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Seasonal variability of physical and chemical properties of the water in lake Kolové pleso, the West Carpathians

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Abstract. This study examines the physical and chemical limnology of lake Kolové pleso in order to understand the response of the high mountain lake ecosystem to seasonal, climatic and anthropogenic impacts. We have combined regular monthly monitoring of physical properties on site and analyzed the chemical composition of the lake, using nutrient photometry, X-ray analysis of elements and COD methods. Fluctuations and concentrations of these variables confirmed that the lake is affected by seasonal fluctuations, subsoil, bioaccumulation of elements, vegetation and atmospheric deposition and climate variables. No potential pollution was detected by these indicators. The GC-MS method was used to qualitatively identify organic substances in the lake that were potentially harmful. PAHs (phenanthrene and pyrene) were found during the heating period (winter months). Due to the extensive rainfall in July 2018, during the experiment, we had the opportunity to observe the effect of flooding on the lake. Flooding has a significant impact on the organic composition of the lake (COD) as well as on some chemical elements (S, K, Rb, Mo, Cd), whose values dropped significantly following the flood. The decrease in COD values influenced the acidity of the lake negatively, as seen in the past.

Key words: high mountain lake, physical and chemical limnology, flood impact, organic pollutants

Introduction

Water is one of the most widespread compounds on Earth. It creates the conditions for the existence of all forms of life, and is a basic biological component and technological raw material (Hanušin 2009). Standing water is characterized by the absence of flow predetermining some of its physicochemical properties, which are significantly different from flowing water. Standing water includes lakes, and this study focuses on glacial lakes. Glacial lakes in the Tatras are called "plesá". They represent 90% of all lakes in Slovakia (Hrabě 1939, 1942; Bitušík *et al.* 2006) and are mostly oligotrophic standing waters with specific characteristics (Psenner 1989; Drever and Zobrist 1992; Beracko *et al.* 2014).

These ecosystems have been identified as key sites for studying global environmental change (Pienitz *et al.* 1997a). Despite their geographical isolation, without direct anthropogenic influences, due to their specific characteristics, alpine lakes are excellent indicators of seasonal changes, as well as increasingly frequent (IPCC 2001) climate change (Wathn *et al.* 1995).

That is why several studies conducted in Arctic region, as well as in Tatra high mountain lakes (e.g. Henriksen *et al.* 1992; Fott *et al.* 1994; Kopáček and Stuchlík 1994; Kopáček *et al.* 2000, Štefková and Šporka 2001; Grimalt *et al.* 2004; Kopáček *et al.* 2004; van Drooge *et al.* 2004; Stuchlík *et al.* 2006; Šporka *et al.* 2006; Kopáček *et al.* 2006; van Drooge *et al.* 2011, 2013), have been devoted to the limnology of such isolated lakes and to this issue.

These studies have shown that aquatic ecosystems are influenced by extensive global environmental changes (Wograth and Psenner 1995; Duff 1999). Research has indicated that global warming is likely to lead to an increase in water temperatures in lakes, a particularly important factor in aquatic ecology (Robertson and Ragotzkie 1990; Hondzo and Stefan 1993; De Stasio *et al.* 1996; Stefan *et al.* 1996; Šporka *et al.* 2006).

Because of fluctuating water levels, floods are notable biochemical events for lake ecosystems (McClain *et al.* 2003). Most lakes are heterotrophic, and dependent on organic inputs from their basins and subsoil (Sobek *et al.* 2007). Floods have the effect of rapidly mobilizing and accumulating organic carbon and nutrients (Nogueira *et al.* 2002; Wantzen *et al.* 2008), which can lead to "wash out" and also cause leaching of heavy metals into the environment from lake bottom sediments; posing a potential risk to water quality (Chrastný *et al.* 2005).

Many studies address the potential negative impact of organic substances accumulating in natural environments (Wania and Mackay 1995) as a result of their extensive use in industrial applications and combustion processes (Douglas and Smol 1994; Antoniades *et al.* 2003; Bruzzoniti *et al.* 2009). Pollutants tend to be transported in the atmosphere over long distances, (van Drooge *et al.* 2004; Landlová 2006; Morales-Baquero *et al.* 2013) and accumulate in isolated regions (Blais *et al.* 1998; Grimalt *et al.* 2001; Zennegg *et al.* 2003; Fernández *et al.* 2005; Meijer *et al.* 2006) such as the Tatra lakes (e.g. Grimalt *et al.* 2004; van

Drooge *et al.* 2004, 2011, 2013). In the High Tatras, which are part of the National Park, there are no industrial or agricultural activities. The closest industrial area is Košice in the south, Ostrava to the west and Polish factories (Krakow, Novy Targ, Zakopane) to the north; almost all of these are located dozens of kilometers from the mountains (van Drooge *et al.* 2004). Despite this, research has found mild PCB and PAH contamination (Grimalt *et al.* 2001; van Drooge *et al.* 2011).

These ecosystems represent the least disturbed inland water environments (Grimalt *et al.* 2001; Meijer *et al.* 2006). They are sensitive environmental indicators for determining changes in air quality and for the long-range transmission of pollutants (van Drooge *et al.* 2013).

Alpine lakes are likely to experience dramatic future physical, chemical and biological changes (Antoniades *et al.* 2003). Therefore, understanding the impact of past, present, and likely future anthropogenic influences and climate change depends on understanding the basic state of lakes (Hamilton *et al.* 2001; Michelutti *et al.* 2002a).

The aim of this study is, therefore, to collect data that will define the natural, present state of lake Kolové pleso, describe the impact of the flood on the lake, and identify and describe potential organic pollution. The data will serve as a reference for future programs for monitoring anthropogenic impacts and global environmental changes (Pienitz *et al.* 1997a).

Material and Methods

Study area

The Tatra Mountains are the highest mountain range in Slovakia. They are about 60 km long and 17 km wide and one-fifth of the range is situated in Poland. They are divided into two geomorphological units, the Western and Eastern Tatra Mts. The Eastern Tatras a further divided into the High Tatras and the Belianske Tatras (Štefková and Šporka 2001).

The valley of Kolová dolina, from the delta of the Kolový potok stream to the foot of Kolový štít peak, is about 2.5 km long. This area is between Jahnence and Bortky. The dominant mountain peaks within this valley are Kolový štít (2418 m a.s.l) and Jahňací štít (2229 m a.s.l) (www.spravatanap.sk 2012).

Fig. 1. Lake Kolové pleso – June 2018 (Photo: V. Ruček).

Lake Kolové pleso (Fig. 1) is situated in Kolová dolina valley at an altitude of 1565 m. It has an area of 18 280 m^2, a perimeter of 735 m, water volume of 10 846 m^3, length of 225 m, width of 123 m, a maximum depth of 1.2 m, and an average depth 0.59 m (Marček 1996).

Climatic conditions of the area

Many specific features (Table 2) that fundamentally determine the existence and development of natural ecosystems, but also environmental phenomena characterize the climate of the High Tatras. Sampling frequency was determined to capture the seasonal variability of the physical and chemical variables of the monitored lake.

