

# The hydrochemistry of high-altitude lakes in selected mountain ranges of Central and Southern Europe

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**Abstract:** The results of hydrochemical investigations of 29 high-altitude lakes in two mountain regions of Europe (Carpathian and Rhodope Mountains), diversified genetically and with respect to present morphogenetic processes, are discussed in relation to local geological, climatic, hydrological conditions and anthropopression. The differences in concentration of major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) are strongly correlated with the altitude of the lakes, and chemical diversity of their water reflects primarily the differences in intensity of chemical weathering and, to a lesser extent, the difference in mineral composition of bedrock. The characteristics of geological structure of the surroundings of lake basin is reflected in chemistry of the lakes located in the area of occurrence of strongly weathered series of metamorphic rock. The ion ratios in water of the investigated lakes are important indicators of anthropogenic influence.

**Keywords:** high-altitude lakes, regional limnology, water chemistry, Carpathian Mountains, Rhodope Mountains

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## Introduction

High-altitude lakes are objects with an extremely low level of biogeochemical equilibrium. They are located in areas consisting mostly of crystalline rock covered with shallow skeletal soils (leptosol, regosol) with scarce plant cover and harsh climate, and they appear to be very susceptible to any environmental changes. Low intensity of weathering in the alpine and subalpine environments makes the hydrochemistry of high-altitude lakes an excellent indicator of not only local anthropogenic interactions but also long-range effects related mainly to atmospheric transport of fossil fuel combustion products (Fott, 1994; Kopáček et al., 1995). High-altitude lakes are also unique due to dissimilarity of local geological and climatic conditions. The relations between geochemical structure of the drainage area and hydrochemistry of high-altitude lakes of various geographical regions reflect the differences in both intensity and direction of denudation processes, and affect their biological diversity. They also allow the study of adaptation processes of living organisms to variable climatic conditions and anthropogenic effect on their natural environment.

The present work aims at describing hydrochemical uniqueness of lakes in two alpine regions of Europe, differing genetically and with respect to present morphogenetic processes: Carpathian Mountains – young fold systems subjected to intense mechanical weathering and domination of gravitational processes (Tatra and Făgăraș Mountains), and Rhodope Mountains – old horst formations subjected to mechanical and chemical weathering, with seasonal flush and local gravitational processes (Pirin, Rila). Additionally, the extent of local transformations of water ecosystems resulting from increasing tourism was estimated.

## Area of investigations

The investigated lakes are located in two geologically different high alpine systems of Europe: Carpathian and Rhodope Mountains. The former system is represented by the lakes of geologically younger Western (Tatra) and Southern (Făgăraș) Carpathians – structural units formed during the Alpine orogenesis, while the latter system is represented by the lakes of Rila and Pirin massifs, being the highest parts of the

Rhodopes, formed during the Hercynian orogenesis and then re-formed during the Alpine period.

The Rila and Pirin massifs, being of horst mountain nature, consist primarily of Paleozoic (Hercynian) igneous rocks (granite, diabase, gneiss), forming intrusive structures within the older Precambrian bedrock made of metamorphic rocks (schist, marble).

The mountain ranges Tatra and Făgăraș, constituting northern and southern extremes of the Carpathian arc, are young fold structures. This orogen has a complex geological structure with well defined flysch, calciferous, magmatic and metamorphic zones of different age. However, in the highest parts of their crystalline core, where the investigated lakes are located, they are made of Paleozoic igneous rocks, mostly granitoids.

Despite clear geological differences between the two regions, basins of the majority of the investigated lakes form clusters of glacial lakes or lakes filling local depressions within the deposits of glacial deposition and formed during the Pleistocene glaciation. Drainage areas of the lakes, with few exceptions (Morskie Oko), are located above the upper limit of forest, which ends at 1400 to 1600 m a.s.l. in the Tatra and Făgăraș Mountains, respectively and at about 1700 m a.s.l. in the Rhodopes (Pirin, Rila), and the predominant plant formations are subalpine shrubs, mostly dwarf mountain pine, as well as alpine meadows and swards.

The climate of these regions is characterized as alpine variations of warm temperate climate; transitional (Tatra Mountains) and intermediate (Făgăraș) and dry continental climate (Pirin, Rila).

The annual precipitation in the Rila is 1000-1200 mm (Musala, 2925 m a.s.l.: 1212 mm), with the maximum precipitation in April, May and June and the minimum during the period August-September. The warmest and coldest months are August (Musala: +5.4°C) and February (-11.8°C), respectively (Maruszczak, 1971). In the Tatra Mountains, the temperature of the warmest month, July, is +3.8°C (Lomnický štít, 2635 m a.s.l.), and that of the coldest month, January, is -11.8°C. The annual precipitation ranges from 1500 to 1700 mm (Lomnický štít: 1561 mm) with the minimum and maximum values in September-October and June-August, respectively (Konček, 1974). In the Făgăraș Mountains, similarly to adjacent mountain ranges, the annual precipitation is slightly lower and ranges from 1200 to 1400 mm (Omul 2507 m a.s.l.: 1346 mm) with the temperatures of the warmest month, July, and the coldest month, January, averaging +5.4°C and -10.5°C, respectively (Maryński, 1973).

## Methods

Twenty nine high-altitude lakes were investigated and their location was as follows: Pirin – 6 lakes, Rila – 9 lakes, Făgăraș – 3 lakes, Tatra – 11 lakes. Basic morphometric characteristics of the investigated lakes are listed in Table 1.

