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Spatial variation of the chemical composition of lake waters in the Tatra National Park

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Abstract: The aim of this study is to determine the factors affecting the spatial variation of the chemical composition of lake waters in the Tatra Mountains. In most cases, the lake waters are acidic and very dilute, with a low ionic content and low conductivity values. In general, HCO_3^- is the predominant anion and Ca^{2+} is the predominant cation in the chemical composition of the analysed water samples. Among nutrients, NO_3^- is the dominant form of nitrogen, but also NH_4^+ may be found in lake waters. By using principal component analysis (PCA) two factors have been identified that explain 63.6% of the variation in the chemical composition of water. Factor 1, which explains 43.2% of the total variability, is associated with Ca^{2+}, SO_4^{2-}, HCO_3^-, Na^+, pH and lake area and is related to weathering and atmospheric deposition. Factor 2 explains 20.4% of the total variability and is associated with Mg^{2+}, K^+, Cl^- and with lake altitude. In terms of chemical composition, based on the projection of cases of the first and second factor, the lakes in the Tatra Mountains may be divided into four groups, representing the following: lakes situated within the subalpine forest at the lowest altitude (<1300 m a.s.l.), characterized by medium mineralization (~14 mg dm^{-3}) and the highest concentration of NH_4^+ and Cl^- (Group I, 8 lakes); slightly alkaline lakes, with the lowest average acidification, medium mineralization (~31 mg dm^{-3}) and the highest concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, SO_4^{2-}, and low concentrations of NO_3^- (Group II, 2 lakes); small lakes (<0.01 ha) located within the alpine meadow and the nival zones at high elevations with the lowest mean mineralization (~4.3 mg dm^{-3}), with the highest ammonium contribution to the sum of ions among all lakes and the largest sensitivity to acidification (Group III, 13 lakes); large lakes with high mineralization and slightly acidic pH (Group IV, 26 lakes) and medium mineralization (~31 mg dm^{-3}).

Key words: chemistry, Tatra National Park, principal component analysis

Introduction

The chemical composition of lakes in mountain areas is usually affected by natural conditions, such as geological structure, lithological cover, topography, climatic conditions, vegetation and soil properties (Psenner and Catalan 1994; Marchetto et al. 1995). Previous studies, especially Scandinavian ones, show that the lakes located in remote areas are particularly susceptible to anthropogenic impact (Skjelkvale and Wright 1998; Skjelkvale et al. 2001). In the highest parts of the Tatra Mountains, in the Tatra National Park, lakes are also subject to various forms of anthropogenic pressure. The main threats towards the Tatra lakes include precipitation-related pollution (i.e. acid rains), intensive mountaineering and the effect of mountain hostel infrastructure (Fott et al. 1994; Kownacki et al. 1996; Kopáček et al. 2001; Kownacki and Łajczak 2002; Rzychoń and Worsztynowicz 2008; Kurzyca et al. 2009).

Waters of the Tatra lakes have been studied since the late nineteenth century in terms of both their origin and hydrochemical parameters (Dziewulski 1880). In the last two decades of the twentieth century, the lake ecosystems were studied in the context of the impact of air pollution, acid rains and climatic changes on their quality. Geochemical and biological studies of high mountain lakes, including the Tatra lakes, were conducted within the projects AL:PE, MOLAR, EMERGE (Mosello et al. 1995; The MOLAR Water Chemistry Group 1999).

The aim of this study was to determine the factors affecting the spatial variability of the chemical composition of water in the Tatra lakes.

Study area

The Tatras are the highest mountains (Mount Gerlach 2655 m a.s.l.) in the Carpathians and are located on the border of Poland and Slovakia (Figure 1). They are mountains of Alpine orogeny and have a high-mountain nature. They are characterized by altitudinal zonation. The mean annual temperature decreases as altitude increases from 4 to 6°C at the foot to −2 and −4°C in the highest parts (Hess 1965). Mean annual total precipitation is high and varies from 1,117.6 mm (Zakopane) to 1,797.7 mm (Kasprowy Wierch / Mount Kasprowy) (Żmudzka 2010). Five altitudinal zones can be distinguished: lower subalpine forest, upper subalpine forest, dwarf pine zone, alpine meadow zone and nival zone (Piękoś-Mirkowa and Mirek 1996). The geological structure is of belt character. The southern part forms the crystalline core and is built of igneous and metamorphic rocks. In contrast, the northern part (tatric and sub-tatric series) is built of sedimentary rocks (Bac-Moszaszwili et al. 1979). The area of the Tatras is legally protected (Tatra National Park, UNESCO Biosphere Reserve, Natura 2000). The studied lakes are of glacial origin and the majority of them are located within the crystalline core of the Tatras (Bac-Moszaszwili et al. 1979).