Fieldwork

Samples were taken monthly between August 2017 and December 2018 (Table 1). This sampling frequency was determined to capture the seasonal variability of the physical and chemical variables of the monitored lake.

To measure physical parameters of the water samples including water temperature, salinity, pH, U (voltage), conductivity, TDS (total dissolved solids) (mg/l), soluble oxygen/(oxygen level) and saturation of the water, we used a portable multimeter WTW 3430 (GEOTECH, Weilheim, Germany). Along with the Multi 3430 we used compatible probes: IDS pH electrode Sen TixR 940-3, conductivity electrode TetraCon 925-3 and an optic oxygen electrode FDO 925-3.

Water samples were taken at 0.5 meters from the left shore of the lake. Samples were processed in the laboratory using gas chromatography. We used a glass container with one liter of content to

Month	Time	Conditions
August 2017	9:30	cloudy, cold, fog
September 2017	13:00	rain, cold
October 2017	12:30	cold, freeze
November 2017	11:30	ice, fog, snow
December 2017	13:00	ice, cloudly
January 2018	13:00	ice cloudly
February 2018	13:30	ice, pathy cloud, -25
March 2018	10:00	ice, sunny, warm
April 2018	8:30	without snow and ice, sunny
May 2018	13:00	sunny, without clouds
June 2018	12:00	cloudly, rain
July 2018	11:30	floods
August 2018	9:30	rain
September 2018	12:30	sunny, warm
October 2018	10:35	ice, first snow, sunny
November 2018	12:30	ice, sunny, without snow
December 2018	10:00	ice, snow

Table 1. Sampling tapping (August 2017-December 2018).

Month	Global radiation [W/m^2]	Air temperature [deg. C]	Air humidity [%]	Wind direction	Precipitation [mm]	Wind speed (m/s)
August 2017	142.5	13.03	78.58	161.36	0.14	0.53
September 2017	84.7	7.03	86.54	163.67	0.3	0.7
October 2017	52.32	2.99	82.04	165.56	0.06	0.48
November 2017	20.0	-0.87	79.23	159.92	0.05	0.7
December 2017	9.35	-4.2	76.72	169.34	0	1.54
January 2018	20.57	-3.16	72.21	150.36	0	1.01
February 2018	18.13	-7.02	89.53	119.76	0	0.35
March 2018	102.56	-4.36	75.86	149.58	0	0.71
April 2018	153.78	7.07	63.12	150.94	0.14	1.31
May 2018	148.39	9.35	78.14	157.15	0.11	0.68
June 2018	100.84	10.18	92.29	159.96	0.22	0.41
July 2018	114.95	11.63	89.78	160.21	0.17	0.37

Table 2. Monthly measurements from a weather station in valley Kolová dolina (August 2017 - July 2018). Note: It should be taken into account that the weather station is not heated, therefore the precipitation totals are not registered exactly in the winter. It is because snow and ice accumulate in the rain gauge through all winter. Data of measurements from the weather station in valley Kolová dolina were kindly provided by the National Forest Center - Forest Research Institute Zvolen.

Fig. 2. Valley Zadné Meďodoly in the day of flood – July 18th, 2018 (Photo: V. Kapusta).

avoid sample contamination because of medium-flowing organic substances in the water. For the purposes of the subsequent analysis, other samples were placed into plastic containers containing 0.7 l. Before the sampling, all containers were properly labeled and disinfected. We were really careful about the proper transportation of the samples and their preservation, trying to keep intervals between sampling and analysis as short as possible. During sampling in the summer (18th of July 2018), the Tatra Mountains were hit by floods (Fig. 2).

Chemical oxygen demand (COD)

We used three boiling flasks with the same sample (100 ml sample of water from lake) to average results for more accurate measurements.

The method is based on the oxidation of organic substances with 20 ml potassium permanganate (K_2MnO_4) solution (0.002 mol/l), in 5 ml acidic sulfuric acid (H_2SO_4, 96%) in a dilution of (1:2) at 10 min boiling. We used 4-5 cooking stones for each boiling flask and a small clock glass was placed on the flask's throat. Oxidation occurs with excess permanganate. After completion of the oxidation, the unreacted $KMnO_4$ is reduced by the excess of standard oxalic acid ($(COOH)_2$) solution (0.005 mol/l), added in the exact quantity (20 ml) to the sample: $2MnO^{-}_{4} + 5\,(COOH)_2 + 6H^{+} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$.

The solution in the boiling flask was completely decolorized to a clear solution. The clear solution was titrated back with potassium permanganate (0.002 mol/l) to $KMnO_4$ until it was stained a faintly pink color. Consumption at titration indicates the consumption of manganese to oxidize organic matter.

Photometry

We used photometry (optical - analytical method) to determine other chemical parameters of water quality (chlorides, sulfates, nitrates, ammonia, phosphorus, and contents of total hardness). The YSI EcoSense 9500 photometer and accessories compatible with this water analyzer determined concentrations of ions in our samples.

X-ray analysis

The x-ray method determines values of some chemical elements (trace elements). We used a handle ED-XRF spectrometer DELTA (Bas, Rudice, CZECH) and analyzed the water sample in a plastic vial. Samples were analyzed with x-ray beams for 80 seconds. Analytical methods and calibration practices used in the laboratory correspond with internationally accepted standards (Spectrapure Standards, Norway). Detections limits (X-ray) differ for different elements and fulfill the criteria described in the manual to Delta XRF.

Gas chromatography/mass spectrometry (GC-MS)

We used LLE: liquid-liquid extraction, a method commonly used for aqueous samples. In this extraction technique we mixed 1l water samples from the tarn with 3 ml of hexane. The sample was shaken for 2 minutes. The hexane layer was isolated on the top of the solution. The isolated extract was evaporated and re-filled with hexane (300 ml). Thus isolated, the sample can be analyzed using a gas chromatograph.

The separation of the components is based on analyte retention between the stationary - liquid phase and the mobile - gas phase. To identify the components of the mixture, the measured retention times are compared with the already known retention times obtained under the same conditions (Agilent Technologies 2013).

Statistics

For statistical analysis (Pearson´s correlation matrix, one way ANOVA and graphs) we used STATISTICA 8 software.

Results

Physical and chemical variables

Physical and chemical values from 12 samples collected between August 2017 and July 2018 are reported in Appendix 1 and Table 3.