On-site measurements included water temperature and conductivity, carried out using a Hanna Combo HI 98129 meter. The measurements were performed during noon hours, between 10:00 a.m. and 3:00 p.m. At the same time, 0.5-L samples of surface water were collected for further detailed hydrochemical determinations. The determination of ionic composition was carried out after two weeks, and prior to analysis the water samples were stored at 4°C (container with ice, refrigerator). The lakes were investigated once during the period August 12-24, 2004. The choice of investigation period was based on the maximum intensity of water circulation and thus the maximum exchange of matter and energy between different parts of the environment. This period is also characterized by substantial changes in the ratio of mechanical to chemical weathering, with the latter being predominant.

The concentration of major anions (sulfate  $\text{SO}_4^{2-}$ , chloride  $\text{Cl}^-$ ) was determined by ion chromatography (Dionex 500) and titration (bicarbonate  $\text{HCO}_3^-$ ). On the other hand, the concentration of major cations was determined by atomic absorption (Buck 210 VGP:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) and atomic emission (Jenway PFP7:  $\text{Na}^+$ ,  $\text{K}^+$ ) spectroscopy.

The experimental data were supplemented with the literature data on the results of hydrochemical measurements of the Tatra lakes carried out in the 1990s (Henriksen et al., 1992).

## Results

In all the investigated lakes the most abundant cation is calcium and the most abundant anions are sulfate or bicarbonate. Domination of one of the two major anions depends on the total concentration of calcium and magnesium and on the altitude of the lake above sea level (Fig. 1). The Carpathian lakes located higher than 1650 m a.s.l. have calcium-sulfate type water. In the Pirin and Rila lakes, this hydrochemical type occurs at altitudes greater than 2400 m a.s.l. Below these threshold altitudes, the lake waters represent the calcium-bicarbonate type. The correlation between the



Table 1. Morphometric characteristics of the lakes under study

Lake	Altitude	Latitude	Longitude	Area	Mean depth	Max. depth
	m a.s.l.	DDMM.mm	DDMM.mm	ha	m	m
<b>Pirin Mountains</b>						
Rybno Ezero	2198	4144.32	2436.95	6.5	–	14.2
Tevnoto Ezero	2515	4141.97	2328.80	4.5	–	–
Popovo Ezero	2240	4142.38	2328.80	12.0	–	29.5
Dalگو Ezero	2310	4144.14	2325.42	4.6	–	10.0
Zabesko Ezero	2325	4144.28	2325.35	0.5	–	–
Bezbozko Ezero	2235	4143.97	2331.50	–	–	–
<b>Rila Mountains</b>						
Grynczar Ezero	2180	4207.25	2335.62	2.9	–	–
Smradlivo Ezero	2285	4207.50	2328.42	21.2	8.1	24.0
Diavolsko Ezero II	2415	4207.00	2326.45	1.2	–	–
Babreka Ezero	2300	4212.18	2318.50	8.5	–	28.0
Musalensko Ezero II	2400	4211.75	2335.32	2.1	–	–
Gorno Ribno Ezero	2235	4206.57	2329.53	12.4	–	–
Diavolsko Ezero I	2395	4207.00	2327.00	2.2	–	–
Salzata Ezero	2530	4211.87	2318.68	0.7	–	4.5
Ledenoto Ezero	2725	4211.05	2335.19	1.5	–	–
<b>Făgăraș Mountains</b>						
Lacul Caltun	2120	4534.90	2434.40	0.8	4.1	11.8
Lacul Balea	2035	4536.22	2436.40	4.7	5.2	11.4
Lacul Podragu	2062	4536.60	2441.45	2.9	6.6	15.5
<b>Tatra Mountains</b>						
Wielki Staw Polski	1665	4912.60	2002.60	34.4	37.7	79.3
Czarny Staw Polski	1722	4912.20	2001.50	12.7	22.2	50.4
Zadni Staw Polski	1890	4912.80	2000.80	6.5	14.2	31.6
Przedni Staw Polski	1668	4912.80	2002.90	7.7	14.6	34.6
Czarny Staw Gașienicowy	1620	4913.95	2001.00	17.4	21.1	51.0
Długi Staw Gașienicowy	1784	4913.70	2000.58	1.6	5.1	10.6
Morskie Oko	1393	4912.08	2004.30	34.9	28.4	50.8
Czarny Staw pod Rysami	1580	4911.44	2004.45	20.6	37.6	76.4
Zielony Staw Gașienicowy	1672	4913.75	2000.10	3.8	6.8	15.1
Kurtkowiec	1686	4913.77	2000.35	1.5	1.4	4.8
Dwoisty Staw	1657	4913.95	2000.40	0.9	2.6	7.9

ratio of major anions ( $\text{SO}_4^{2-}/\text{HCO}_3^-$ ) and the altitude is stronger for the lakes of Pirin and Rila ( $r^2 = 0.87$ ;  $p < 0.001$ ;  $n = 7$ ) than for the Carpathian lakes ( $r^2 = 0.65$ ;  $p < 0.005$ ;  $n = 11$ ). The concentrations of calcium range from 71.9 to 633.7  $\mu\text{eq}\cdot\text{L}^{-1}$ , while those of sulfate and bicarbonate vary from 47.0 to 108.8  $\mu\text{eq}\cdot\text{L}^{-1}$  and from 30.4 to 727.0  $\mu\text{eq}\cdot\text{L}^{-1}$ , respectively. The significance of bicarbonate is emphasized by the strong correlation between concentration of this ion and the conductivity (Fig. 1), while the sulfate ion does not reveal such a correlation ( $r^2 = 0.38$ ). The cation with the second highest concentration is sodium: 3.9-19.4  $\mu\text{eq}\cdot\text{L}^{-1}$ . Only in the lake Podragu concentration of magnesium ion exceeds that of sodium ion. Consequently, as far as the cation composition is concerned, the lake waters represent the calcium-sodium type.

