

Analysis of water chemistry in the alpine lake Kolové pleso, the Tatra Mountains

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Abstract. The study focuses on the long-term observation of physical variables as well as inorganic and organic contents in the water of the lake Kolové pleso (High Tatras). Physical variables were measured directly at the sampling site at regular monthly intervals. The chemical composition of the collected water samples was analysed by photometric method. Organic substances were detected by GC/MS and chemical oxygen demand (COD) method. The study confirmed the seasonal dependence in water temperature, total water hardness and oxygen saturation. The amount of sulphates and nitrates also varied over the seasons. Significant inter-annual differences were also observed in the amount of atracene.

Key words: high mountain lake, seasonal variability, water chemistry, physical parameters of water, PAH

Introduction

Alpine lakes are considered sensitive indicators of the effects of natural and anthropogenic factors, including atmospheric deposition and climate change (Catalan *et al.* 2006; Rogora *et al.* 2020). High elevation areas are characterized by demanding and rapidly changing climatic and environmental gradients (Thompson *et al.* 2005; Moser *et al.* 2019), which equally influence lake ecological factors. Organisms living in the lakes have to adapt to severe environmental conditions such as low nutrient availability, low temperature, short growing seasons, extreme changes in light conditions, and periods of strong solar UV radiation (Sommaruga 2001), yet lakes are considered hotspots of biodiversity and habitats for endemic species and specific fauna.

These water bodies are located close to or above the upper forest boundary, are characterized by an extended period of ice coverage, but also by low direct impact of anthropogenic pollution. Most such lakes are of glacial origin. In the upper parts of the valley where they were the source of glaciers, the accumulated mass of ice pushed the bedrock

and formed glacial kettles or craters. They may also have been formed by geological processes such as volcanic activity or landslides.

The high mountain lakes in the High Tatras are also of glacial origin and were formed during the retreat of the Würm glaciation, roughly 20,000 years ago (Pacl and Gregor 2010). According to their origin, they are divided into karst lakes, where water fills glacial carvings excavated in the compact bedrock of the valley, and moraine lakes, which were formed after the melting of the glacier behind its frontal or even lateral moraines, which prevent the water from draining away. Most of the Tatra's lakes were formed in both ways (Vološčuk *et al.* 1994).

The hydrological regime of Tatra lakes is mainly related to their location, and the hydrology of alpine lake basins seems to have a significant influence on the chemical characteristics and nutrient availability (Xenopoulos *et al.* 2003; Perga *et al.* 2018). The main sources of water are direct precipitation and tributary catchments. The water-level of the lakes in the Tatra Mountains corresponds to the precipitation during the year, with maximum precipitation and thus highest water-levels in summer, and minimum levels typical for winter. Water from melting snow cover is also an important source of water in the spring months (Santoková 2015).

The influx of precipitation also represents an increase in the wet deposition of pollutants that are transported into the mountains from distant, often anthropogenic sources, so high elevation lakes are highly susceptible to deposition of atmospheric pollutants transported from lowland areas (Mosello *et al.* 2002; Curtis *et al.* 2005). The lakes also respond sensitively to climate change due to very significant changes in ice and snow cover (Thompson *et al.* 2005), or temperature increases (Dokulil 2022). These changes have a greater impact on chemistry than atmospheric deposition (Mast *et al.* 2011; Preston *et al.* 2016). Because these are remote and pristine ecosystems, high elevation lakes are minimally exposed to local anthropogenic pressures that could confound the influence of climate patterns (Bertani *et al.* 2016). In the absence of local point sources such as mountain cottages or grazing, the water chemistry of mountain lakes is driven primarily by atmospheric deposition (quantity and chemical composition) and trapping processes (weathering of rocks and soils) (Camarero *et al.* 2009). Climate change may accelerate or delay recovery from acidification, nitrogen saturation, or other aeration-related processes (Rogora *et al.* 2020).

Research on the water chemistry of Kolové pleso has been ongoing since 2018. This study summarises inter-annual comparisons of physical and chemical characteristics from the years 2021-2022. Kolové pleso (1565 m a.s.l.) is a tributary-fed lake located in the Kolová valley (Javorová dolina, High Tatras). It is a relatively small and shallow lake (area: 18,280 m², volume: 10,846 m³, depth: 1 m) (Bohuš 1996). The shallow depth, area and catchment area make the mountain bogs extremely sensitive to external influences on global, regional and local scales, which is why they are considered as early warning or patrol systems and are ideal for long-term monitoring (Slovak Forestry Society 2012). Kolové pleso is not accessible to tourists, therefore no direct impact of anthropogenic pollution is expected here. Possible pollutants are therefore mainly deposited by atmospheric precipitation. In our research we focused on the physical and chemical parameters of the water of Kolové pleso during the year. We expect changes in parameters naturally linked to the season, such as temperature, oxygen, but also changes in the levels of organic pollutants.