Methods

Hydrochemical surveys were conducted twice – in 2007 and 2008 – and 49 lakes in total in the Tatra National Park were considered. Temperature, pH and electrical conductivity (EC_{25oC}) were measured during field work using Mutli 350i (WTW) meters equipped with a combined glass electrode with a gel electrolyte type POLYPLAST PRO (Hamilton) and LR-325/01 (WTW) conductivity sensor with constant k = 0.1. Additionally, CPC 401 and CX 401 (Elmetron) meters with glass electrodes ERH-11 and conductivity cells CFT-201 (k = 0.1) and CDT-2 (Hydromet) with constant k = 0.45 were used in the field. Water samples were collected into polyethylene bottles with a volume of 0.5 dm^3 at the lake shores or from their outflows. pH and conductivity were measured again in the laboratory and the chemical composition of water was determined by ion chromatography in the Hydrochemical Laboratory of the Institute of Geography and Spatial Management of the Jagiellonian University. Two chromatographic modules (DIONEX ICS-2000) enabled the simultaneous separation and determination of 14 ions: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Li^+, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, F^-, Br^-. The gradient elution (KOH) was used in the anion module equipped with

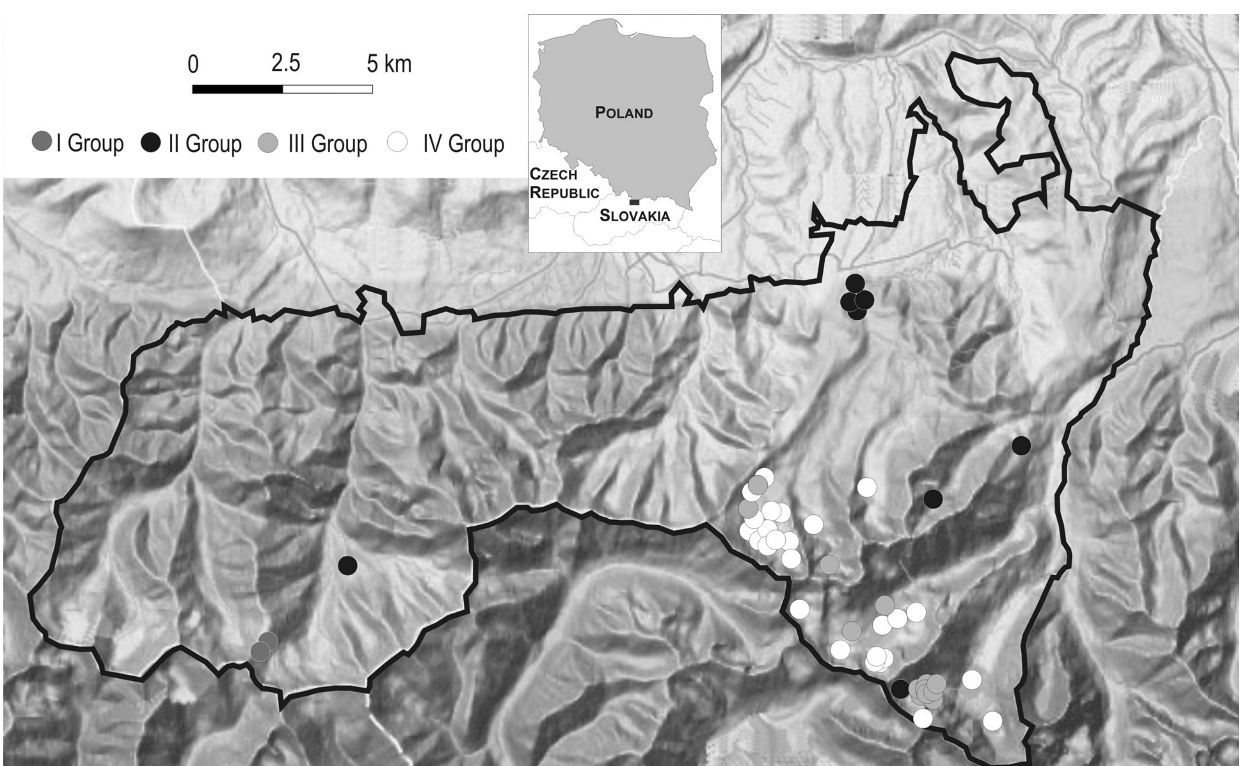

Fig. 1. Study area and spatial diversity of lake groups

an AS18 column (2 mm) and suppressor ASRS 300 (2 mm), while isocratic elution (MSA) was used in the cation module equipped with a CS16 column (5 mm) and suppressor CSRS 300 (4 mm).

The quality of the analytical results was checked using certified reference materials: AES-02 –a low pH acid rain sample; and Trois-94 –a coloured soft water from Quebec. For each sample the ionic balance was also calculated. Mineralization (TDS) was calculated as the sum of concentrations of determined ions expressed in mg dm^{-3} Watersheds of the sub-catchments were identified based on mapping and geographical and morphological characteristics, i.e. area and altitude, geological structure and land cover, were determined for lakes and their sub-catchments.

Statistical analyses were performed in STATISTICA 10. The interpretation of the chemical composition of waters was conducted both for the ion concentrations and their percentage contribution to the total ionic content. To organize the information on the chemical composition of lakes, waters were divided into several types. The name of the hydrochemical types included ions whose share was ≥10% μeq dm^{-3} in relation to the group of anions or cations. In order