Chemical characteristics of the investigated lakes are shown in Table 2. The total dissolved salt content is low, ranging from 181.1 to 1691.3  $\mu\text{eq}\cdot\text{L}^{-1}$ ,

while the corresponding conductivity ( $\text{Cond}_{25}$ ) varies from 11.4 to 96.7  $\mu\text{S}\cdot\text{cm}^{-1}$ . The conductivity is strongly correlated not only with the dissolved salt content ( $r^2 = 0.98$ ;  $p < 0.001$ ) but also with the concentration of predominant calcium ion ( $r^2 = 0.96$ ;  $p < 0.001$ ) and bicarbonate ion ( $r^2 = 0.99$ ;  $p < 0.001$ ).

The ion structure of waters of the investigated lakes, expressed as the cation (CR) and anion (AR) ratio reveals that most of them are characterized by the AR values below 2.0 with the CR values less than 15.0 (Fig. 2). The values of both indices are strongly correlated with the altitude of surface of the lake: the higher the lake altitude, the smaller the values of CR and AR. For four of the investigated lakes (Balea, Diavolsko II, Podragu and Przedni Staw Polski), both the CR and AR values differ from those observed for the remaining lakes. The values are much larger and they reflect the effect of local conditions, such as geological structure and hydrological type of the reservoir (Diavolsko

II, and probably Diavolsko I, for which complete analytical results of the ion composition were unavailable) or the effect of tourist infrastructure (Balea, Podragu, Przedni Staw). When determining the effect of lake altitude on the concentration of individual ions these lakes were omitted as being unrepresentative.

The concentrations of major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ) are strongly correlated with the altitude of water level of a lake (Fig. 3). Only for chloride ion the relationship is statistically insignificant ( $r^2 = 0.157$ ;  $p < 0.1$ ;  $n = 19$ ), and the variability in  $\text{Cl}^-$  concentration cannot be explained by the effect

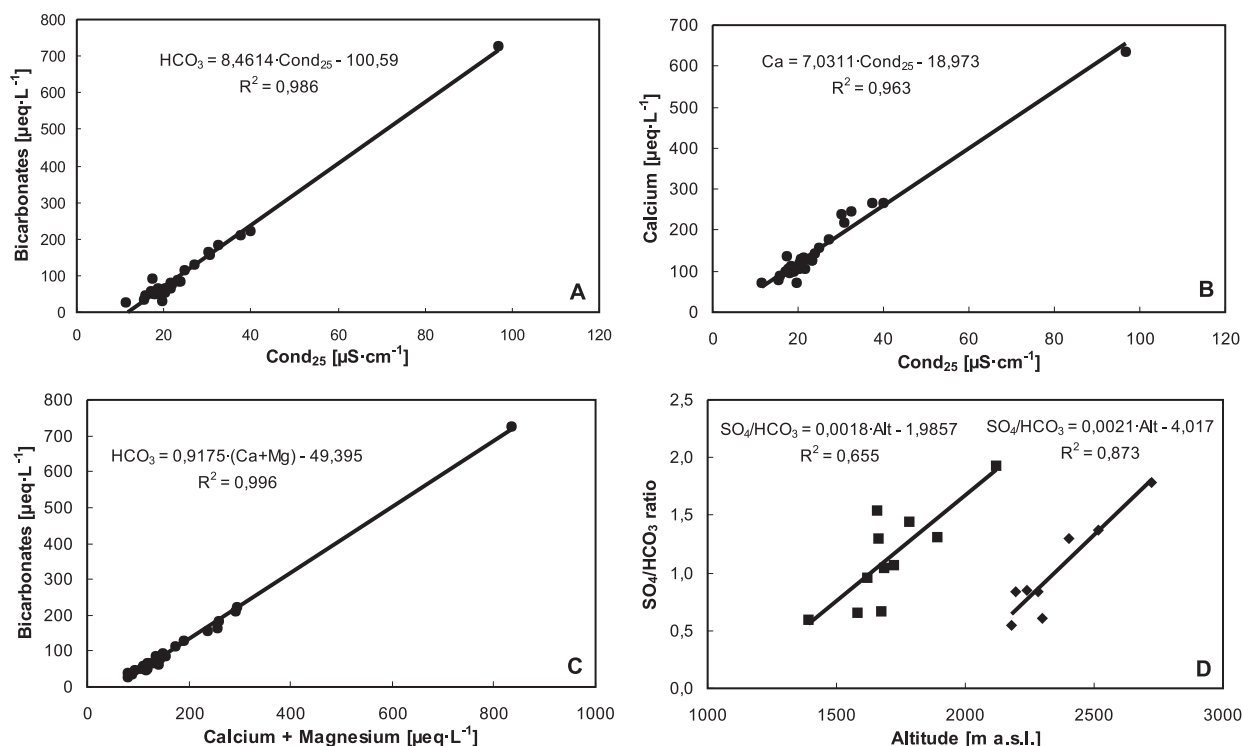


Fig. 1. Relationships between bicarbonate and conductivity (a), calcium and conductivity (b), bicarbonate and sum of calcium and magnesium (c),  $\text{SO}_4/\text{HCO}_3$  ratio and altitude (d). In part (d) squares denote Carpathian lakes and diamonds Rhodopean lakes