Material and Methods

Study area and sampling

Research on the physicochemical properties of the lake Kolové pleso (Kolová dolina; High Tatras) began in 2017 and has continued until now. Previous results are published in Hrináková (2019), and Potecká (2021). The results of the research presented in this study are from the period 2021-2022. Water sampling and *in situ* measurements of physical properties were carried out regularly at monthly intervals at the same sampling point (N 49.220972° ; E 20.192500° ; 1565 m a.s.l.) in the mountain lake Kolové pleso.

At the sampling point, the physical properties of water (temperature, pH, conductivity, TDS, oxygen level and saturation) were measured using a WTW Multi 3430 SET G portable multimeter (WTW, Germany). A one liter water sample was also collected in a dark glass sampling bottle. The water samples were transferred to the IHMB laboratory where analysis for the presence of organic matter was carried out within 24 hours.

Laboratory analysis

Optical-analytical method

Determination of chemical parameters (chloride, nitrate, phosphorus, ammonia, sulphate) and determination of total water hardness was carried out by direct photometry using a YSI EcoSense 9500 photometer (YSI Inc., Ohio, USA) and accessories compatible with this instrument. Total hardness (CaCO₃ in mg/L), phosphates (P, PO₄³⁻ in mg/L), nitrates (N, NO₃ in mg/L), ammonia (N, NH₃, NH₄ in mg/L) and chlorides (Cl, NaCl in mg/L) of the samples were measured using chemical reagents (PALINTEST Ltd., Gateshead, UK).

Chemical oxygen demand (COD)

The chemical oxygen demand test is a commonly used method to indirectly measure the amount of

organic compounds in liquid waste. It is expressed in milligrams/grams per liter, which indicates the amount of oxygen consumed per liter of solution. The test was carried out simultaneously in three samples (100 mL of water from the lake) and the resulting COD was determined by averaging their values. To the volume of water analysed, 5 mL of H₂SO₄ (diluted at a concentration of 1:2) and 20 mL of KMnO₄ were added. The flasks were placed on a heat source and heated to boiling (96-98 °C) for 10 minutes. After 10' of boiling, 20 mL of (COOH)₂ was added to completely decolorize the solution. The clear solution was titrated with 0.002 mol/L KMnO₄ until it turned slightly pink again.

Extraction - chromatographic analysis for polycyclic aromatic hydrocarbons (PAHs)

Laboratory analysis uses the solubility of PAHs in organic solvents followed by determination of the concentration of individual PAHs in the sample by GC/MS (gas chromatography with mass spectrometry). The process is carried out in two steps. In the first step, the pollutants are concentrated in 1 mL of hexane by extraction. The control substance D-pyrene (30 µL) was added to 1 L of the sample and the mixture was stirred in a closed Erlenmeyer flask. In the next step, 1 mL of n-hexane was added, the mixture was then stirred in a closed flask for 2 minutes. The mixture was allowed to stand at rest for 2-5 hours depending on the laboratory and sample temperature. After equilibration, the separated n-hexane phase (extract) was pipetted from the Erlenmeyer flask into a labeled container where the amount ranged from 0.5 to 1.0 mL. The extract was allowed to evaporate to an amount of 0.3 mL. The extract was analysed in a gas chromatograph used for the detection of organic compounds. Analysis were performed using an Agilent Technologies 5977A stand-alone capillary GC detector (Agilent Technologies 2013) and an Agilent 7890B mass selective detector with MassHunter software. An automated liquid sampler (ALS) was used to inject 2 µL (injection volume) of extract. Helium of purity 6.0 was used as a carrier gas, which can create a vacuum system and increases the separation efficiency of the instrument (Vékey 2001). Evaluation of chromatograms was performed using Agilent Technologies software (2013).

Statistical analysis

Statistical analysis were performed using Statistica 12 (StatSoft, USA). Normality of data were tested by Shapiro-Wilk test. Kruskal Wallis H test (KW-H) was used to test differences between the measured values for variables without normal distribution. One-Way ANOVA test was used for variables with normal distribution of data.