to determine the factors affecting the spatial variability in the chemical composition of waters, the principal component analysis (PCA) was used, based on 12 parameters. Two parameters were related to the morphometric characteristics of lakes: altitude (m a.s.l.) and area (ha), while the remaining variables were pH and concentration of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}, NO_3^{-}, F^{-}. Calculations were performed using standardized and normalized data. Cattell's scree test was used to limit the number of analysed factors (Cattell 1966). The analysis was performed on both the ion concentrations (mg dm^{-3}) and their relative contribution to the total ionic content (μeq dm^{-3}).

Results

In terms of the natural characteristics, the analysed lakes are extremely different. The largest group consists of the lakes with a small area up to 0.01 ha (47%); the second group is formed by slightly larger lakes – from 0.01 to 1 ha – 30.6%; while the lakes with an area >1 ha constitute 22.5%. Morskie Oko (34.93 ha) is the largest lake, while the Mnichowe and Szpiglasowe Stawki lakes are the smallest ones. Toporowy Stawek No. 4 is located at the lowest elevation (1093 m a.s.l.), and the highest is Zadni Mnichowy Stawek (2070 m a.s.l.). As regards the area land cover of the sub-catchments, the lakes are mostly located within the alpine tundra zone (Table 1).

The analysis of the chemical composition of the Tatra lake waters showed a significant variation in the ion concentrations (mg dm^{-3}) and their relative contribution to the total ionic content (Table 2). The chemical composition of waters is dominated by HCO_3^{-} among anions (34.63% μeq dm^{-3}) and by Ca^{2+} among cations (38.20% μeq dm^{-3}). Large variability among cations was observed, especially in the case of Mg^{2+} as shown by the coefficient of variation (Cv = 183.2%), SO_4^{2-} and nitrogen compounds. Among nutrients, mineral nitrogen in the form of NO_3^{-} and less often NH_4^{+} is usually found in the lake waters. The majority of lake waters are acidic, which is confirmed by numerous studies of the Tatra lakes (Rzychoń 1998, 2009; Fott 1994; Kopáček et al. 2001; Rzychoń and Worsztynowicz 2008). The values of pH of lake waters ranged from 4.61 to 7.40 and the median value was 6.15 pH units. These lakes are characterized by extremely dilute waters, with conductivity values between 5.6 and 39.2 μS cm^{-1}. The contribution of nitrogen compounds to the total ionic content reached up to 18.77% μeq dm^{-3} in the case of NH_4^{+} and 12.77% μeq dm^{-3} for NO_3^{-}.