Physical variables

Water temperature values are seasonally dependent (Comparison between two half a year samples - summer versus winter: $F(1.10) = 7.9815$, $p=0.01800$), falling in the summer months and increasing during winter. Based on our research, the water temperature was low all year round (Appendix 1) with a mean value of 5˚ C. A maximum temperature of 14.1˚ C was recorded in May and a minimum temperature of -0.1˚ C was measured in December (Table 3). Water temperature also affects oxygen ratios (Appendix 2), which can be seen in the annual seasonal fluctuations when oxygen levels fall in the summer months and increases at lower temperatures in winter (Appendix 1). The dissolved oxygen values in the lake were high - mean 10.12 mg/l and 98.36% (Table 3). These values correlate negatively with those of titanium and potassium (Appendix 2). The mean pH of the lake was 7.5 with a range of 5.8 to 9.4 (Table 3). The pH also influences the concentration and solubility of some elements (Appendix 2) such as chlorine, potassium, and titanium. The highest pH values were measured in June - July, while the electric voltage, which is inversely proportional to pH (Appendix 2), decreases with temperature rise (Appendix 1). Positive correlation (Appendix 2) of molybdenum with electrical voltage is an interesting result. Electrical voltage had higher values in August, January, and February than in the other months, as did molybdenum, indicating this correlation (Appendix 2). Conductivity is directly proportional to ion concentration (TDS) and

Parameter	Mean	Median	SD	Minimum	Maximum	Detection limit & units
t	5.008	3.85	3.620	-0.1	14.1	**˚C**
pH	7.460	7.548	1.087	5.705	9.437	
U	-53.409	-40.65	35.867	-131.96	-0.33	**mV**
Concent. O_2	10.123	10.26	1.026	8.31	11.99	**mg/l**
Sat. O_2	98.359	99.7	5.777	88.33	110.47	**%**
O_2	172.521	172.7	8.821	155.10	193.10	**mbar**
Conductivity	15.148	13.38	6.563	7.70	27.23	**μS/cm**
TDS	15.066	13	6.675	8	28	**mg/l**
p	*78.926*	79.23	28.401	37.23	130.20	**kΩ*cm**
COD	3.375	2.82	2.664	0.82	10.59	**ml**
Cl^-	7.5	3.7	7.996	0.5	22.2	**0-50 mg/l**
NaCl	13.183	8.55	12.990	0.8	36.7	**0-50,000 mg/l**
tot. hardness $CaCO_3$	12.567	10	11.679	Det limit	40	**0-500 mg/l**
chlorides $CaCO_3$	11.958	7.3	11.026	0.7	31.3	**mg/l**
SO_4^{2-}	12.517	5.35	21.903	0.0	83.3	**0-200 mg/l**
S	4.217	1.85	7.449	0.0	28.3	**0- 200 mg/l**
ammonia N	0.209	0.095	0.256	Det limit	0.72	**0-1.0 mg/l**
PO_4^{3-}	0.107	0.075	0.103	Det limit	0.34	**0-4.0 mg/l**
P	0.035	0.025	0.034	Det limit	0.11	**0-1.3 mg/l**

Table 3. Measured limnological variables from lake Kolové pleso including mean, median, standard deviation (SD), minimum value, maximum value, and analytical detection limit. Det limit - measurement under the detection limit.

Parameter	Climatic variables									
	Global radiation [W/m²]		Air temperature [deg. C]		Air humidity [%]		Wind direction		Precipitation [mm]	
	r	p	r	p	r	p	r	p	r	p
t (° C)	0.5931	0.0421	0.611	0.0348						
U (mV)					-0.5771	0.0494				
O_2 (mbar)	0.5788	0.0487								
Conductivity (μS/cm)			-0.7356	0.0064			-0.6825	0.0145	-0.6824	0.0145
TDS (mg/l)			-0.7592	0.0042			-0.7193	0.0084	-0.6757	0.0159
p (kohm*cm)			0.7147	0.009					0.6617	0.0191
Cl (ppm)	-0.7139	0.0091	-0.695	0.0121					-0.591	0.043
K (ppm)	-0.7488	0.0051	-0.6445	0.0237						
Ti (ppm)	-0.6225	0.0307								
Sn (ppm)									0.5796	0.0483
Sb (ppm)			0.5766	0.0497						

Table 4. Correlation coefficients of selected climatic variables. Only significant values ($p<0.05$) are listed. Climatic variables were kindly provided by the National Forest Center - Forest Research Institute Zvolen.