Results

No significant differences were observed between years for physical variables and most organic matter. Significant inter-annual differences were only observed for anthracene, which was significantly higher in 2021 (Fig. 1).

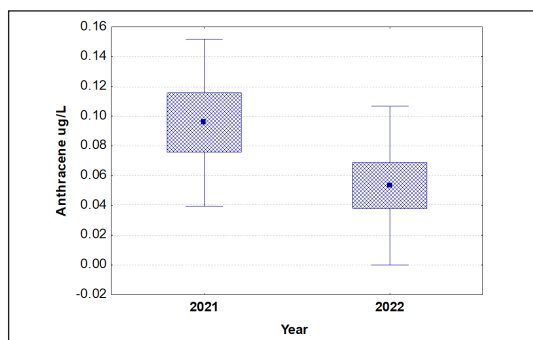


Fig. 1. Differences in anthracene levels in the water of Kolové pleso in 2021 and 2022. K-W H (1; 20) = 5.3612; $p = 0.0206$. (Middle points: means; Boxes: +/- standard errors of mean; Whiskers: +/- standard deviations of mean).

The results of the study cover a period of two years (2021-2022), due to the larger amount of data, differences between seasons (spring, summer, autumn, winter) were also analysed. Significant differences were found between seasons, especially between temperature, oxygen, sulphur, SO_4 , nitrogen, NO_3 , and water hardness levels. The significance of the differences between years and seasons, in the observed transformations is presented in Table 1.

Physical parameters of water

Of the physical characteristics of the water, presumably temperature was the most seasonally dependent. It is significantly higher in the summer months compared to the winter months (Fig. 2). Over the two-year period measured, the mean water temperature was 6.88°C . The highest measured temperature was recorded in August 2021 with a value of 17.40°C and the lowest in December 2021 with a value of 0.1°C .

Differences in oxygen (O_2) content were also significantly different between seasons (Fig. 3). The lowest measured values for all three oxygen parameters (O_2 concentration; O_2 partial pressure; O_2 saturation) were measured in March 2022 (O_2 concentration: 6.36 mg/L , partial pressure O_2 : 99.9 mbar and O_2 saturation: 58.88%). Given that in other winter months, when O_2 levels are lowest, the measured values have never been this low, we assume that

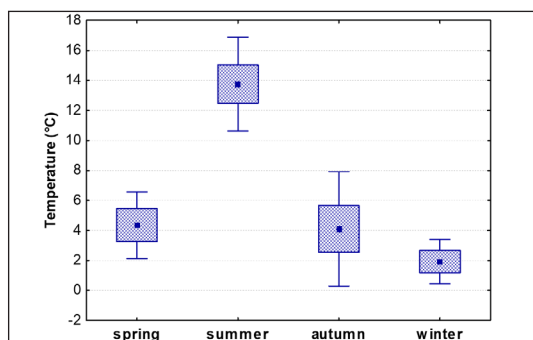


Fig. 2. Differences in water temperatures of Kolové pleso in different seasons. K-W H (3; 20) = 12.8817; $p = 0.0049$. (Middle points: means; Boxes: +/- standard errors of mean; Whiskers: +/- standard deviations of mean).

Variables	p		Units
	Years	Season	
Anthracene	0.0206	0.6016	$\mu\text{g/L}$
Fluoranthene	0.1090	0.8759	$\mu\text{g/L}$
Pyrene	0.4404	0.4035	$\mu\text{g/L}$
Chrysene	0.2316	0.1335	$\mu\text{g/L}$
Benzo[a]pyrene	0.1026	0.3596	$\mu\text{g/L}$
Temperature	0.6159	0.0049	$^\circ\text{C}$
COD	0.4875	0.6222	mL
pH	0.1427	0.1106	
Concentration O_2	0.8774	0.1893	mg/L
Partial pressure O_2	0.1052	0.1709	Mbar
Saturation O_2	0.4177	0.0354	%
Conductivity	0.4177	0.1821	$\mu\text{S/cm}$
TDS	0.7553	0.1092	mg/L
Cl	0.9383	0.5840	mg/L
Chlorides CaCO_3	0.9383	0.5840	mg/L
NaCl	0.9383	0.5840	mg/L
Total hardness CaCO_3	0.7529	*0.0361	mg/L
S	0.3498	0.0293	mg/L
SO_4^{2-}	0.5986	0.0229	mg/L
Ammonia N	0.4392	0.8885	mg/L
NH_3	0.4392	0.8885	mg/L
NH_4	0.4392	0.8885	mg/L
Nitrates N	0.3347	*0.0104	mg/L
NO_3	0.3545	*0.0103	mg/L
PO_4^{3-}	0.8767	0.2847	mg/L
P	0.6917	0.5041	mg/L