In terms of hydrochemical properties, the lake waters belong to 11 hydrochemical types (Table 3). These are simple or complex waters, from two- to five-ion. The most common types include complex three-ion waters: HCO_3–SO_4–Ca (32.7%) and waters belonging to a simple, two-ion type HCO_3–Ca (30.6%). It is noteworthy that also nutrients, even though present in low concentrations, are part of some hydrochemical types, forming unusual types with ions of anthropogenic origin, e.g.: HCO_3–SO_4–NO_3–Ca, HCO_3–Ca–NH_4. Due to low pH and extremely low mineralization of water, an element related to the H^{+} ion appeared in the hydrochemical type of water in several lakes (e.g. HCO_3–SO_4–H–Ca).

Principal component analysis (PCA) based on ion concentrations and environmental variables enabled the determination of two independent factors that explain most (63.6%) of the total variability (Table 4). Factor 1 explains 43.2% of the total variability and is associated with Ca^{2+}, SO_4^{2-}, HCO_3^{-}, Na^{+}, pH and lake area. Ca^{2+}, HCO_3^{-} and Na^{+} ions are related to the natural processes of weathering. Na^{+} and Ca^{2+} ions originate from the chemical weathering of aluminosilicates, e.g. quartz diorite, granite, sienna granite

Table 1. Lake characteristics

Lake	Valley	Land-cover	Area	Elevation
			[a]	[m a.s.l.]
Czarny	Pięciu Stawów	meadows	1270.0	1891
Mały	Pięciu Stawów	meadows	18.0	1664
to the north of Wielki	Pięciu Stawów	meadows	0.1	1696
Przedni	Pięciu Stawów	meadows	770.0	1668
Stara Koleba	Pięciu Stawów	meadows	0.5	1781
Szpiglasowy 1	Pięciu Stawów	meadows	0.1	1774
Szpiglasowy 2	Pięciu Stawów	meadows	0.1	1774
Szpiglasowy 3	Pięciu Stawów	meadows	0.1	1990
Szpiglasowy 4	Pięciu Stawów	meadows	0.1	1774
Wielki	Pięciu Stawów	meadows	3414.0	1553
Zadni	Pięciu Stawów	bare rock	647.0	1668
Siwy (Northern)	Kościeliska	meadows	4.6	1722
Siwy (Southern)	Kościeliska	meadows	3.7	1725
Smreczyński	Kościeliska	forests	75.0	1226
Zadni Mnichowy	Rybiego Potoku	bare rock	0.4	1863
Czarny Staw	Rybiego Potoku	meadows	2064.0	1470
Mnichowy 1	Rybiego Potoku	meadows	0.3	1779
Mnichowy 2	Rybiego Potoku	meadows	0.3	1836
Mnichowy 3	Rybiego Potoku	meadows	0.3	1795
Mnichowy 4	Rybiego Potoku	meadows	0.3	1825
Mnichowy 5	Rybiego Potoku	meadows	0.3	1854
Mnichowy 6	Rybiego Potoku	meadows	0.3	1831
Mnichowy 7	Rybiego Potoku	meadows	0.3	1516
Mnichowy 8	Rybiego Potoku	meadows	0.3	1858
Morskie Oko	Rybiego Potoku	dwarf	3493.0	1516
Na Kopkach	Rybiego Potoku	meadows	0.6	1794
Pod Wołoszynem	Rybiego Potoku	forests	1.0	1244
Staszica (Northern)	Rybiego Potoku	meadows	0.1	1625
Czarny	Sucha Woda	dwarf	1794.0	1575
Czerwony Pańszczycki	Sucha Woda	dwarf	30.0	1652
Czerwony Pańszczycki	Sucha Woda	dwarf	30.0	1653
Czerwony (Eastern)	Sucha Woda	meadows	15.0	1700
Czerwony (Western)	Sucha Woda	meadows	27.0	1697
Długi	Sucha Woda	meadows	156.4	1624
Dwoisty (Eastern)	Sucha Woda	dwarf	141.0	1652
Dwoisty (Western)	Sucha Woda	dwarf	90.0	1656
Kurtkowiec	Sucha Woda	dwarf	153.6	1095
Litworowy	Sucha Woda	dwarf	40.7	1620
above Zadni	Sucha Woda	bare rock	0.1	1881
Samotniak	Sucha Woda	dwarf	0.1	1594
Toporowy 1	Sucha Woda	forests	0.1	1133
Toporowy 2	Sucha Woda	forests	0.1	1129
Toporowy 3	Sucha Woda	forests	3,0	1123
Toporowy 4	Sucha Woda	forests	61.7	1093
Trójniak	Sucha Woda	dwarf	0.01	1620
Zadni	Sucha Woda	meadows	51.5	1856
Zielony	Sucha Woda	dwarf	376.4	1679
Zmarzły	Sucha Woda	bare rock	28.0	1794
Waksmundzkie Rówienki	Waksmundzka	forests	0.1	1278

