose concentrations are higher in the High Tatras.

Regardless of the location, Ca^{2+} and HCO_3^- have the largest share in the chemical composition of springs, and their variability expressed as Ψ is the lowest, except for the ridge part of the High Tatras (> 1,800 m a.s.l.), where the variability of HCO_3^- increases (Table 2). High variability of ion concentration expressed as the interquartile range occurs up to a height of 1,300 m a.s.l. (Fig. 3), with the greatest variability of Na^+ ions (Ψ =1.05) in the range of 1,200-1,300 m a.s.l. (Table 2). Changes in the share of ions (% mval) in the structure of chemical composition in relation to height is more complicated. The share of HCO_3^- ions (% mval) in the chemical composition of TNP springs unevenly decreases with increasing height (from 1,100 m a.s.l.) and the share of Na^+ and SO_4^{2-} increases (Table 2),

Table 1. Chemical composition parameters of TNP spring waters.

Feature	Unit	Mean	Median	Min	Max	Q_1	Q_3	Ψ
pH		6.46	7.54	4.76	8.87	6.96	7.97	0.07
EC	$\mu S \cdot cm^{-1}$	153.6	87.1	3.8	515.0	39.2	282.0	1.39
Mineralization	$mg \cdot dm^{-3}$	145.8	77.6	2.5	504.5	31.8	273.2	1.55
Ca^{2+}		25.095	10.648	0.408	92.397	5.120	46.360	1.94
Mg^{2+}		7.163	3.738	0.020	32.790	0.569	12.144	1.55
Na^+		0.911	0.871	0.048	3.809	0.508	1.177	0.38
K^+		0.570	0.475	0.027	3.107	0.264	0.787	0.55
NH_4^+		0.029	0.003	0.001	1.516	0.002	0.036	5.43
HCO_3^-		102.250	54.222	0.648	382.864	17.899	193.372	1.62
SO_4^{2-}		7.546	5.664	0.252	85.981	3.309	8.948	0.50
Cl^-		0.409	0.339	0.050	1.790	0.192	0.563	0.55
NO_3^-		1.752	1.578	0.001	7.915	0.952	2.291	0.42
F-		0.025	0.023	0.000	0.905	0.0003	0.034	0.72
Ca^{2+}	% mval	32.64	31.34	15.96	47.78	27.25	38.23	0.2
Mg^{2+}		12.88	12.91	0.99	32.36	6.31	19.03	0.5
Na^+		3.48	2.16	0.11	17.96	0.50	5.49	1.2
K^+		0.73	0.52	0.04	5.79	0.30	0.98	0.7
NH_4^+		0.11	0.02	0.001	18.29	0.008	0.05	0.9
HCO_3^-		39.64	41.62	10.26	48.91	35.32	46.16	0.1
SO_4^{2-}		7.69	6.63	0.67	34.26	2.79	11.08	0.6
Cl^-		0.68	0.41	0.07	8.35	0.23	0.84	0.7
NO_3^-		1.84	0.92	0.0001	19.44	0.54	2.12	0.9
F^-		0.12	0.08	0.0001	1.01	0.0005	0.18	1.2