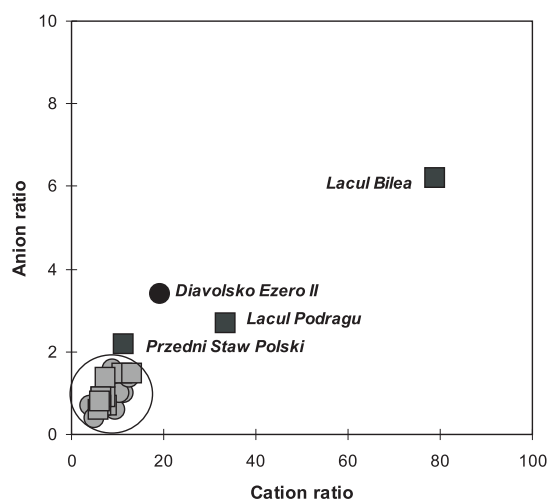


Fig. 2. Ionic composition of water of the investigated lakes expressed as the cation and anion ratios

of altitude. In crystalline regions deficient in chloride, the lack of this correlation can be related to variable atmospheric deposition of this component resulting from different conditions of atmospheric circulation of the investigated regions, their different exposure to rain-carrying winds or a different distance from the sea, which is indicated by the low chloride concentration in lake water ( $2.8\text{--}9.9 \mu\text{eq}\cdot\text{L}^{-1}$ ). Similarly, the weakest correlations between the chloride concentration and the altitude were found for the river water in the drainage area of the upper Iskar, Rila (Gassama & Violette, 1997).

A strong correlation between the concentration of sulfate and altitude ( $r^2 = 0.762$ ;  $p < 0.001$ ;  $n = 19$ ) reveals that the supply of this component is related to the intensity of weathering of bedrock. The effect



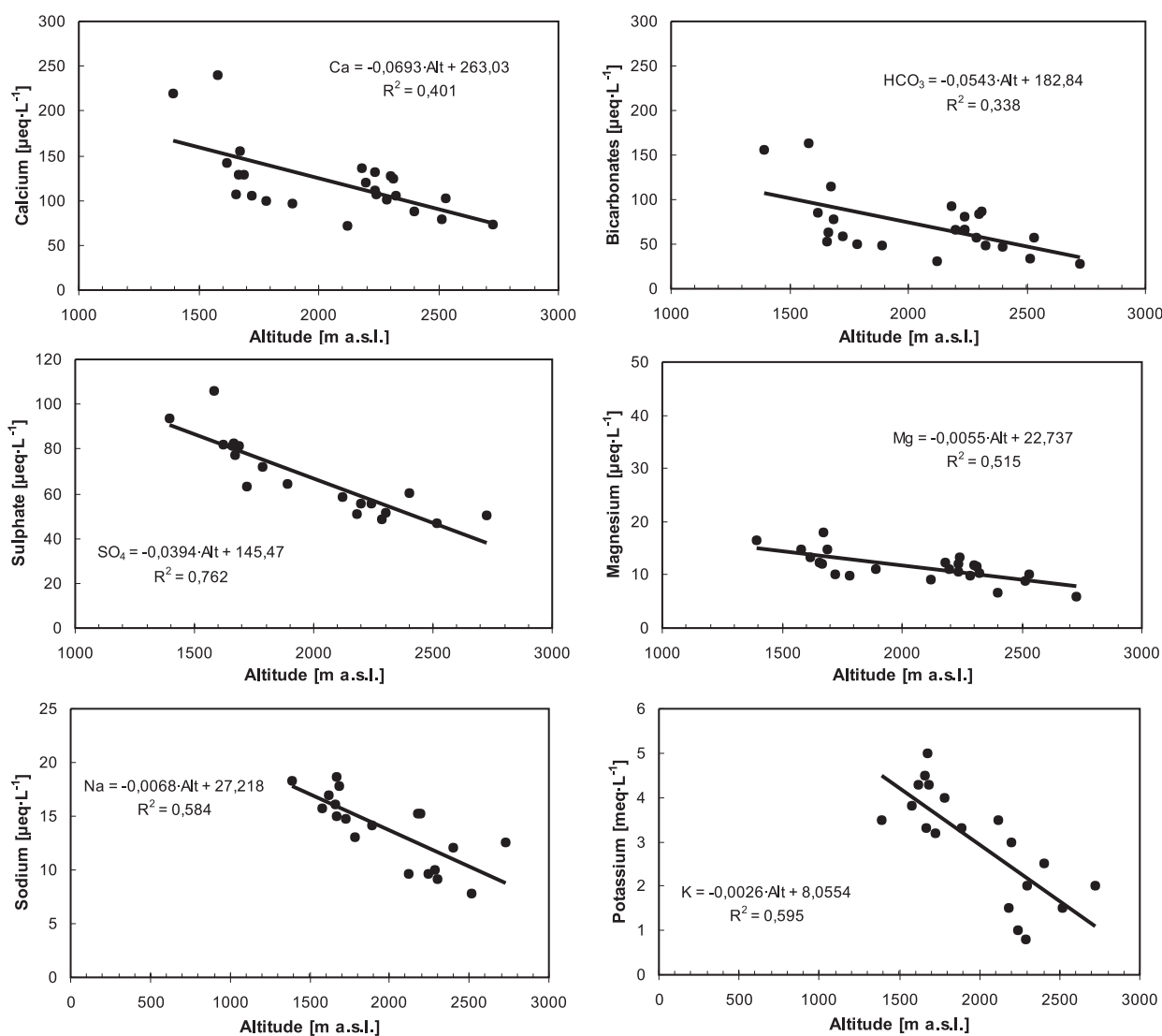
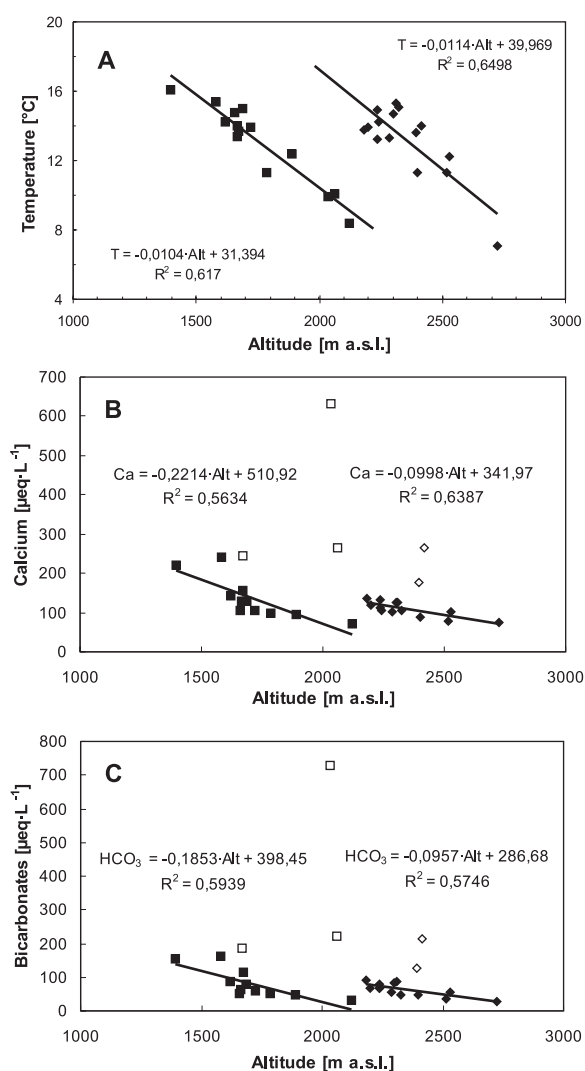