Table 2. Characteristics of physico-chemical parameters of lakes (n = 49)

Feature	Unit	Mean	Median	Min	Max	$Q_{25\%}$	$Q_{75\%}$	CV [%]
$EC_{25°C}$	µS cm^{-1}	17.77	15.28	5.56	39.20	11.55	23.70	51.55
TDS	mg dm^{-3}	13.78	12.90	2.80	32.44	6.96	19.32	61.63
pH		5.42	6.15	4.61	7.40	5.19	6.99	14.74
Ca^{2+}	mg dm^{-3}	2.551	2.447	0.241	7.378	0.739	3.415	73.41
Mg^{2+}		0.258	0.105	0.034	2.354	0.084	0.156	183.22
Na^{+}		0.338	0.354	0.066	0.601	0.250	0.418	40.24
K^{+}		0.172	0.133	0.046	0.820	0.111	0.180	72.22
NH_4^{+}		0.138	0.042	0.002	1.159	0.018	0.210	159.01
HCO_3^{-}		7.789	6.031	1.077	21.503	2.302	11.055	76.31
SO_4^{2-}		1.590	1.544	0.560	3.056	1.040	1.982	37.86
Cl^{-}		0.200	0.158	0.043	0.589	0.129	0.246	53.69
NO_3^{-}		0.688	0.631	0.001	1.925	0.100	1.183	93.66
F^{-}		0.0181	0.0174	0.0003	0.0497	0.0115	0.0231	48.75
H^{+}	% µeq dm^{-3}	2.41	0.30	0.01	12.17	0.02	4.50	143.45
Ca^{2+}		32.01	38.20	13.75	44.86	21.06	41.48	34.26
Mg^{2+}		5.08	3.24	1.16	24.16	2.43	4.16	101.54
Na^{+}		5.12	4.64	1.39	15.89	3.21	5.57	54.87
K^{+}		1.85	1.06	0.28	6.13	0.79	1.93	91.96
NH_4^{+}		3.42	0.77	0.02	18.77	0.20	5.03	139.50
HCO_3^{-}		31.98	34.63	14.86	43.28	25.82	37.64	24.16
SO_4^{2-}		11.71	10.85	3.11	23.02	7.62	14.83	45.34
Cl^{-}		2.39	1.36	0.38	8.76	0.85	3.06	88.52
NO_3^{-}		3.32	1.78	0.00	12.77	0.58	5.83	101.28
F^{-}		0.34	0.32	0.01	0.89	0.18	0.45	55.67

Table 3. Diversity of hydrochemical types of lakes

Hydrochemical types	N	[%]	Cumulative [%]
HCO_3 – Ca	15	30.6	30.6
HCO_3 – SO_4 – Ca	16	32.7	63.3
HCO_3 – Ca – Mg	5	10.2	73.5
HCO_3 – SO_4 – Ca – NH_4	3	6.1	79.6
HCO_3 – Ca – NH_4	2	4.1	83.7
HCO_3 – SO_4 – Ca – Na	2	4.1	87.8
HCO_3 – SO_4 – NO_3 – Ca	2	4.1	91.8
HCO_3 – SO_4 – Ca – Mg	1	2.0	93.9
HCO_3 – SO_4 – H – Ca	1	2.0	95.9
HCO_3 – SO_4 – H – Ca – Na	1	2.0	98.0
HCO_3 – SO_4 – H – Ca – NH_4	1	2.0	100.0

Table 4. Factor matrix and accounted variance

Features	Factor 1	Factor 2
area of lakes (ha)	-0.65	0.23
elevation (m a.s.l.)	0.08	0.57
pH	-0.83	0.22
Ca^{2+}	-0.94	-0.11
Mg^{2+}	-0.48	-0.73
Na^{+}	-0.82	-0.07
K^{+}	0.12	-0.77
HCO_3^{-}	-0.83	-0.38
SO_4^{2-}	-0.84	-0.01
Cl^{-}	0.29	-0.74
NO_3^{-}	-0.67	0.43
F^{-}	-0.58	-0.08
Accounted variance [%]	43.2	20.4
Cumulative variance [%]	43.2	63.6