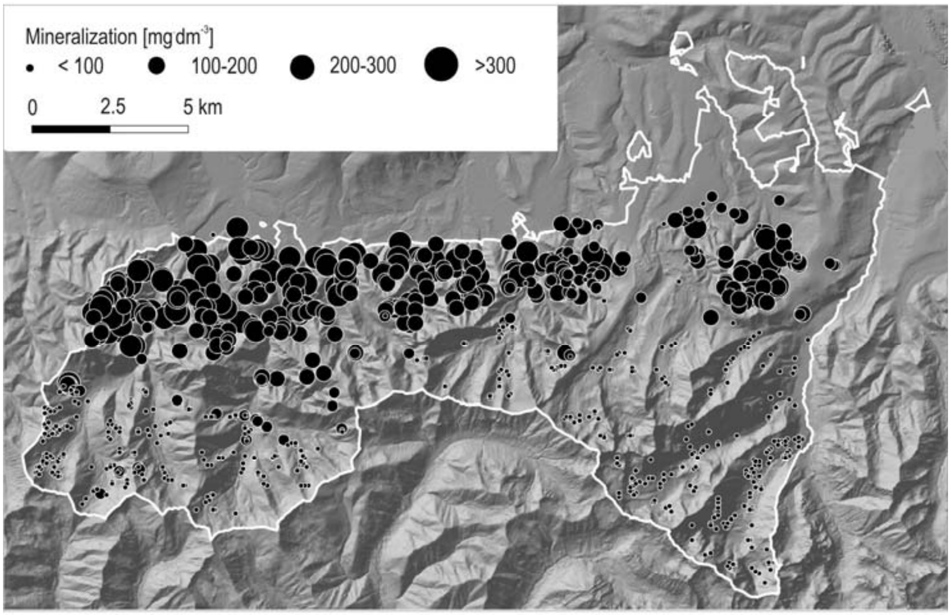

Fig. 2. Mineralization of Tatra spring waters.

Table 2. Changes in the share of ions [% mval], with elevation.

Elevation [m a.s.l.]	Ions [% mval]	Tatra National Park				High Tatras				Western Tatras			
		Median	Q_1	Q_3	ψ	Median	Q_1	Q_3	ψ	Median	Q_1	Q_3	ψ
900-1,000	Ca^{2+}	35.18	29.79	38.38	0.12	38.38	36.19	39.61	0.04	33.29	29.22	37.62	0.13
	Mg^{2+}	13.01	9.54	19.20	0.37	9.10	8.38	10.62	0.12	15.36	10.97	20.02	0.29
	Na^{+}	0.67	0.31	1.22	0.68	1.43	1.23	1.88	0.23	0.54	0.28	0.80	0.49
	HCO_3^{-}	45.19	42.90	47.30	0.05	43.29	41.50	44.10	0.03	46.11	43.47	47.40	0.04
	SO_4^{2-}	3.61	2.01	6.00	0.55	5.09	4.52	7.37	0.28	2.87	1.76	5.80	0.70
1,000-1,100	Ca^{2+}	30.05	27.88	37.49	0.16	42.74	34.81	43.92	0.11	29.90	27.76	36.79	0.15
	Mg^{2+}	18.27	10.81	21.10	0.28	6.16	5.29	7.76	0.20	18.60	12.19	21.16	0.24
	Na^{+}	0.38	0.17	0.83	0.86	0.81	0.48	1.06	0.35	0.35	0.17	0.83	0.94
	HCO_3^{-}	46.62	42.78	47.56	0.05	45.82	44.28	46.81	0.03	46.64	42.53	47.60	0.05
	SO_4^{2-}	2.55	1.65	6.37	0.92	3.55	2.52	4.22	0.24	2.42	1.63	6.51	1.01
1,100-1,200	Ca^{2+}	32.63	28.44	37.98	0.15	35.36	31.84	41.34	0.13	31.50	26.81	36.94	0.16
	Mg^{2+}	14.42	9.66	19.41	0.34	6.31	5.48	13.24	0.61	16.46	11.52	20.54	0.27
	Na^{+}	0.64	0.35	1.75	1.09	1.66	0.50	8.37	2.36	0.59	0.30	1.31	0.85
	HCO_3^{-}	44.64	39.93	46.73	0.08	43.70	31.80	44.94	0.15	45.03	40.95	47.01	0.07
	SO_4^{2-}	4.35	2.34	8.66	0.73	5.44	4.45	13.25	0.81	3.54	2.13	7.91	0.82
1,200-1,300	Ca^{2+}	29.82	26.39	37.78	0.19	40.59	36.50	41.52	0.06	27.30	26.05	31.35	0.10
	Mg^{2+}	13.51	7.76	18.81	0.41	4.33	3.11	7.00	0.45	16.06	12.72	20.07	0.23
	Na^{+}	3.05	0.52	6.03	0.90	5.02	0.90	6.16	0.52	2.58	0.50	5.90	1.05