Fig. 3. Relationship between the concentration of major ions and altitude

of altitude on the conductivity and concentrations of calcium and bicarbonate clearly indicates a bipartite set of the experimental data (Fig. 4), which is related to regional differences in biogeochemical conditions of the investigated high-altitude regions (Carpathian Mountains, Rhodopes). In general, however, the transformation of chemical composition of water of the investigated lakes reveals a clear correlation with their altitude, which is associated mainly with the change in retention time of the drainage basin and the surface area of soils and rocks being washed.

## Conclusions

Cluster analysis of the experimental data reveals the diversity of hydrochemical structures of the lakes being studied (Fig. 5). It follows from cluster analysis, in which such parameters of ion composition as the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  as well as  $\text{Cond}_{25}$  were used, that the investigated population of lakes falls into four categories. The first two categories are the clusters of lakes, whose chemistry is determined by natural factors, such as geology of the drainage area, vegetation cover or intensity of chemical weathering. The third and fourth category are the lakes, whose water chemistry is strongly af-



ected by anthropogenic interactions (Balea, Podragu, Przedni Staw Polski, partly Morskie Oko), or whose chemistry is influenced by specific local conditions, as is the case with Lake Diavolsko II. A shallow basin of the latter lake is formed in strongly weathered schists, and in summer the lake is drainage free. Such a state favors chemical weathering and concentration of dissolved species in water of the lake. Lake Diavolsko I has similar hydrochemical properties; however, a rheolimnic nature of this reservoir and a larger volume of water stored result in concentrations of calcium and magnesium being lower by about one-third (Table 2). On the other hand, Lakes Balea, Podragu, Przedni Staw Polski, and Morskie Oko are reservoirs, which are located close to mountain lodges and their shores are used as a resting place for numerous tourists. In addition, the altitude of water surface of Lake Morskie Oko is the lowest of all the investigated lakes. The lake is the only one that lies below the upper limit of forest and has the most extensive drainage area, which favors natural supply of mineral matter.

Factor analysis carried out on the set of hydrochemical data of the entire population of the investigated lakes reveals the existence of two main factors,

Fig. 4. Relationships between lake water surface temperature and altitude (a); calcium and altitude (b); bicarbonate and altitude (c) with division into Carpathian (squares) and Rhodopean (diamonds) lakes. Empty squares and diamonds denote the lakes excluded from the analysis