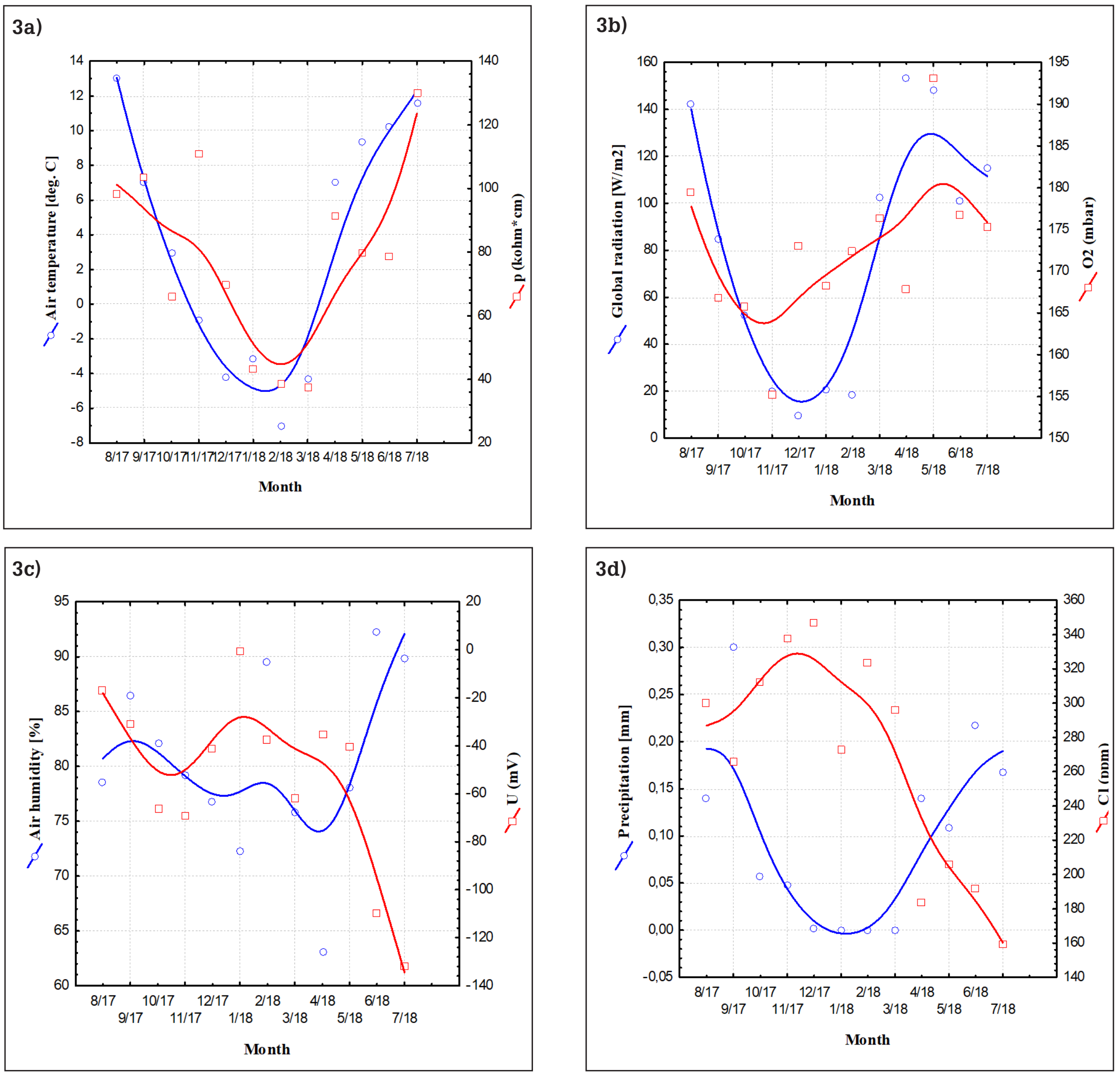

Fig. 3. Fluctuating of multiple variables (negative exponential smoothing) of the lake with climatic variables during the year. The fluctuating of global radiation in conjunction with O_2 (mbar) (3a), air temperature in conjunction with resistance (3b), the air humidity in conjunction electrical voltage (3c), precipitation in conjunction with chlorine (3d), and wind direction in conjunction with conductivity values with respect to the month.

is the inverted value of the electrical resistance of the water (Appendix 2 - high values of the same sign). Seasonally interdependent variables (Comparison between two half a year samples - summer versus winter: Resistance: One way ANOVA: F(1.10) = 6.6758, p=0.02724, Conductivity: One way ANOVA: F(1.10) = 6.4953, p=0.02893, TDS: One way ANOVA: F(1.10) = 7.2196, p=0.02282). Conductivity and TDS values were higher in the winter months (January-March), and dropped during summer months (July- September) (Appendix 1). Resistance negatively correlated with these values during the year (Appendix 2). Salinity showed zero values throughout the experiment.

Nutrients

Four of the 13 original environmental variables ($N\text{-}NH_4$, $N\text{-}NH_3$, NO_3^- and N) were not included in the statistical analysis because they were commonly found outside the detection boundaries. Nutrient concentrations were lower and in some months they were below the detection limit (Appendix 1). Chloride values gradually increased in winter (November - April) and decreased between spring and winter (May - October) (Appendix 1). The most widespread chloride (NaCl) values ranged from 0.8 - 36.7 mg/l (Table 3). Total hardness has a fluctuating tendency (Appendix 1). Peaks occurred in November, January and May and the maximum value was 40 mg/l (Table 3). The lowest values were observed in September, December and March. In Appendix 1, we can see that the sulfates gradually increased in direct proportion to the total hardness during the year. With the exception of one peak in August, when sulfates reached the highest value of 83.3 mg/l (Appendix 1). Phosphate values were higher in the months of October, November, January, and June, and decreased during summer (July-September) (Appendix 1). The highest value was measured in June at 0.34 mg/l (Table 3). Ammonia (N) values gradually increased in direct proportion to the sulfur values during the year. Ammonia (N) had higher values in April, June, November, and December (Appendix 1) than in other months, as did sulfur, suggesting a positive correlation between them (Appendix 2). The highest COD values were observed in the autumn (August-November), and decreased in the following months (Appendix 1). During the year, COD values were low, with the exception of one maximum value of 10.59 ml (Table 3) in November 2017.

Chemical elements

Potassium is seasonally affected (Comparison between two half a year samples - summer versus winter: One way ANOVA: F(1.10) = 12.999, p=0.00480) and had higher values in the winter months (October - February) (Table 3) than in the summer months (April - August). It has a similar fluctuating tendency to titanium, suggesting a positive correlation between them (Appendix 2). Appendix 2 shows the positive relationship between titanium, NaCl and chlorides ($CaCO_3$). The decrease in the second alkali metal measured in the lake - rubidium (Appendix 1) was recorded at the beginning of spring and summer (March - April, and July) and the highest values were observed from August to February. A smaller decrease in molybdenum values was recorded at the beginning of winter and a more pronounced decrease was recorded in spring (March - July). The highest values were in August, January, and February (Appendix 1). Tin values peaked in September, January, and June (Appendix 1) though in other months, the values were lower. Antimony is affected by temperature (Appendix 2) and thus by season (Comparison between two half a year samples - summer versus winter: One way ANOVA: F(1.10) = 6.6568, p=0.02741). In summer it gradually increased (Appendix 1). During the winter season it declined between September and April. Chlorine had higher values in winter (October - March) (Appendix 1) and lower values in summer months (April - July), similar to potassium, suggesting a positive correlation between them (Appendix 2) as well as a seasonal dependence (Comparison between two half a year samples - summer versus winter: One way ANOVA: F(1.10) = 15.518, p=0.00278). Sulfur has a fluctuating tendency (Appendix 1); peaking in November and December as well as between April and June, while in recent months the values were lower.

Direct climate variables also affect the lake, which can be seen in many correlations with lake properties (Table 4). Global radiation positively correlates (Table 4) with water temperature and O_2 (mbar), as seen in the same fluctuations during the year (Fig. 3b). This climate indicator negatively correlates (Table 4) with the chemical composition of the lake, namely the values of chlorine, titanium, and potassium. The temperature as a major climate variable affects the negative conductivity, TDS and chlorine and potassium correlations (Table 4). However, the correlation with resistance is positive, which can be seen in the same fluctuations during the year (Fig. 3a). As shown in Figure 3c, air humidity negatively correlates with electrical voltage. The amount of precipitation correlates favorably with resistance and tin and negative with conductivity, TDS (Table 4) and chlorine in water (Fig. 3d). The dependence of conductivity and TDS on the weather is shown in Table 4.

Effects of flooding

In July of 2018 the High Tatras experienced an extensive flood and significant decrease in concentration was observed in sulfur (S), molybdenum (Mo), potassium (K) and rubidium (Rb) values (Table 5 and Fig. 4a-d). The other mentioned measured elements were unchanged.

The second impact of the flood was on the organic composition of the lake (COD). As we saw with element concentration, COD values (Fig. 5a) also decreases following the flood. The difference is that the decrease in COD was also observed on the day of the flood and thus in the sample from July 18, unlike the other elements whose values fell during the following month, as can be seen in Table 5. However, with the decrease in COD during the summer, pH values (Fig. 5c) are increasing. In July, 2018, values between 7.7 to 9.4 were measured. The highest pH values over the entirety of the sampling pe-