	HCO_3^{-}	37.50	33.00	46.58	0.18	37.49	36.28	42.98	0.09	38.00	32.00	47.26	0.20
	SO_4^{2-}	8.83	2.46	13.74	0.64	8.77	5.74	9.58	0.22	9.67	1.77	14.12	0.64
1,300-1,400	Ca^{2+}	31.34	27.50	37.17	0.15	36.91	33.22	41.41	0.11	29.35	26.66	32.62	0.10
	Mg^{2+}	11.14	4.58	16.47	0.53	3.82	2.50	5.15	0.35	14.81	11.43	18.77	0.25
	Na^{+}	4.30	2.93	7.65	0.55	7.46	4.65	9.34	0.31	3.57	1.09	5.19	0.57
	HCO_3^{-}	36.94	32.73	41.50	0.12	33.26	29.47	40.29	0.16	38.21	34.76	42.60	0.10
	SO_4^{2-}	10.07	6.11	12.59	0.32	11.28	7.03	14.62	0.34	9.38	5.45	11.91	0.34
1,400-1,500	Ca^{2+}	31.22	26.59	38.42	0.19	39.22	37.81	41.82	0.05	27.78	26.01	30.55	0.08
	Mg^{2+}	10.33	3.25	16.24	0.63	3.08	2.04	3.31	0.21	15.08	11.31	19.26	0.26
	Na^{+}	5.05	3.36	7.42	0.40	6.79	5.43	7.67	0.16	3.95	2.78	6.44	0.46
	HCO_3^{-}	40.15	35.32	41.53	0.08	40.22	38.25	41.02	0.03	40.15	33.60	41.62	0.10
	SO_4^{2-}	7.37	6.35	10.24	0.26	6.84	6.05	8.92	0.21	8.28	6.41	12.82	0.39
1,500-1,600	Ca^{2+}	26.71	23.18	30.57	0.14	39.87	35.55	41.13	0.07	25.92	22.75	29.46	0.13
	Mg^{2+}	16.07	8.61	24.18	0.48	2.63	2.22	3.18	0.18	16.81	11.02	24.60	0.40
	Na^{+}	4.25	2.13	7.51	0.63	6.28	5.66	10.17	0.36	3.63	1.81	7.51	0.79
	HCO_3^{-}	40.29	34.67	43.14	0.11	34.79	27.77	36.57	0.13	41.42	35.87	43.17	0.09
	SO_4^{2-}	7.68	5.68	11.00	0.35	10.22	9.07	16.44	0.36	7.53	5.47	11.00	0.37
1,600-1,700	Ca^{2+}	30.71	27.28	38.53	0.18	41.05	37.49	43.18	0.07	28.38	26.79	30.84	0.07
	Mg^{2+}	10.33	3.41	16.47	0.63	2.20	2.08	3.35	0.29	12.27	10.30	18.37	0.33
	Na^{+}	5.28	3.28	7.48	0.40	5.53	3.92	6.04	0.19	5.20	2.45	8.43	0.58
	HCO_3^{-}	36.29	31.94	41.39	0.13	34.80	28.06	37.54	0.14	37.01	33.34	43.74	0.14
	SO_4^{2-}	10.02	6.52	12.46	0.30	12.02	7.91	12.48	0.19	10.01	4.64	12.34	0.38