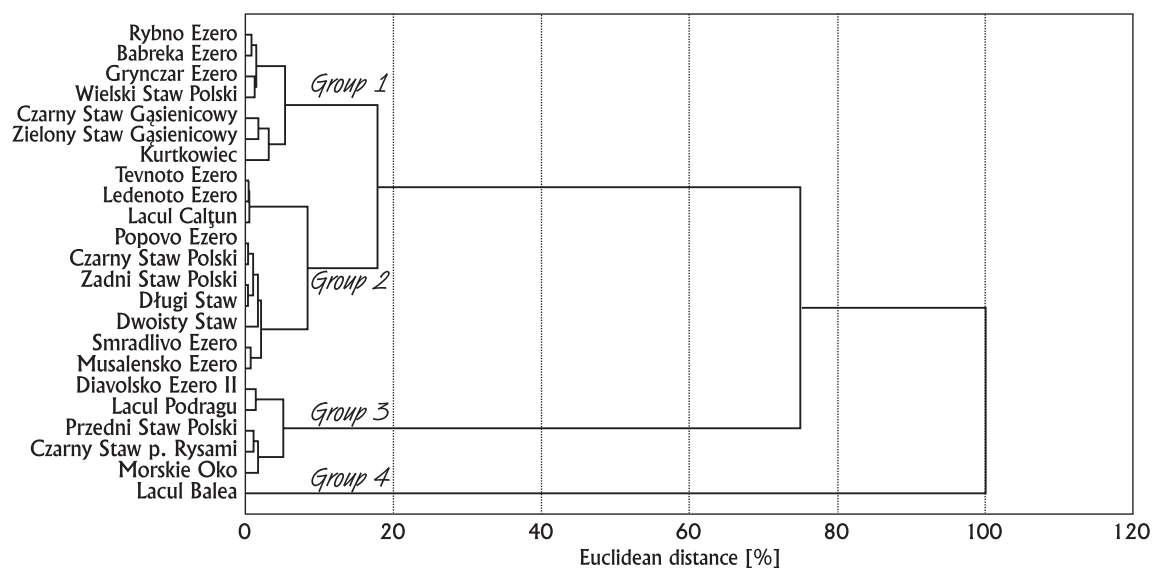


Fig. 5. Classification of the lakes under study into different hydrochemical groups (cluster analysis – Ward's method)

Table 2. Altitude, temperature, conductivity and concentrations of major ions

Lake	Altitude m a.s.l.	Temp. °C	Cond <sub>25</sub> µS/cm <sup>-1</sup>	Na <sup>+</sup> µeq/l	K <sup>+</sup> µeq/l	Mg <sup>2+</sup> µeq/l	Ca <sup>2+</sup> µeq/l	Cl <sup>-</sup> µeq/l	SO <sub>4</sub> <sup>2-</sup> µeq/l	HCO <sub>3</sub> <sup>-</sup> µeq/l	Anions µeq/l	Cations µeq/l	Ions µeq/l	Cationic ratio (Ca+Mg)/(Na+K)	Anionic ratio HCO <sub>3</sub> <sup>-</sup> /(Cl+SO <sub>4</sub> )
<b>Pirin Mountains</b>															
Rybno Ezero	2198	13.9	20.3	15.2	3.0	11.2	119.3	9.9	55.5	65.7	131.1	148.7	279.8	7.2	1.0
Tevnoto Ezero	2515	11.3	15.4	7.8	1.5	8.9	79.3	7.1	47.0	34.3	88.4	97.5	185.9	9.5	0.6
Popovo Ezero	2240	14.2	21.5	9.6	1.0	13.2	106.3	7.9	55.7	65.5	129.1	130.1	259.2	11.3	1.0
Dalgo Ezero	2310	15.3	23.3	–	–	11.5	124.7	–	–	86.6	–	–	–	–	–
Zabesko Ezero	2325	15.1	17.6	–	–	10.3	104.8	–	–	48.3	–	–	–	–	–
Bezbozko Ezero	2235	14.9	18.5	–	–	10.7	111.3	–	–	65.9	–	–	–	–	–
<b>Rila Mountains</b>															
Grynczar Ezero	2180	13.8	17.5	15.2	1.5	12.3	136.7	5.4	50.9	92.7	149.0	165.7	314.7	8.9	1.6
Smradlivo Ezero	2285	13.3	16.9	10.0	0.8	9.9	100.3	6.8	48.5	57.4	112.7	121.0	233.7	10.2	1.0
Diavolsko Ezero II	2415	14.0	37.5	10.9	4.3	25.5	266.5	6.5	56.6	212.4	275.5	307.2	582.7	19.2	3.4
Babreka Ezero	2300	14.7	23.4	9.1	2.0	11.7	127.2	9.0	51.4	83.9	144.3	150.0	294.3	12.5	1.4
Musalensko Ezero II	2400	11.3	15.7	12.1	2.5	6.6	88.3	7.9	60.5	46.5	114.9	109.5	224.4	3.9	0.7
Gorno Ribno Ezero	2235	13.2	21.4	–	–	12.0	131.5	–	–	80.5	–	–	–	–	–
Džendemske Ezero I	2395	13.6	27.1	–	–	15.3	176.0	–	–	128.7	–	–	–	–	–
Salzata Ezero	2530	12.2	18.6	–	–	10.1	101.8	–	–	56.8	–	–	–	–	–
Ledenoto Ezero	2725	7.1	11.4	12.6	2.0	5.8	73.4	8.4	50.5	28.4	87.3	93.8	181.1	4.8	0.4
<b>Făgăraş Mountains</b>															
Lacul Caltun	2120	8.4	19.6	9.6	3.5	9.0	71.9	5.1	58.7	30.4	94.2	94.0	188.2	6.2	0.8
Lacul Balea	2035	9.9	96.7	6.1	4.5	202.2	633.7	9.0	108.8	727.0	844.8	846.5	1691.3	78.9	6.2
Lacul Podragu	2062	10.1	39.9	3.9	5.0	29.6	266.5	2.8	79.0	223.3	305.1	305.0	610.1	33.3	2.7
<b>Tatra Mountains</b>															
Wielki Staw Polski	1665	13.4	20.5	15.0	3.3	12.0	129.0	5.4	82.5	63.7	151.6	159.3	310.9	7.7	0.7
Czarny Staw Polski	1722	13.9	18.7	14.8	3.2	10.2	105.8	5.5	63.1	59.2	127.8	134.0	261.8	6.4	0.9
Zadni Staw Polski	1890	12.4	17.9	14.2	3.3	11.0	96.4	6.0	64.3	49.2	119.5	124.9	244.4	6.1	0.7
Przedni Staw Polski	1668	14.0	32.6	19.4	3.7	14.4	245.3	4.9	78.0	185.1	268.0	282.8	550.8	11.2	2.2
Czarny Staw Gašienic. <sup>(1)</sup>	1620	14.2	23.9	17.0	4.3	13.2	142.2	8.5	82.2	85.7	176.4	176.6	353.0	7.3	0.9
Długi Staw Gašienic. <sup>(1)</sup>	1784	11.3	19.1	13.1	4.0	9.9	98.8	4.2	71.8	49.9	125.9	125.7	251.6	6.4	0.7
Morskie Oko <sup>(1)</sup>	1393	16.1	30.7	18.3	3.5	16.4	219.6	8.5	93.6	155.8	257.9	257.8	515.7	10.8	1.5
Czarny Staw p. Rysami <sup>(1)</sup>	1580	15.4	30.3	15.7	3.8	14.8	240.5	5.6	106.1	162.7	274.4	274.7	549.1	13.1	1.5
Zielony Staw Gašienic. <sup>(1)</sup>	1672	13.7	24.8	18.7	5.0	18.1	155.7	5.6	77.0	114.8	197.4	197.5	394.9	7.3	1.4
Kurtkowiec <sup>(1)</sup>	1686	15.0	22.0	17.8	4.3	14.8	128.2	5.6	81.1	78.2	165.0	165.1	330.1	6.5	0.9
Dwoisty Staw <sup>(1)</sup>	1657	14.8	20.2	16.1	4.5	12.3	106.3	5.6	81.1	52.5	139.2	139.2	278.4	5.8	0.6