Month	COD (ml)	S (ppm)	K (ppm)	Rb (ppm)	Mo (ppm)	Cd (ppm)
August 2017	6.25	76 ± 64	187 ± 12	1.6 ± 0.6	1.3 ± 0.5	Det limit ± 6
September 2017	4.7	Det limit ± 62	196 ± 12	1.6 ± 1.1	1.1 ± 1	Det limit ± 6
October 2017	2.79	59 ± 48	210 ± 10	1.2 ± 0.8	1.1 ± 0.8	Det limit ± 4
November 2017	10.59	96 ± 67	252 ± 15	1.5 ± 0.5	1.1 ± 1	Det limit ± 6
December 2017	3.27	93 ± 34	193 ± 13	1.5 ± 0.6	Det limit ± 1	Det limit ± 6
January 2018	0.93	Det limit ± 56	203 ± 11	1 ± 1	1.3 ± 0.9	Det limit ± 5
February 2018	0.92	Det limit ± 57	215 ± 12	1.2 ± 0.5	1.3 ± 0.4	Det limit ± 5
March 2018	2.18	Det limit ± 63	187 ± 13	Det limit ± 1.1	Det limit ± 1	Det limit ± 6
April 2018	2.85	196 ± 145	134 ± 9	Det limit ± 0.4	Det limit ± 0.1	Det limit ± 6
May 2018	1.8	Det limit ± 138	152 ± 9	1.3 ± 0.2	Det limit ± 0.1	Det limit ± 6
June 2018	3.41	187 + 144	133 ± 8	1 ± 0.4	Det limit ± 0.1	Det limit ± 6
18th of July 2018	**0.82**	Det limit ± 137	137 ± 8	Det limit ± 0.4	Det limit ± 0.1	Det limit ± 6
August 2018	**0.8**	16 ± 12	1 ± 0.1	Det limit ± 0	Det limit ± 0	Det limit ± 0
September 2018	**0.91**	Det limit ± 11	1 ± 0.1	Det limit ± 0	Det limit ± 0	Det limit ± 0
October 2018	**0.66**	Det limit ± 12	1.1 ± 0.1	Det limit ± 0	Det limit ± 0	Det limit ± 0
November 2018	**0.98**	Det limit ± 12	1.1 ± 0.1	Det limit ± 0	Det limit ± 0	Det limit ± 0
December 2018	**0.77**	13 ± 6	1 ± 0.1	Det limit ± 0	Det limit ± 0	Det limit ± 0

Table 5. Average amount of chemical elements (and COD amount) ± displayed error (deviation from measurement) during a one and half year experiment. Det limit - measurement under the detection limit.

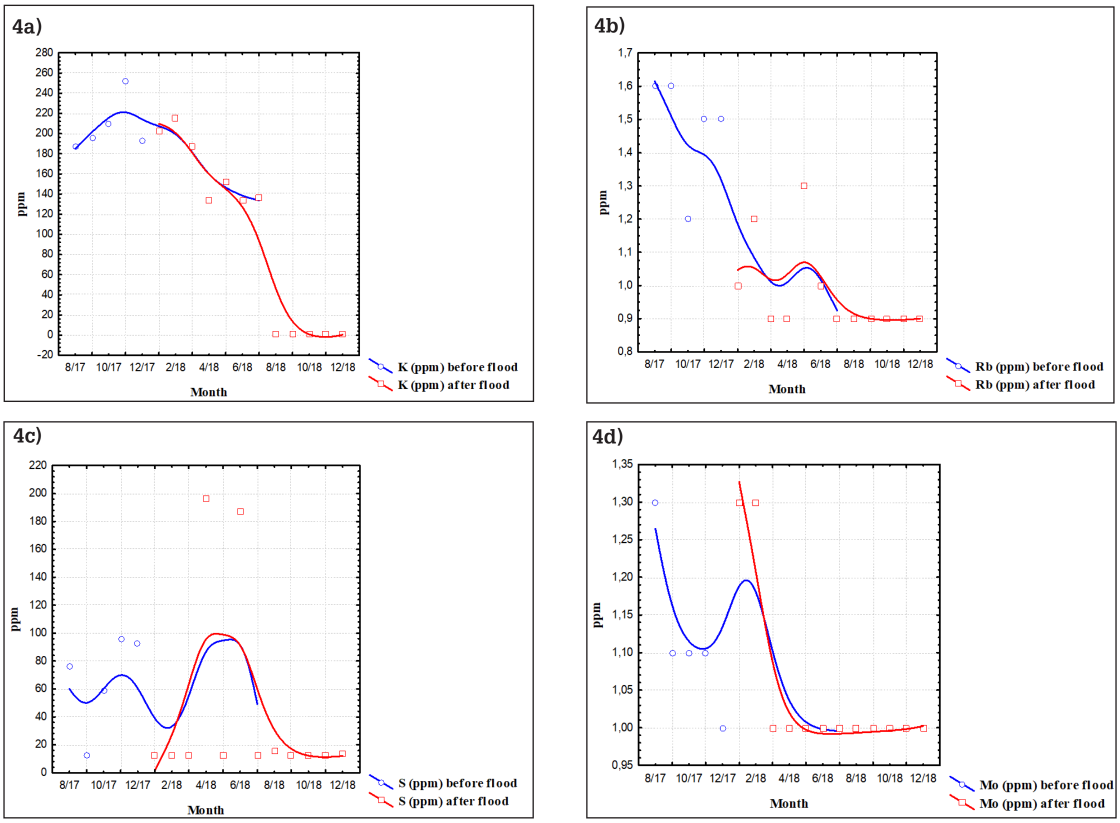

Fig. 4. The fluctuation of elements (K, Rb, S, Mo) prior to the flood (blue line) and post-flood change (red line) in July 2018. A decrease in the amount of potassium (4a), rubidium (4b), sulfur (4c) and molybdenum (4d) after July of 2018.

riod was also on the day of the flood. This negative correlation (pH: COD (ml): r = -0.6003; p = 0.0108) indicates that pH (Fig. 5b) is affected by flood and can be seen in Fig.5c and Fig. 5d. For other measured physical and chemical variables, no changes due to floods were observed.

Organic pollutants

All organic compounds found in the lake and the months in which they were measured are presented in Table 6, except for the phthalates that originated from the laboratory contamination and are therefore