Table 2. Continued.

Elevation [m a.s.l.]	Ions [% mval]	Tatra National Park				High Tatras				Western Tatras			
		Median	Q_1	Q_3	ψ	Median	Q_1	Q_3	ψ	Median	Q_1	Q_3	ψ
1,700-1,800	Ca^{2+}	38.60	33.27	41.85	0.11	39.49	35.38	42.04	0.08	21.72	21.20	22.93	0.04
	Mg^{2+}	2.67	1.95	3.33	0.26	2.55	1.85	2.98	0.22	25.53	25.18	26.55	0.03
	Na^{+}	5.42	4.15	8.66	0.42	5.56	4.58	8.82	0.38	1.67	1.46	2.68	0.36
	HCO_3^-	34.23	25.98	40.01	0.20	33.74	25.23	36.34	0.16	43.22	41.43	43.62	0.03
	SO_4^{2-}	9.81	7.30	14.28	0.36	11.67	8.36	15.04	0.29	5.67	5.63	8.02	0.21
1,800-1,900	Ca^{2+}	39.14	37.35	40.84	0.04	38.75	37.33	40.61	0.04	43.20	39.67	46.73	0.08
	Mg^{2+}	2.91	2.62	3.94	0.23	2.91	2.54	3.64	0.19	5.27	2.82	7.73	0.47
	Na^{+}	5.73	3.60	6.48	0.25	5.78	4.79	6.54	0.15	1.01	0.29	1.72	0.71
	HCO_3^-	24.17	15.06	42.25	0.56	19.93	14.85	32.26	0.44	46.64	45.45	47.82	0.03
	SO_4^{2-}	12.31	5.19	16.92	0.48	13.55	9.83	17.39	0.28	2.37	1.39	3.35	0.41
1,900-2,115	Ca^{2+}	38.85	27.38	41.53	0.18	38.85	27.38	41.53	0.18				
	Mg^{2+}	2.30	2.00	2.68	0.15	2.30	2.00	2.68	0.15				
	Na^{+}	5.79	3.65	9.60	0.51	5.79	3.65	9.60	0.51				
	HCO_3^-	17.88	14.72	24.58	0.28	17.88	14.72	24.58	0.28				
	SO_4^{2-}	16.16	13.47	20.88	0.23	16.16	13.47	20.88	0.23				

while in the highest part of TNP we observe a small percentage of Mg^{2+} (<3%). An interesting relationship was noticed in the structure of the chemical composition between the springs in the Western and the High Tatras. The share of Mg^{2+} in the Western Tatras is usually higher than in the High Tatras, while in the case of SO_4^{2-} the situation is the opposite, i.e. the share of SO_4^{2-} in the High Tatras is higher beyond the zone of 1,300-1,500 m a.s.l. (Table 2).

Given the share of ions (% mval) in the structure of the chemical composition of springs, a hydrochemical diversity in the Western and High Tatras is observed. The share of most ions in different elevation ranges shows enormous variability (Table 2). Generally, HCO_3^- and Ca^{2+} occur in the chemical composition of waters in all elevation ranges, but their share is changing as, locally, other ions (Mg^{2+}, SO_4^{2-}, Na^+, and sometimes NO_3^- and others) have greater significance. In the Western Tatras, the highest share of Na^+, K^+, SO_4^{2-}, Cl^-, and NO_3^- is observed in springs situated at an elevation of 1,300-1,700 m a.s.l., but it decreases above and below this elevation range.

Spring waters of TNP may be assigned into 13 hydrochemical classes, but according to Szczukariew-Prikłoński, strict criteria there are 8 hydrochemical classes (98.1%), and the remaining five create the so-called "new classes." HCO_3-Ca-Mg is the most common class among the spring waters of TNP, and in the Western Tatras it is usually the dominant one (>50%), while in the High Tatras waters of this class take fourth place (Table 3).

The pattern of increasing the number of classes with the increase of absolute height may be observed in the hypsometric variability in the chemical composition of TNP spring waters, starting from two classes at the foothills to six classes from 1,300 to 1,700 m a.s.l. (Fig. 4, Table 3). It is worth noting that hydrochemical variability of spring waters in the Western Tatras is greater (max. 7 classes) than in the High Tatras (max. 5 classes).

The analysis of the frequency of the occurrence of hydrochemical classes in each TNP elevation indicates the dominance of complex water containing three types of ions HCO_3-Ca-Mg up to a height of 1,700 m a.s.l. The HCO_3-SO_4-Ca-Mg springs appear more frequently with increasing elevation from the foot of the mountains. It is noteworthy that this class of spring waters does not occur in the High Tatras from an elevation of 1,400 m a.s.l., while in the Western Tatras this class is still significant in elevations of 1,200-1,400 and 1,600-1,700 m a.s.l. The highest parts of the mountains also are characterized by the fact of frequent occurrence of waters "off classification," of which the water containing four types of ions HCO_3-SO_4-NO_3-Ca is the most frequent in the High Tatras. The share of the two most numerous hydrochemical classes (HCO_3-Ca-Mg and HCO_3-Ca) of spring waters systematically decrease from the foot where in the range of 900-1,000 m a.s.l. it is ~97% to only 10% in the highest ridge part of the High Tatras (Fig. 4).