Table 1. Inter-annual differences in the monitored water parameters of Kolové pleso. Significant differences ($p < 0.05$) are in bold. (Differences tested by K-W H test and marked by * tested by One-Way ANOVA test).

this may have been an instrument error. The second lowest measured values for oxygen (O_2 concentration: 10.43 mg/L , partial pressure O_2 : 174.47 mbar , and O_2 saturation: 102.86%) were in the month of

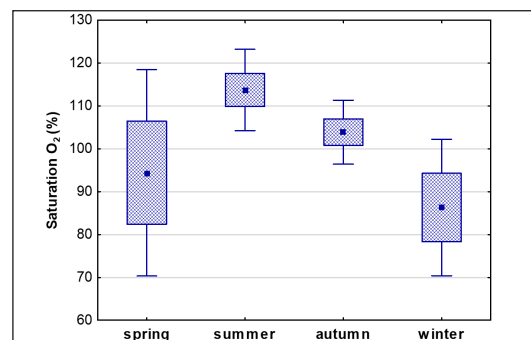


Fig. 3. Seasonal differences in oxygen levels in the water of Kolové pleso. K-W H (3; 20) = 8.5803; $p = 0.0354$. (Middle points: means; Boxes: +/- standard errors of mean; Whiskers: +/- standard deviations of mean).

December 2021, when the lowest water temperatures were also recorded in the same month.

The average pH for the overall measurement period was 7.64, with the lowest and highest measured values occurring in the fall of 2022. The lowest water pH was measured in September with a value of 6.08 and the highest pH was measured in November with a value of 8.82. Conductivity, TDS, and water hardness also increased during this month as well as pH. The average values of these variables were: conductivity: 15.68 $\mu\text{S}/\text{cm}$, TDS: 15.24 mg/L, and CaCO_3 : 17.05 mg/L.

Conductivity and TDS had measured minimums in May 2021 (conductivity: 7.5 $\mu\text{S}/\text{cm}$ and TDS: 8 mg/L) and maximums in February 2022, (conductivity: 25 $\mu\text{S}/\text{cm}$; TDS: 25 mg/L). The average values for both years were a level for conductivity: 15.68 $\mu\text{S}/\text{cm}$ and TDS: 15.24 mg/L.

Chemical parameters of water

For the identification of chlorides in water, the concentration of chlorine (Cl), chloride (NaCl) and calcium carbonate (CaCO_3) are detected, and their concentration levels are correlated with each other. On average, Cl: 6.4 mg/L, CaCO_3 : 9.46 mg/L and NaCl: 11.09 mg/L, were detected in lake Kolové pleso. The highest chloride levels were measured in November 2021: Cl: 25.5 mg/L, CaCO_3 : 35.5 mg/L and NaCl with a value of 41.5 mg/L. No chloride values (0 mg/L) were detected a total of four times,

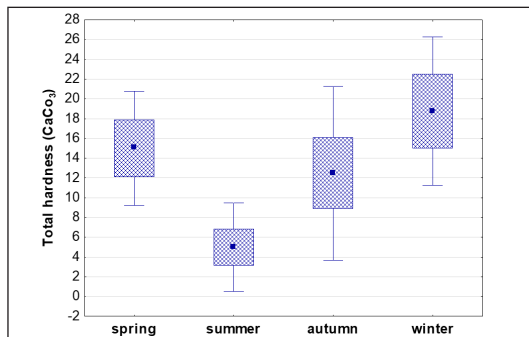
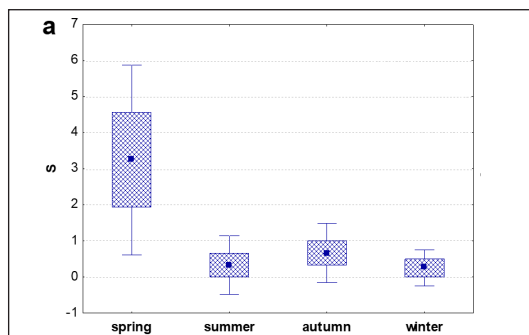


Fig. 4. Seasonal differences in total water hardness CaCO_3 ; $F(3; 16) = 3.6231$; $p = 0.0361$. (Middle points: means; Boxes: \pm standard errors of mean; Whiskers: \pm standard deviations of mean).



once in each season (October 2021, December 2021, May 2022 and July 2022).