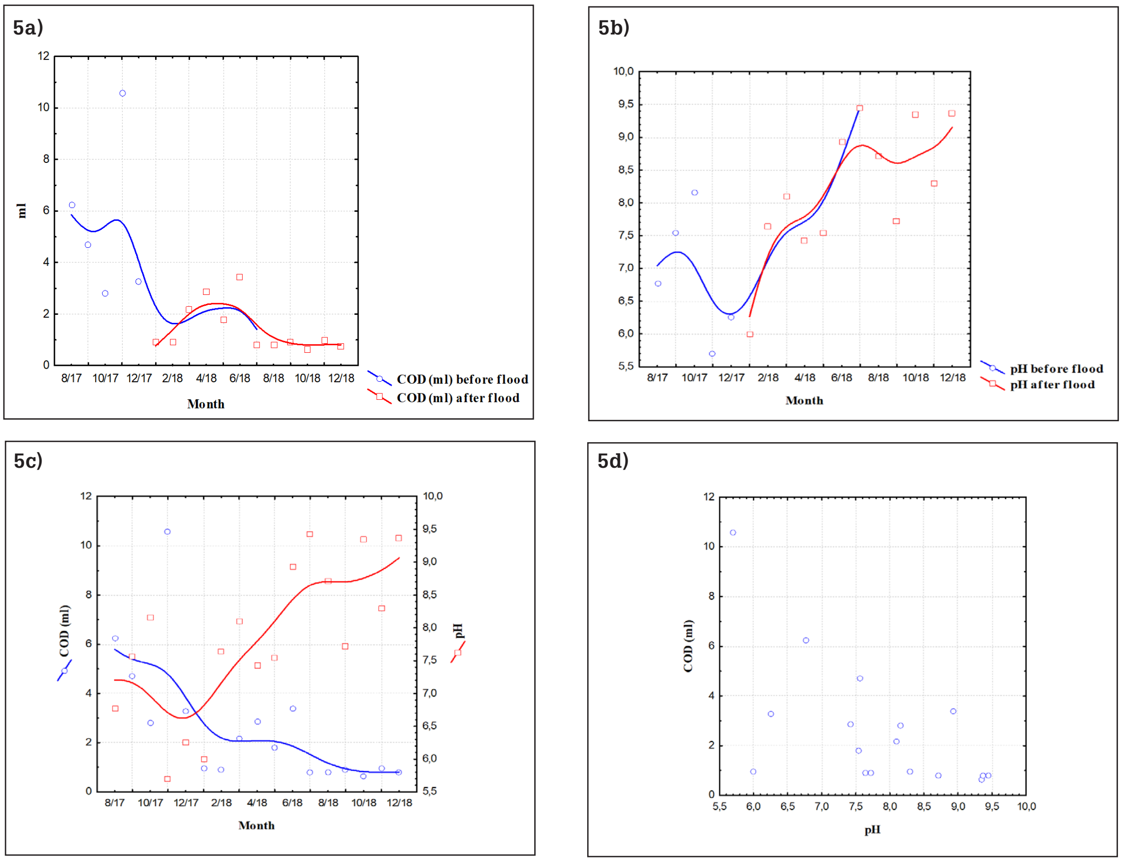

Fig. 5. Changes in COD and pH values due to floods and their interdependence. The fluctuation of values of COD and pH prior to the flood (blue line) and post-flood change (red line) in July 2018 is shown in figures 5a and 5b. Figures 5c and 5d show the correlation (pH: COD (ml): r = -0.6003; p = 0.0108) of pH values against the COD, during an experimental period.

Organic compounds	Formula	RT	Month	
			2017	2018
1-Decanol, 2-hexyl-	$C_{16}H_{34}O$	13.6	August	February
1-Dodecanol	$C_{12}H_{26}O$	16.5	-	May
4-Methyl-2,4-bis(p-hydroxyphenyl) pent-1-ene, 2TMS d.	$C_{24}H_{36}O_2Si_2$	18.3	-	November
6-Hepten-3-one, 5-hydroxy-4-methyl-	$C_8H_{14}O_2$	3.1	October	February, June, October
Borinic acid, diethyl-	$C_4H_{11}BO$	4.6	October	January, June, October
Carbonic acid, eicosyl vinyl ester	$C_{23}H_{44}O_3$	12.5	August, December	January, February
Dotriacontane, 1-iodo-	$C_{32}H_{65}I$	13.5	August	February
Eicosane, 1-iodo-	$C_{20}H_{41}I$	12.5	-	January
Eicosyl octyl ether	$C_{28}H_{58}O$	19.3	-	February
Fumaronitrile	$C_4H_2N_2$	3.3	-	November
Hexadecane, 2,6,11,15-tetramethyl-	$C_{20}H_{42}$	13.5	-	January
i-Propyl 14-methyl-pentadecanoate	$C_{19}H_{38}O_2$	20.4	-	January, March
Isopropyl palmitate	$C_{19}H_{38}O_2$	20.4	-	May
Phenanthrene	$C_{14}H_{10}$	14.2	December	January, February
Pyrene	$C_{16}H_{10}$	21.1	December	-
Sebacic acid, but-2-enyl propyl ester	$C_{17}H_{30}O_4$	15.8	-	January
Sulfurous acid, 2-ethylhexyl tetradecyl ester	$C_{22}H_{46}O_3S$	13.9	-	January

Table 6. List of detected organic compounds in analyzed samples of water during August 2017 – December 2018 from lake Kolové pleso. RT – retention time.

not reported in the results. In September of 2017, November of 2017, April of 2018, July of 2018, August of 2018, September of 2018, December of 2019 no organic compounds were found.

Compounds from all analyzed samples belong to the chemical groups of carboxylic acids, acid esters, ethers of various compounds, alcohols, isoprenoids, PAH and others. In Table 6, we can see that some potentially polluting organic substances were measured in several months during the experimental period. Most of the substances were found in the winter months, when the lake is covered with snow, namely substances from the group PAHs (Phenanthrene; Pyrene), esters (Sebacic acid, but-2-enyl propyl ester; Sulfurous acid, 2-ethylhexyl tetradecyl ester), isoprenoids (Hexadecane, 2,6,11,15-tetramethyl; i-propyl 14-methylpentadecanoate), ethers (Eicosyl octyl ether; Fumaronitrile; Eicosyl octyl ether), but also Eicosane, 1-iodo. Substances analyzed in both summer and winter are from the group of fatty alcohols (1-Decanol, 2-hexyl-) and acids (Dotriacontane, 1-iodo; Carbonic acid, eicosyl vinyl ester). Isopropyl palmitate was measured only in May as well as 1-Dodecanol. Interestingly, acids (6-Hepten-3-one, 5-hydroxy-4-methyl-; Borinic acid, diethyl) were detected in the same months (October, January, and February).