Discussion

Generally, the chemical composition of water depends on the relationship of precipitation, and the geological

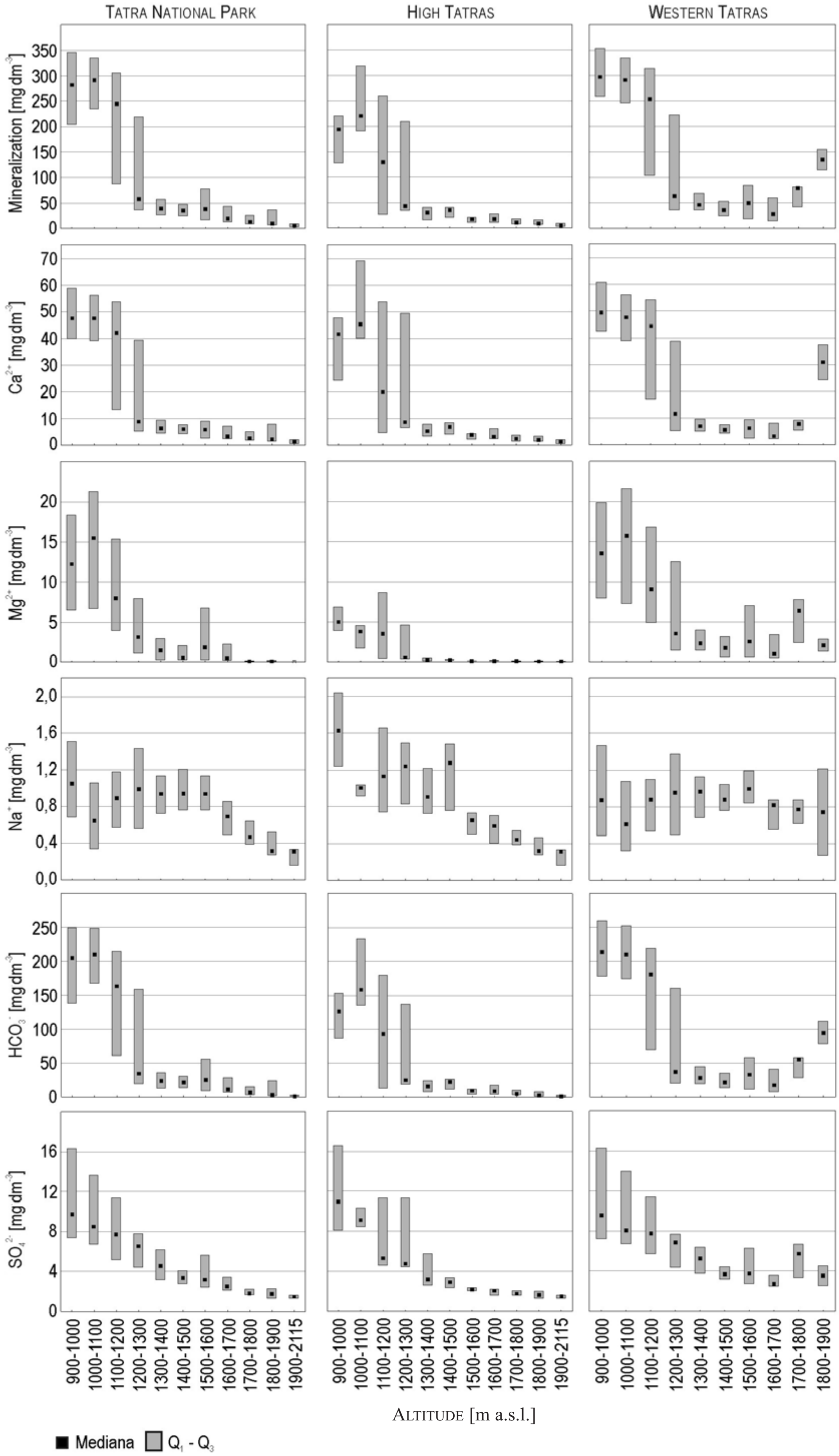

Fig. 3. Changes in ion concentrations in spring waters, with elevation.