(Gawęda 2001, 2008). SO_4^{2-} originates from atmospheric deposition (dry and wet) and a part from the decomposition of organic matter. Factor 2 explains 20.4% of the total variability and is associated with Mg^{2+}, K^+ and Cl^- and with a negative relationship, with lake altitude. Different levels of magnesium concentration in lake waters derived from the geological structure and strictly refer to the lithological cover of lake catchments. Tatra granites are deficient in magnesium-containing minerals, while metamorphic rocks (gneisses, amphibolites) are richer in these minerals. The genesis of K^+ should be associated with processes of rock weathering and organic matter decomposition. In contrast, Cl^- ions are probably of atmospheric origin (precipitation).

Four groups (I, II, III, IV) of Tatra lakes can be distinguished (Table 5), based on the analysis of the projection of cases (lakes) in the plane of factors F1 and F2. The first group (I) consists of 8 lakes, situated within the subalpine forests (e.g. Toporowe Stawki). In terms of morphology, these are the lowest (<1300 m a.s.l.) Tatra lakes. They are characterized by medium mineralization (~14 mg dm^{-3}), the highest concentration of NH_4^+ and Cl^-, high concentration of Mg^{2+} and K^+, F^- and low concentration of Ca^{2+}, HCO_3^-, SO_4^{2-} and NO_3^-. The medium hydrochemical type is represented by simple HCO_3–Ca waters; however, also Mg^{2+}, NH_4^+, SO_4^{2-} and Na^+ ions can occur in the water type. The second group (II) includes only two lakes, i.e. Siwe Stawki N and S located in the Kościeliska Valley (Fig. 1). They are characterized by a medium mineralization (~31 mg dm^{-3}) and the highest concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, and SO_4^{2-} among all lakes, and low concentrations of NO_3^-. The lake waters are slightly alkaline and their average acidification is the lowest in the Tatras. The average hydrochemical type is HCO_3–Mg–Ca. In terms of hydrochemical characteristics these lake waters are extremely interesting, because the relevance of magnesium in the chemical composition of water is greater than that of calcium. Group III consists of 13 small lakes (<0.01 ha), located at high elevation. The majority of them are Mnichowe Stawki from the Rybi Potok Valley. They are located within the alpine meadow and the nival zones. This type of waters is represented by the group of lakes with the lowest mean mineralization (~4.3 mg dm^{-3}) and the largest sensitivity to acidification. The majority of ions in the lake waters – similarly as in the case of mineralization – is characterized by the lowest mean concentration of, for example, Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-}, NO_3^- and F^-. Only the ammonium concentration is high and its contribution to the sum of ions reaches a maximum of 15.54% μeq dm^{-3}. An extremely interesting feature of this group of lakes is the greater relevance of Na^+ with respect to Mg^{2+} in the chemical composition of water. The average hydrochemical type is HCO_3–SO_4–Ca. The contribution of SO_4^{2-} in the chemical composition is the highest among all groups of lakes. The mosaic character of hydrochemical types is the characteristic feature of this group of lakes, as the contribution of 5 ions (H^+, Na^+, NH_4^+, SO_4^{2-}, NO_3^-) to the total ionic content is greater than 10% μeq dm^{-3}. In general, magnesium is absent in this hydrochemical type (max = 9.93% μeq dm^{-3}).