(1) (according to Henriksen et al., 1997)

Table 3. Results of principal components analysis of hydrochemical properties of lake water

Variable	Factor 1	Factor 2
Conductivity, Cond <sub>25</sub>	-0,991	-0,031
Sodium, Na <sup>+</sup>	0,295	0,617
Potassium, K <sup>+</sup>	-0,500	0,605
Magnesium, Mg <sup>2+</sup>	-0,938	-0,085
Calcium, Ca <sup>2+</sup>	-0,981	0,000
Chloride, Cl <sup>-</sup>	-0,109	-0,369
Sulphate, SO <sub>4</sub> <sup>2-</sup>	-0,696	0,461
Bicarbonates, HCO <sub>3</sub> <sup>-</sup>	-0,983	-0,043
Cationic ratio, CR	0,141	0,821
Anionic ratio, AR	0,159	0,829
% of variance explained	46,7	24,7

Table 4. Surface water temperature characteristics of European high-altitude mountain lakes. Data referring to Alpine and Tatra lakes according to Livingstone et al. (2005) and Šporka et al. (2005)

Region	Date	Temperature gradient	2000 m intercept	r <sup>2</sup>	Number of lakes
Carpathes	Aug 2004	1.0 °C/100 m	10.6 °C	0.62	14
Rhodopes	Aug 2004	1.1 °C/100 m	17.2 °C	0.65	15
Tatras	Jul 2001	1.4 °C/100 m	5.4 °C	0.65	9
Tatras	Aug 2001	0.7 °C/100 m	10.8 °C	0.38	9
Alps (lakes below 2000 m a.s.l.)	Jul 2000	0.7 °C/100 m	11.1 °C	0.91	15
Alps (lakes below 2000 m a.s.l.)	Aug 2000	0.7 °C/100 m	13.0 °C	0.91	15
Alps (lakes above 2000 m a.s.l.)	Jul 2000	1.3 °C/100 m	10.2 °C	0.38	14
Alps (lakes above 2000 m a.s.l.)	Aug 2000	0.9 °C/100 m	13.3 °C	0.30	14

which jointly account for over 71% of the total variability (Table 3). The first component, determined by the presence of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> ions (to a lesser extent also SO<sub>4</sub><sup>2-</sup> ions) and Cond<sub>25</sub>, and accounting for 47% of the variability of chemical properties of the examined lakes, can be interpreted as the effect of intensity of weathering, mostly chemical weathering, as well as the effect of the altitude factor, determining the weathering process. The second major component (24.7%), correlated with the ion ratios described by the CR and AR coefficients, is related to the intensity of anthropogenic interactions superimposed on the natural cycles of elements in the drainage area.