Table 3. Total springs in each hydrochemical class in elevation ranges.

Elevation [m a.s.l.]	Region	HCO_3-Ca	HCO_3-Ca-Mg	HCO_3-SO_4-Ca	HCO_3-SO_4-Ca-Mg	HCO_3-SO_4-Ca-Mg-Na	HCO_3-SO_4-Ca-Na	HCO_3-SO_4-NO_3-Ca	Other	Total
900-1,000	**TNP:**	**25**	**59**	**0**	**3**	**0**	**0**	**0**	**0**	**87**
	High Tatras	11	7	0	0	0	0	0	0	18
	Western Tatras	14	52	0	3	0	0	0	0	69
1,000-1,100	**TNP:**	**34**	**99**	**0**	**11**	**0**	**1**	**0**	**0**	**145**
	High Tatras	6	2	0	0	0	1	0	0	9
	Western Tatras	28	97	0	11	0	0	0	0	136
1,100-1,200	**TNP:**	**26**	**90**	**8**	**18**	**0**	**5**	**1**	**0**	**148**
	High Tatras	7	11	7	0	0	5	1	0	31
	Western Tatras	19	79	1	18	0	0	0	0	117
1,200-1,300	**TNP:**	**21**	**35**	**6**	**30**	**0**	**4**	**0**	**0**	**96**
	High Tatras	16	2	2	0	0	3	0	0	23
	Western Tatras	5	33	4	30	0	1	0	0	73
1,300-1,400	**TNP:**	**27**	**40**	**22**	**32**	**1**	**13**	**0**	**0**	**135**
	High Tatras	18	6	17	0	0	12	0	0	53
	Western Tatras	9	34	5	32	1	1	0	0	82
1,400-1,500	**TNP:**	**27**	**28**	**4**	**6**	**5**	**5**	**0**	**2**	**77**
	High Tatras	23	0	1	0	0	2	0	2	30
	Western Tatras	2	28	3	6	5	3	0	0	47
1,500-1,600	**TNP:**	**5**	**40**	**7**	**5**	**1**	**9**	**0**	**3**	**70**
	High Tatras	4	0	2	0	0	2	0	0	8
	Western Tatras	1	40	5	5	1	7	0	3	62
1,600-1,700	**TNP:**	**8**	**15**	**12**	**9**	**1**	**3**	**0**	**0**	**48**
	High Tatras	7	0	8	0	0	0	0	0	15
	Western Tatras	1	15	4	9	1	3	0	0	33
1,700-1,800	**TNP:**	**15**	**6**	**15**	**0**	**0**	**3**	**2**	**1**	**42**
	High Tatras	15	0	15	0	0	3	2	1	36
	Western Tatras	0	6	0	0	0	0	0	0	6
1,800-1,900	**TNP:**	**6**	**0**	**1**	**0**	**0**	**1**	**5**	**1**	**14**
	High Tatras	4	0	1	0	0	1	5	1	12
	Western Tatras	2	0	0	0	0	0	0	0	2
1,900-2,115	**TNP:**	**1**	**0**	**2**	**0**	**0**	**2**	**4**	**1**	**10**
	High Tatras	1	0	2	0	0	2	4	1	10
	-	-	-	-	-	-	-	-	-	-
Total	**TNP:**	**195**	**412**	**77**	**114**	**8**	**46**	**12**	**8**	**872**
	High Tatras	112	28	55	0	0	31	12	5	245
	Western Tatras	81	384	22	114	8	15	0	3	627

structure of the ground, soils, and plants [40]. Related to the hypsometry, the presented chemical composition of springs draining the high-mountain part of TNP, where the characteristic zoning of many environmental elements occurs, confirms the well-known regularity of the ion concentration increase from ridges to the foot of the mountains [10, 11, 22-24, 26, 30]. According to Małecka [9, 10, 23], groundwaters in the top part of the Tatras are 90% formed by the chemical composition of precipitation. The importance of bedrock is less because of the high resistance to leaching of crystalline rocks and very fast water circulation [10, 30, 41].