Discussion

Physical and chemical variables

In alpine lakes such as Kolové pleso, water temperatures have very low values throughout the year (Appendix 1), even during periods when the lake is not frozen (Juriš *et al.* 1965; Šporka *et al.* 2006). Although water temperature is dependent on the season, even in summer months the water temperature does not significantly exceed 10° C (Juriš *et al.* 1965). The average water temperature in Kolové pleso was 5° C (Table 3) and during the measurement period, it only rose above 10° C once, and reached a maximum measured value of 14.1° C in May (Table 3). The thermal balance of the lake depends on global radiation absorption (Table 4) and heat exchange with air (Edinger *et al.* 1968; Sweers 1976). Water temperature of the lake has often followed the air temperature closely (Table 4), according to several studies (e.g., McCombie 1959; Edinger *et al.* 1968; Webb 1974; Sweers 1976; Shuter *et al.* 1983; Marti and Imboden 1986; Livingstone and Imboden 1989; Douglas and Smol 1994; Lister *et al.* 1998; Livingstone and Lotter 1998; Kettle *et al.* 2004; Šporka *et al.* 2006). Surface water temperature of the lake more faithfully reflects air temperature during the warmer months (Livingstone *et al.* 1999, 2005; Šporka *et al.* 2006). The highest temperature value (14.1° C) (Table 3) was measured on the warmest day (13.22° C) according to weather station data (weather station data APVV-16-0325 - NFC). Water temperature is also important for the assessment of oxygen ratios (Doláková and Janýšková 2012), as oxygen ratios depend on water temperature (Appendix 2). Saturation in the lake increases in winter and its decrease is caused by the temperature increase in summer (Appendix 1) (Sedláková and Halabuk 2003; Judová *et al.* 2015). The intensity of global radiation (Table 4 and Fig. 3b) also affects dissolved oxygen, which in turn affects photosynthesis in water, as the processes are interrelated. Oxygen concentration in Kolové pleso was around 10.12 mg/l (Table 3) and the average saturation was 98%, which is characteristic for chemically pure waters (Diviš 2008) such as Tatra Mountain lakes (Juriš *et al.* 1965). Based on these parameters, particularly pH values, we can classify the Kolové pleso among oligotrophic lakes (Beracko *et al.* 2014). pH during the analyzed annual cycle (Appendix 1) ranged from 5.7-9.4 (Table 3), which are typical values for this type of lake (Douglas and Smol 1994; Antoniades *et al.* 2000; Hamilton *et al.* 2001; Lim *et al.* 2001; Michelutti *et al.* 2002a, b; Kopáček *et al.* 2006). In these circumstances, pH is most influenced by rock composition (Fyles 1963; McNeely *et al.* 1979; Michelutti *et al.* 2002a) and its values affect ion concentration (Faure 1991; Hamilton *et al.* 2001), which is likely why pH correlates with a number of elements (Appendix 2) measured in the lake. The electrical voltage as an inverted value of pH has a negative effect in the lake (Appendix 2), specifically on the bioaccumulation capacity (Orolínová 2009) of molybdenum in winter months. Other seasonally dependent physical parameters of the lake include conductivity, TDS and resistance. These values are inverted, (Appendix 2) (Doláková and Janýšková 2012; Judová *et al.* 2015) and were also influenced by climatic variables such as air temperature (Table 4 and Fig. 3a) (Tölgyessy *et al.* 1984; Doláková and Janýšková 2012), precipitation and wind conditions (Table 4). Values are (Appendix 1) below the limit (The law 296/2005 Coll. Requirements for surface water quality and water pollution limits), because of the oligotrophy of the lake.

Similarly to studies by Douglas and Smol (1994); Antoniades *et al.* (2000); Lim *et al.* (2001); and Michelutti *et al.* (2002a,b), measurements showed nutrients in the lower range of recorded values. COD (Table 3) concentrations in the alpine environment range from 0.6 to 10 ml (Pienitz *et al.* 1997b). Low values (Appendix 1) and limited range are related to an almost complete absence of vegetation and poor drainage in the area (Antoniades *et al.* 2003). Sulfate concentrations in alpine lakes are generally influenced by sedimentary subsoil (Oswald and Senyk 1977; Pienitz *et al.* 1997b). Due to the oxidation of minerals, they increased from October to March (Appendix 1) and subsequently decreased as a result of reduced conditions (Wograth and Psenner 1995). Sulfate values were low (Appendix 1), implying nearly complete regeneration from events taking place in the 80's (Stuchlík *et al.* 1985; Kopáček and Stuchlík 1994; Kopáček *et al.* 2001; Evans *et al.* 2001; Veselý *et al.* 2002). The solubility of sulfuric minerals is a property of water hardness (Howard-Williams and Vincent 1989; Howard-Williams *et al.* 1989; Hamilton *et al.* 2001) and can be influenced by the trend that sulfates in the lake Kolové pleso grow in direct proportion to total water hardness (Appendix 1). Phosphate concentration (Appendix 1) (Wetzel 1983; Hobbie 1984; Pienitz *et al.* 1997a) is also related to the catchment area (Kopáček *et al.* 2006) of the lake. These nutrients are in the range typical for oligotrophic lakes (Wetzel 2001) and values were near to of below the detection limit (Appendix 1 and Table 3), (Juriš *et al.* 1965; Kopáček *et al.* (2006). Nitrate levels in the lake are also at or near the detection level (Rühland and Smol 1998; Hamilton *et al.* 2001; Kopáček *et al.* 2006). Ammonia nitrogen, as an important indicator of water pollution (Doláková and Janýšková 2012), is below or near the analytical value in high-altitude clean lakes (Appendix 1) (Pienitz *et al.* 1997b). The content of ammonia nitrogen (Table 3) is in the range of 0.01-0.72 mg/l for Kolové pleso and is similar to other Tatra lakes (Juriš *et al.* 1965; Kopáček *et al.* 2006).

Ionic composition of Kolové pleso depends on several factors. Most ions and especially trace elements are in very small concentrations in the lake, or are below the detection limit (Appendix 1), which is typical. (Hamilton *et al.* 2001). Lake chemistry is clearly related to climatic variables. As a result of precipitation (Welch and Legault 1986; Pienitz *et al.* 1997a; Kopáček *et al.* 2006), but also due to wind influence (Marchetto *et al.* 1995; Kamenik *et al.* 2001), concentration of elements in the lake (Table 4) and their conductivity were changed. Precipitation (Kerekes 1975) can reduce the content of chloride compounds in the lake (Table 4, Fig. 3d). Another factor that influences the chemical composition of the lake is the geochemistry of the bedrock (Hutchinson 1957; Wetzel 1983) and thus mineralogy (Kamenik *et al.* 2001), which is related to the concentration of sulfate anions and ammonia (Kopáček *et al.* 2006). This also explains the correlation between them (Appendix 2). High continuity (Appendix 1 and Appendix 2) and concentration of potassium and chlorine elements indicate that they are the most commonly (Kerekes 1973, 1975) found in the lake in the form of chloride minerals (chloride salts) such as sylvite, KCl, or similarly to other water bodies, common rock salt (NaCl) (Muck 2006). Dependence of these major ions (K, Cl) both seasonal (Vondrka *et al.* 2013), and due to temperature can be explained by less salt measured in winter than in warmer months. Chlorine levels (Appendix 1) rise in autumn and winter due to chloride leakage from degrading vegetation (Psenner and Catalan 1994; Kamenik *et al.* 2001; Mikuš 2012). The same effect is also observed with potassium (Prentiki *et al.* 1980; Michelluti *et al.* 2002a). However, other water-soluble minerals (Petránek 1993) also accompany major elements dissolved in water. Common chlorides include titanium tetrachloride ($TiCl_4$) and titanium chloride ($TiCl_3$) (www.britannica.com 2019) as seen in the correlation of Titanium with chlorides (Appendix 2). Other elements are also subject to seasonal effects. Molybdenum dependence is due to its significant bioaccumulation capacity (Orolínová 2009), which in winter, due to weaker current (Appendix 1,2) has better conditions for accumulation and has higher values.