Total water hardness varied significantly between seasons (Fig. 4). The average hardness for the two-year period compared was 12 mg/L, with the lowest value of 0 mg/L measured in June 2021 and the highest value of 30 mg/L measured in winter, December 2021. In general, higher values were recorded in winter and the lowest values in spring and summer.

Sulfides also had a significant seasonal pattern, with the highest values measured in spring. The highest value was measured in May, S: 7 mg/L (Fig. 5a) and SO_4^{2-} : 22 mg/L (Fig. 5b). The lowest value of 0 mg/L was measured for several times. (for SO_4^{2-} nine times and for S eleven times). During summer and winter the values were low, the highest values and a large dispersion occurred in spring.

Ammonia values were not higher than 1 mg/L during the whole monitoring period. On average, it remained at N: 0.16 mg/L, NH_3 : 0.19 mg/L and NH_4 : 0.2 mg/L. Their values increased in the last half of the second year of monitoring, with the highest values measured for all three variables in July 2022.

Nitrates were dependent on seasonality during the study period. The measured values in both cases (N, NO_3) were higher in spring and had the highest variance of values, while in winter they had the lowest variance. The lowest values were measured in autumn, in September 2022 for N: 0.11 mg/L (Fig. 6a) and for NO_3 : 0.49 mg/L (Fig. 6b). The highest values for nitrates were measured in May 2022, for N: 0.88 mg/L and for NO_3 : 3.9 mg/L.

Phosphates did not show seasonal dependence. They were at, or just above, 0 for most of the two-year measurement period. The average value was for P: 0.03 mg/L and for PO_4^{3-} : 0.09 mg/L. The highest values were measured in June 2021. The highest values measured were for P: 0.15 mg/L and for PO_4^{3-} : 0.39 mg/L.

Discussion

Alpine lakes are sensitive environmental sensors, typically unaffected by anthropogenic disturbance, and are therefore considered high-quality water resources (Arnaud *et al.* 2016; Moser *et al.* 2019; Han *et al.* 2023). However, they are particularly sensitive to pollution and climate change (Flaim *et al.* 2020).

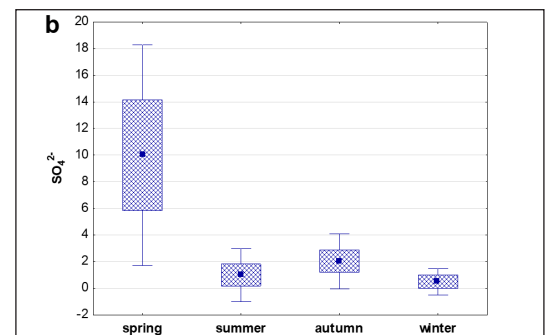


Fig. 5. Seasonal differences in sulphate content. a) S: K-W H(3; 20) = 8.9958; $p = 0.0293$. b) SO_4^{2-} : K-W H(3; 20) = 9.54; $p = 0.0229$. (Middle points: means; Boxes: \pm standard errors of mean; Whiskers: \pm standard deviations of mean).

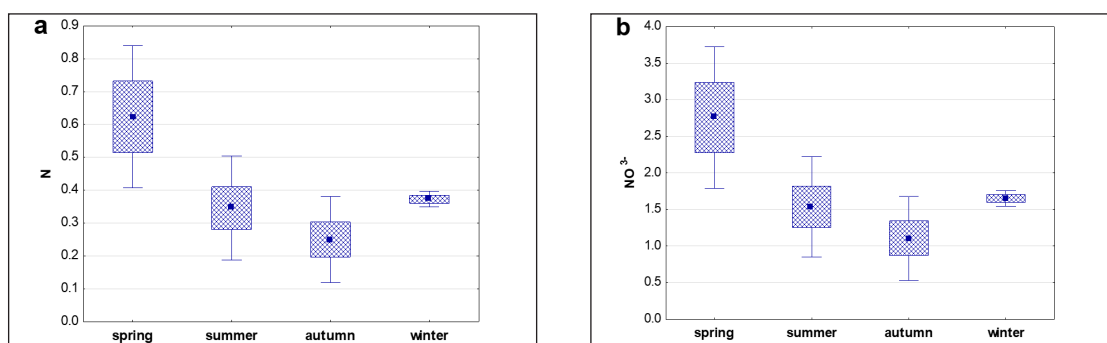


Fig. 6. Seasonal differences of Nitrates in mountain lake Kolové pleso. a) N: (One-Way ANOVA $F(3; 16) = 5.235$; $p = 0.0104$). b) NO_3^- : (One-Way ANOVA $F(3; 16) = 5.2551$; $p = 0.0103$). (Middle points: means; Boxes: \pm standard errors of mean; Whiskers: \pm standard deviations of mean).