The effect of geological structures is reflected particularly in the concentration of Mg^{2+} in the crystalline part of TNP. Igneous rocks of the High Tatras are characterized by lower content of this ion, while it is significantly higher in metamorphic rocks of the Western Tatras [42, 43]. This geological regularity is expressed by significantly higher Mg^{2+} concentrations in springs of the Western Tatras than in springs of the High Tatras, and was already noticed in the 1960s by Oleksynowa and Komornicki [8, 12-22]. Ion concentrations and spring water mineralization slowly increase from the peaks of the Tatras to the elevation of 1,300 m a.s.l., although the geological structure remains the same (crystalline rocks). Increased ion concentration is associated with prolonged water circulation within the slope, particularly in the moraine deposits, which are characterized by higher retention capacity [33, 41]. According to Małecka [23], there is an increase in the concentration of ions, especially Na^+ and K^+ in waters circulating in moraine deposits. Lower parts of the Tatras are characterized by several times higher mineralization, since they are constructed from a variety of sedimentary rocks, mostly carbonate rocks with easily soluble calcite. According to a geological map at a scale 1:30,000 [28], the majority of these are: Mesozoic-Paleogene limestone, dolomites, marls, and conglomerates, and sometimes sandstones, shales, and others. In this part of the TNP the factors affecting high concentrations of Ca^{2+}, Mg^{2+}, and HCO_3^- are the large share of karst and definitely longer time of water circulation in the massif.

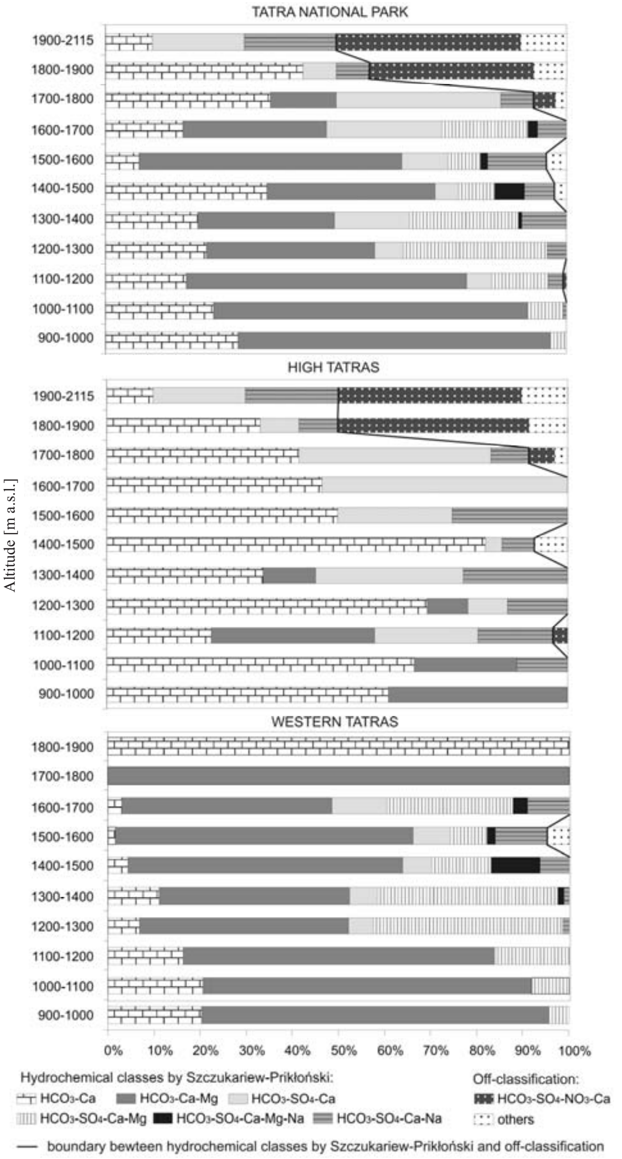

Fig. 4. The share of hydrochemical classes in elevation ranges.