Table 5. Characteristics of chemical parameters of lake groups

Feature [mg dm^{-3}]		Group I	Group II	Group III	Group IV
Mineralization	Mean	13.74	31.47	4.33	17.15
	Min	6.96	31.20	2.80	8.51
	Max	19.56	31.74	10.78	32.44
Ca^{2+}	Mean	1.82	3.45	0.48	3.74
	Min	0.63	3.42	0.24	1.66
	Max	2.89	3.48	1.40	7.38
Mg^{2+}	Mean	0.46	2.32	0.06	0.13
	Min	0.10	2.29	0.03	0.07
	Max	1.12	2.35	0.13	0.30
Na^+	Mean	0.33	0.48	0.17	0.41
	Min	0.13	0.46	0.07	0.29
	Max	0.53	0.50	0.35	0.60
K^+	Mean	0.32	0.39	0.15	0.12
	Min	0.14	0.37	0.05	0.08
	Max	0.82	0.41	0.24	0.18
NH_4^+	Mean	0.43	0.15	0.17	0.03
	Min	0.03	0.09	0.02	0.00
	Max	1.16	0.21	0.49	0.23
HCO_3^-	Mean	8.44	21.26	1.92	9.49
	Min	2.30	21.02	1.08	3.07
	Max	13.45	21.50	6.95	20.57
SO_4^{2-}	Mean	1.22	3.03	0.99	1.89
	Min	0.56	3.00	0.56	1.39
	Max	2.25	3.06	1.50	2.77
Cl^-	Mean	0.36	0.22	0.20	0.15
	Min	0.15	0.20	0.04	0.08
	Max	0.59	0.25	0.35	0.28
NO_3^-	Mean	0.22	0.15	0.14	1.15
	Min	0.00	0.12	0.00	0.17
	Max	0.73	0.17	0.94	1.92

Group (IV) comprises a group of 26 large lakes (e.g. Morskie Oko, Czarny Staw), characterized by slightly acidic pH and high mineralization. Among ions, Ca^{2+}, NO_3^- and F^- show the greatest mean concentration; this group also shows high concentrations of HCO_3^-, SO_4^{2-} and a low concentration of Mg^{2+}, K^+, NH_4^+, Cl^-. The average hydrochemical type of lake waters is HCO_3–Ca. Additionally, the HCO_3–SO_4–Ca type of waters occurs frequently and yet only NO_3^- happens to be the type-forming ion.