The high mountain lake of Kolové pleso is located above the upper forest boundary and is not exposed to direct sources of pollution. It is a unique setting for monitoring ecosystem loading from atmospheric deposition.

There are several studies that have concluded that climate change can have a strong impact on these areas, as documented in a study from the Pyrenees region by Catalan *et al.* (2006). Climate change is also reflected in the increase in air temperature. The increase in lake water temperature increases evaporation, lowers lake levels and changes water quality. Thus, surface temperature is a particularly key factor (Cogălniceanu and Miaud 2004). In this study, the maximum temperature was 17.4°C , the minimum was 0.1°C , and the average over two years was 6.88°C . In a comparison of previous measurements for the period between 2017 and 2018, the minimum temperature was also 0.1°C , while the maximum was 14.1°C and the median was 5°C (Hrivnáková 2019). In the following period (2019-2020), the minimum temperature was 1.3°C , the maximum was 16.2°C and the median was 6.33°C (Potecká 2021). Temperatures have an increasing trend in the comparison of monitoring periods. Climate change can alter water composition and quality by influencing precipitation, which dilutes contaminants and affects flow to surface waters. Increased flows may also affect sediment transport to lakes, which may affect future life in lakes (Whitehead *et al.* 2009). Temperature values in our study had a large variance, which is likely due to the shallow depth of the lake ($\sim 1\text{ m}$), making it difficult to maintain a constant temperature (Ivanković *et al.* 2011).

Temperature values are positively correlated with oxygen levels in Kolové pleso. Taking into account that the lowest measured values were probably measured incorrectly, and thus the second lowest values were measured in December, the results support the hypothesis that the level of oxygen present is influenced by water temperature but also by the season, meaning that the lowest oxygen levels occur in winter when the lake is covered with ice and the water temperature in the lake is also low. Otherwise, oxygen concentrations were high throughout the year. The same conclusion is confirmed by Catalan *et al.* (2002) in a study monitoring nine mountain lakes in different European countries.

Comparison of our results with previous monitoring periods did not confirm a seasonal depen-

dence for TDS, conductivity, and water department.

Previous studies on the lake Kolové pleso show a negative correlation between water temperature and sulphides (Hrivnáková 2019), confirmed in this work for the period under study. Chlorides were not mentioned in connection with the same tendency to decrease with temperature as sulfides.

In previous work (Hrivnáková 2019; Potecká 2021), chlorides had extremely low values or were below the measured level. In this study, although they did not have high values throughout the year, they never fell below the detection limit. We therefore conclude that nitrate levels have increased. Increases in nitrate in lakes have also been reported by Palacin-Lizarbe *et al.* (2020). They concluded that, despite increased denitrification rates, there was an increase in nitrate because the denitrification process itself was not able to sufficiently compensate for the increase in these elements. The study was carried out on Lake Sabocos in the Pyrenees, which is situated at an altitude of 1905 metres above sea level (higher than Lake Cologne). Atmospheric deposition is probably the main source of elevated N (Palacin-Lizarbe *et al.* 2020).

COD has a higher number than in previous study periods immediately after the flood (y. 2018). The flood radically changed some water parameters (Hrivnáková 2019). During the second monitoring period, the parameters returned to normal except for COD. Our results confirm the higher values for COD.

The aim of the research in the monitoring period 2021-2022 was to compare the physical and chemical parameters of the water in the mountain lake Kolové pleso.

No significant differences were observed between most of the organic and physical compounds in the year-to-year comparison. Significant year-to-year difference was observed only for anthracene. Significant differences were observed in the seasonal comparison for the parameters studied, namely water temperature, oxygen level, sulphur (as a separate element), SO_4^{2-} , nitrogen, NO_3^- and water hardness. Oxygen and temperature were positively correlated, but oxygen levels remained high throughout the year.

In 2018, a flood occurred in the region of valley Javorová dolina area that rapidly changed some water parameters. During the second monitoring period (2019-2020), COD values remained high, while other parameters gradually regained their pre-flood values.

During the monitoring period (2021-2022), COD values remained elevated. The research continues to be ongoing in the 2023-2024 monitoring period.

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