The effect of precipitation on the chemical composition of water does not exceed 30% in the lower parts of the Tatras [10]. In the mountain forest zone there is a low concentration and share of NO_3^- and slightly higher concentration of SO_4^{2-}. The origin of SO_4^{2-} in the alpine zone is complicated, because apart from weathering of rocks, these ions are derived from precipitation and result from biological and biochemical processes, particularly in soils [44, 45]. The above brief discussion shows that the concentration and origin of ions in waters draining high mountain slopes is affected by numerous factors, therefore hydrochemical classes were used to determine the general regularities in the hypsometric and spatial distribution of chemical composition of spring waters at TNP. Chowaniec [30] distinguished 18 hydrochemical types of water, from containing two to six types of ions, in the western part of the Polish Carpathians. Based on the performed research, it may be stated that the spring waters of TNP belong to 13 hydrochemical classes: from containing two to five types of ions. So far, studies have shown that waters of the Tatra Mountains contain from two to three types of ions: HCO_3-Ca, HCO_3-Ca-Mg [10, 46]. Indeed, the share of these two classes is dominant (~70%), and in lower parts of the mountains it is even >90%. However, in the upper part of TNP their share is reduced to <50%, and in the highest elevation range it is only 10%. Certain regularities can be observed with regard to the chemical composition of spring waters of the High and Western Tatras, particularly with varying concentrations and shares of SO_4^{2-} and Mg^{2+} in waters, which is usually related to the geological structure. In the Western Tatras HCO_3-Ca-Mg types of waters are predominant, but the second largest group consists of springs with HCO_3-SO_4-Ca-Mg water types. HCO_3-Ca springs are predominant in the High Tatras, and the second largest group is HCO_3-SO_4-Ca. Małecka also mentioned a large share of waters containing four types of ions: HCO_3-SO_4-Ca-Mg [47], while waters containing HCO_3-SO_4-Ca were referred to by Chowaniec [30]. Waters containing SO_4^{2-}:

type SO_4-HCO_3-Ca occur in the crystalline part, type SO_4-HCO_3-Mg-Ca occur in the mountain part, and type HCO_3-Mg-Ca in the peak part in the hydrochemical regions distinguished by Kostrakiewicz [26]. It is worth noting that waters with Na^+ appear in the upper parts of the Tatras.

Conclusions

The results showed greater hydrochemical diversity of spring waters of shallow circulation than has been demonstrated in the existing hydrochemical reference books. Regardless of height and geological structure, HCO_3^- and Ca^{2+} generally occur in each hydrochemical class. Most often Mg^{2+}, SO_4^{2-}, and Na^+ and less frequently NO_3^- are the differentiating ions that form hydrochemical classes and in various combinations produce 13 hydrochemical classes of spring water. The geological structure of TNP in a natural way implies fundamental hydrochemical differences between springs of the High and Western Tatras, which concerns not only the well-known relationship referred to mineralization. The predominance of springs containing Mg^{2+} (HCO_3-Ca-Mg) is characteristic of the Western Tatras, while in the High Tatras there are usually spring waters containing two types of ions: HCO_3-Ca often having an additional SO_4^{2-} ion, forming complex water containing three types of ions: HCO_3-SO_4-Ca. The role of absolute height in the formation of chemical composition of spring waters is reflected throughout TNP as a systematic reduction of the importance of two major hydrochemical classes of spring waters (HCO_3-Ca, HCO_3-Ca-Mg) in favor of waters containing a large share of SO_4^{2-}, particularly in the High Tatras. In the middle part of TNP, in the range of 1,300-1,700 m. a.s.l., we may indicate the presence of spring water zones characterized by the greatest hydrochemical variation, expressed as the number of hydrochemical classes. The lower parts of the mountains are characterized by low hydrochemical diversity for the whole Tatra Mountains, while the ridge part of the High Tatras is characterized by considerable diversity, which is particularly emphasized by the fact of frequent occurrence of waters in which the share of NO_3^- is >20%.

In relation to elevation intervals, there is a decrease in the share of springs belonging to the two most common classes (HCO_3-Ca, HCO_3-Ca-Mg), from 97% at the elevation of 900-1,000 m to only 10 % in the ridge part of the High Tatras. They are often replaced by waters with a large share of SO_4^{2-} and sometimes Na^+. The complicated geological structure of TNP results in a huge natural hydrochemical diversity of spring waters.

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