The present study revealed definite regional differences in concentration of predominant cations (Ca<sup>2+</sup>) and anions (HCO<sub>3</sub><sup>-</sup>) in the investigated clusters of lakes. For the ions with lower concentrations (SO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>), the differences are not as clear-cut. The correlations between the predominant ions and altitude of the water surface of the lakes are described by different linear regression equations for the two high-altitude regions. For the Carpathian lakes, the change in lake altitude by 100 m results in an increase/decrease in the concentration of calcium ion by 22.1 µeq·L<sup>-1</sup>, while for the Pirin and Rila lakes the respective change is only about 10 µeq·L<sup>-1</sup>. For bicarbonate ion, the respective values are 18.5 and 9.6 µeq·L<sup>-1</sup>. Similar concentration levels of the major ions (Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>) are observed in the Carpathian

lakes at altitudes lower by ca. 500-600 m compared to the lakes of Pirin and Rila. This is the denivelation value, at which the intensity of chemical weathering in the two regions becomes equal. This denivelation value is directly related to the changes in thermal conditions of lake water. The altitude gradients of surface temperature of water of the two investigated groups of lakes are similar, but the absolute temperatures referred to the 2000 m above sea-level differ in August by 6.6°C (Table 4). The obtained values of gradients as well as average interregional thermal differences are similar to the results of earlier measurements of temperature of surface water of the Tatra (Šporka et al., 2005) and Alpine lakes (Livingstone et al., 2005). It can thus be concluded that the investigated period of time did not significantly deviate from other periods of time with respect of prevailing thermal conditions and the results obtained are representative of average conditions.

Hydrochemical differentiation of water of high-altitude lakes of the selected regions of the Carpathian and Rhodope Mountains largely reflects the differences in intensity of chemical weathering and, to a lesser extent, the differences in petrographic composition of bedrock. The differences in geological structure of the environs of lake basins were revealed only for the Diavolsko Lakes, located in the area of deposition of strongly weathered metamorphic rocks.





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## Streszczenie

Wyniki badań hydrochemicznych 29 jezior wysokogórskich położonych w dwóch, zróżnicowanych pod względem genetycznym oraz współcześnie przebiegających procesów morfogenetycznych, obszarów wysokogórskich Europy: Karpat i Rodopów (tab. 1), rozpatrywane były w odniesieniu do lokalnych warunków geologicznych, klimatycznych, hydrologicznych oraz intensywności antropopresji. W badanych jeziorach dominującym kationem jest  $\text{Ca}^{2+}$ , natomiast wśród anionów  $\text{SO}_4^{2-}$  lub  $\text{HCO}_3^-$  (tab. 2). Dominacja jednego z dwóch głównych anionów uzależniona jest od sumy stężeń jonów  $\text{Ca}^{2+}$  i  $\text{Mg}^{2+}$  oraz położenia jeziora nad poziomem morza (ryc. 1). Jeziora karpackie położone powyżej 1650 m n.p.m. mają wody typu wapniowo-siarczanowego. Stężenia wapnia wahają się od 71,9 do 633,7  $\mu\text{eq}\cdot\text{L}^{-1}$ , wodorowęglanów od 30,4 do 727,0  $\mu\text{eq}\cdot\text{L}^{-1}$ , a siarczanów od 47,0 do 108,8  $\mu\text{eq}\cdot\text{L}^{-1}$ . Znaczenie wodorowęglanów podkreślone jest również istnieniem silnej zależności tego jonu od przewodności (ryc. 1). Struktura jonowa wód jeziornych, wyrażona współczynnikiem kationów (CR) oraz anionów (AR) pokazuje, że większość z nich charakteryzuje się wartościami AR poniżej 2,0 przy wartościach CR nie przekraczających 15,0 (ryc. 2). Wartości obu wskaźników są silnie powiązane z wysokościowym położeniem jeziora. Zmiany koncentracji głównych jonów ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  i  $\text{HCO}_3^-$ ) także wykazują mocne skorelowanie z bezwzględną wysokością jeziora (ryc. 3). Wysokościowe zmiany przewodności oraz koncentracji wapnia i wodorowęglanów wskazują na wyraźną dwudzielność zbioru danych pomiarowych (ryc. 4), która nawiązuje do regionalnych odrębności biogeochemicznych badanych obszarów.

Badana zbiorowość jezior dzieli się na cztery grupy hydrochemiczne (ryc. 5). Dwie pierwsze to jeziora, których chemizm kształtowany jest czynnikami naturalnymi (geologia zlewni, szata roślinna, intensywność wietrzenia chemicznego). Grupy trzecia i czwarta, to jeziora o silnie zmienionym, oddziaływaniami antropogenicznymi, chemizmie (Balea, Podragu, Przedni Staw Polski, częściowo Morskie Oko), lub jeziora których hydrochemia wynika ze specyfiki lokalnych uwarunkowań.

Analiza składowych głównych wskazuje na istnienie dwóch głównych czynników, które łącznie wyjaśniają 71% całkowitej zmienności badanej grupy jezior (tab. 3). Pierwszy z nich (47%), zdeterminowany obecnością jonów  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$  (w mniejszym stopniu jonów  $\text{SO}_4^{2-}$ ) i  $\text{Cond}_{25}$ , może być interpretowany jako efekt intensywności wietrzenia chemicznego, a pośrednio także czynnika wysokościowego wpływającego na warunki termiczne (tab. 4). Druga składowa główna (24,7%), skorelowana ze stosunkami jonowymi opisanymi współczynnikami; anionowym i kationowym, jest powiązana z natężeniem oddziaływań antropogenicznych nakładających się na naturalne warunki obiegu pierwiastków w zlewni.

Chemiczne odrębności wód badanych jezior odzwierciedlają zasadniczo różnice w intensywności wietrzenia chemicznego, w mniejszym zaś stopniu różnice składu mineralnego skał podłoża. Specyfika budowy geologicznej otoczenia niecek jeziornych uwidacznia się w chemizmie jezior położonych na obszarze zalegania mocno zwietrzalnych serii skał metamorficznych. Przekształcenie stosunków jonowych w wodach badanych jezior jest istotnym wskaźnikiem wskazującym na oddziaływania antropogeniczne.