Discussion

The chemical composition of the Tatra lakes is characterized by extremely dilute waters, with low buffer capacity and the highest concentrations of main ions associated with shallow hypergenic circulation. The Tatra crystalline core has low water permeability as it is cracked only to the depth of 20-30 m (Chowaniec 2009). Therefore, water circulation in crystalline formations occurs only in the shallow, surface crack zone. There is no common reservoir of underground water but many separate slitlike systems. Because of the high inclination of the mountain sides, water circulation is fast, so any longer water retention in the covers is inhibited. Some small water-bearing systems were formed within glacial moraines and fluvioglacial structures (Ziemońska 1966, 1973, 1974; Łajczak 1988, 1996; Małecka 1989). Very low ionic concentrations in lake waters result from the resistance of crystalline rocks to weathering (Oleksynowa 1970; Łajczak 2006; Małecka et al. 2007; Chowaniec 2009). Low levels of ion concentration in lake waters have also been observed in other mountain regions, e.g. in Scandinavia (Camerero et al. 2009). The literature concerning the Tatra Mountains has demonstrated that lakes are usually acidic (pH <7) (Rzychoń 1998, 2009; Kopáček et al. 2004; Kopáček et al. 2006; Stuchlík et al. 2006). Studies have shown that although acidic water prevails, still 20% of lake waters are not acidified. This applies especially to large lakes belonging to group IV, in which 35% is represented by water of slightly alkaline pH (>7 pH). In other mountain regions of Europe (the Alps) and South America (Patagonia) lake waters are predominantly alkaline (Rogora et al. 2008; Camerero et al. 2009). Lakes in group III are entirely different in terms of acidification, as all waters in this group were acidic with pH <5.40. Among cations, regardless of the type, Ca^{2+} occurs usually in the highest concentration, and then depending on the lithology, there is much lower concentration of Mg^{2+} (group I and II) or Na^+ (group III and IV). In the study of Camarero at al. (2009) it was shown that calcium is the dominant cation in the lake waters in Europe and also depends on the lithology. It needs to be stressed that in lakes belonging to groups I and II the relevance of Mg^{2+} is greater than that of Na^+, whereas the ratio is different in lakes of groups III and IV. Lithological-mineralogical studies of granitoids of the High Tatras conducted by Gawęda (2008); Burda and Gawęda (2009) showed that these rocks are characterized by a high proportion of sodium while there are virtually no magnesium-containing minerals. Thus, the fact that the concentration of sodium exceeds the concentration of magnesium in lake waters results from lithological features. It is worth noting that only in group II is Mg^{2+} more important in the chemical composition of water than Ca^{2+}. This is an extremely rare hydrochemical relation, considering that the analysed waters are very low mineralized. Magnesium in the Western Tatras is probably of amphibolite origin, which can be verified on the Geological map of the Tatra Mountains on a scale 1 : 50 000 (Nemčok et al. 1994). Studies by Gawęda (2001) showed that the concentration of magnesium in the Western Tatras is high in the mica group (e.g. biotite, muscovite), and it is particularly high in the pegmatite segregation in alaskites of the Starorobociański Wierch (Mount Starorobociański) and in chlorites of biotite alaskite from the Western Tatras, e.g. on Ornak Ridge (MgO 10.86-11.71%). Studies by Żelazny (2012) showed that the rCa^{2+}/rMg^{2+} ratio in the spring waters draining metamorphic rocks in some areas of the western Tatras (e.g. the slope of Czubik in the catchment of Jarząbczy Potok) is less than one, i.e. in terms of equivalence there is more Mg^{2+} than Ca^{2+}. Thus, a source of magnesium is associated with the lithological and mineral structure of metamorphic rocks of some parts of the Western Tatras. Probably high concentrations of K^+ were observed in lakes located in the forest zone, which should be associated with the organic matter decomposition. Various studies emphasized that K^+ ions originated from the decomposition of organic matter and from soil (Avila et al. 1992; Likens et al. 1994). The sequence of anion concentrations is typically represented by the order: $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$ except for waters from the group IV, in which the concentrations of NO_3^- are greater than Cl^-. The chemical composition of lake waters in the upper parts of the Tatras depends only to a small extent on soil cover, due the lack of it or to the fact that soils are poorly developed. Also within the subcatchments of lakes there is virtually no vegetation. What mainly influences the chemical composition of the lakes in this group is atmospheric deposition. A similar relationship was found in Camarero's research (Camarero et al. 2009), where the source of NO_3^- and NH_4^+ ions was also related to atmospheric deposition. The observed elevated concentrations of nutrients, especially NH_4^+ and NO_3^- in lakes located at high elevations above sea level are usually the result of poor assimilation of those ions by plants. When atmospheric deposition exceeds the uptake capacity by plants and microorganisms, the NO_3^- excess is leached into water and increases its acidity (Rzychoń 2009). On the other hand, the group of lakes located within the alpine forest contains lower concentrations of NO_3^- ions due to the vegetation-related uptake. Plants, by taking up nitrogen compounds cause the release of H^+ and OH^- ions, thus increasing acidification of soil and water (Rzychoń 2009). Kopáček et al. (2006) noted that the poorer the vegetation and soil cover, the greater the concentration of NO_3^-. High concentrations of NO_3^- were recorded in waters of large lakes, such as Morskie Oko, Czarny and Zielony Staw Gąsienicowy as well as Czarny Staw Pod Rysami. Perhaps this is the result of conducting the studies in late summer, when the plant demand for nitrogen is not as high as in spring or early summer. The environmental pressure associated with massive tourism probably has a certain effect on the nitrogen concentration. It is also worth noting that the stock of fish in lakes, which results in an increased fertility of the Tatra lakes, is an additional aspect affecting the increase in nutrient concentration in Morskie Oko, Czarny and Zielony Staw Gąsienicowy and Kurtkowiec (Kownacki et al. 1996).

Conclusion

The analysis of the chemical composition of lake waters in the Tatra National Park showed significant spatial variation of pH, level of mineralization and ionic concentrations as well as their structure expressed by hydrochemical types. Two independent main factors, determined by PCA, explain ~63.6% of the total variability of the chemical composition of lake waters. Of the two morphometric features considered in the analysis, lake size is more strictly associated (factor 1) with ion concentration and pH value of water. The second environmental variable affecting ion concentration is the ordinate of its altitude, which is strictly negatively associated with the concentration of magnesium, chlorides and potassium. This factor, strongly differentiating chemical composition of lake waters, can be called the lithological one. The distinguished four groups of lakes revealed the differences in the chemical composition of lake waters, resulting from the geological structure and the lithology in particular. It is worth noting that the generalization of the chemical composition allows subtle differences to be identified in the chemical composition of water resulting from different geological structure. Frequent occurrence of hydrochemically atypical waters is associated with extremely low concentrations of main ions. In these cases small changes in their concentrations, also of the mineral forms of nitrogen (NO_3^-, NH_4^+), result in the creation of many hydrochemical types that are rare in nature. This mosaic variation of the chemical composition of water is, however, of a natural character.

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