Effects of flooding on the lake

Increasingly frequent phenomena (IPCC 2001) such as extreme rainfall and consequently flooding, affected lake Kolové pleso in July 2018, giving the opportunity to observe the way water level fluctuations and flooding affect the alpine lake. The first effect was observed in the decrease of COD values (Fig. 5a) - total organic matter immediately on the day of flood events (Table 5). At the present stage of knowledge and based on studies of water fluctuations and its effects (Junk *et al.* 1989; Tockner *et al.* 2000; Nogueira *et al.* 2002; Junk and Wantzen 2004), we can only speculate that such a fluctuation is caused by a higher density of dissolved sediments. Due to the flood, these substances were precipitated on land and stored in ATTZ (Grossart and Simon 1998). The behavior of the lake, and its COD levels has thus shown that floods mobilize and accumulate organic nutrients in the lake (Keddy and Fraser 2000; Nogueira *et al.* 2002; Coops *et al.* 2003; Mooij *et al.* 2005; Wantzen *et al.* 2008) which are probably washed out and stored on land. We believe that this effect also caused the observed decrease (Table 5, Fig. 4a-d) in some element values and their displayed errors (measurement deviation) (explained in Materials and Methods). The decrease in element values and their deviations likely occurred due to washout following the flood, as more elements were left behind as part of the mineralization process (inorganic compounds). The instrument measures more accurately for values that bind to inorganic compounds than organic, which affects the resulting measurement error. As already mentioned in the results, the deviation for cadmium was also reduced after the flood, although it had values below the detection limit at all times. This finding is also confirmed by the work of Chrastný *et al.* (2005) whose study of the impact of floods on heavy metals revealed that floods may in particular cause the release of cadmium into the environment, as well as other elements (especially their organic compounds). In connection with the decline in COD values, we observed another interesting fact in the results after the flood situation. With decreasing COD values, pH (Fig. 5c) values increased (pH: COD (ml): $r = -0.6003$; $p = 0.0108$, Fig. 5d), which suggests the importance of organic substances for acidic lakes. This negative correlation has been observed in the past by acidification (Donahue *et al.* 1998; Evans and Monteith 2001; Kopáček *et al.* 2003; Kopáček *et al.* 2006). In such poorly polluted surface waters, the pH is most influenced by sedimentation (Fyles 1963; McNeely *et al.* 1979; Michelluti *et al.* 2002b) and precipitation (Judová *et al.* 2015). The highest pH value was measured on the day of the flood when extreme rainfall occured. Harriman and Taylor (1999) point out in their work that, regardless of the cause, the rising values of organic composition will have a significant impact on the lake's acidity (Fig. 5b), as floods and precipitation have also affected the acidity of lake Kolové pleso, with the opposite effect.

Potential organic pollution in the lake

Due to the low solubility of POPs and their extremely low concentration, it is difficult to determine these substances in aqueous samples (Bruzzoniti *et al.* 2009), which is why most studies around the world focus on the analysis of these substances in sediments (Borghini *et al.* 2005; Appleby and Piliposian 2006; Meijer *et al.* 2006; Evenset *et al.* 2007; Pozo *et al.* 2007; Schmidt *et* *al.* 2011). For this reason, our analysis in water samples was only qualitative. Analysis of samples from the lake detected several organic compounds from different chemical groups (Table 6). The main external factor affecting the amount of measured organic substances entering the lake systems is precipitation (Pozo *et al.* 2007). Snow effectively traps organic pollutants, making them easier to detect in the winter months in areas such as the Tatra lakes that experience a high volume of precipitation in the form of snow (Wania *et al.* 1998, 1999; Arellano *et al.* 2011). In most cases, these substances are not included in the lists of priority pollutants (Wania and Mackay 1995) because of their low levels or lack of toxicity and small spread around the world. However, PAHs classified as mutagenic, carcinogenic and teratogenic compounds have also been qualitatively analyzed (Pérez-Cadahía *et al.* 2004; Oliveira *et al.* 2012) and can be rapidly absorbed by both organic matter and water (Mitra *et al.* 1999). The first PAH substance detected is phenanthrene, a substance that is highly toxic to the environment, especially for water, because it accumulates in aquatic organisms. The second is pyrene, which is one of the most widespread pollutants in aquatic environments (Oliveira *et al.* 2012). These substances arise as a result of pyrolytic processes such as imperfect combustion (they are part of coal tar) and industrial activity (WHO 1987). A potential source for this pollution are industrial areas such as Košice in the south, Ostrava in the west and Polish factories (Krakow, Nowy Targ, Zakopane) (van Drooge *et al.* 2004). These industrial areas are a substantial distance from the Tatra mountains, but due to the properties of these substances and their ability to be transported over long distances atmosphereically (van Drooge *et al.* 2004; Morales-Baquero *et al.* 2013), they still pollute these areas (Landlová 2006). The lake Kolové pleso is located in the most remote area of the High Tatras, but due to its altitude it has a similar effect to the global distillation effect (Grimalt *et al.* 2001; Meijer *et al.* 2006). Additionally, the High Tatras mountain range constitutes a natural barrier to air flow due to its orientation. The Northwestern sides, where the lake is located, have higher rainfall loads due to exposure to North Atlantic air (Zasadni and Klapyta 2009). These substances in the form of wet deposition enter the mountain ecosystems and thus the lake (www.scientica.sk 2012). PAHs substances were measured in the months when the heating effect and wind is strongest (December 2017, January 2018, February 2018) (www.shmu.sk 2019). Other substances that have been measured and may cause a potential risk of contamination are Dodecanol, which is harmful to aquatic organisms (Noweck and Grafahrend 2006); toxic fumaronitrile - LT2300000 ($C_4H_2N_2$); and isopropyl palmitate ($C_{19}H_{38}O_2$) (Table 6). However, we do not know their sources. Our measurements, although only qualitative, have been confirmed by recent studies on contamination in European alpine regions (Blais *et al.* 1998; Grimalt *et al.* 2001; Zennegg *et al.* 2003; Fernández *et al.* 2005; Meijer *et al.* 2006) as well as in the High Tatras specifically (Grimalt *et al.* 2004; van Drooge *et al.* 2004, 2011, 2013).

Conclusions

Our research has confirmed that monitoring water quality and the impact of seasonal and climate change on isolated high mountain lakes is important in the context of global climate change. Based on the physical properties and chemical composition of the lake, we have been able to observe its seasonal changes, confirming some well-known ideas about how alpine lakes function during the year. These changes will be very important for the aquatic environment in the future. Due to the rise in water temperature from global warming or water level fluctuations, and the impact of floods, we can see an effect on the organic composition of the lake, and measure concentrations of heavy metals leached into the environment. The effects of industy on the environment, including the deposition of compounds like PAH (pyrene and phenanthrene) are also becoming an increasingly serious issue. This study defines the natural present state of lake Kolové pleso, which will serve as a reference for future programs for monitoring anthropogenic impacts and global environmental changes.

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Appendix 1. Measured limnological variables from lake Kolové pleso during from year period (August 2017 – July 2018). Det limit - measurement under the detection limit.

	Aug.17	Sep.17	Oct.17	Nov.17	Dec.17	Jan.2018	Feb.18	Mar.18	Apr.18	May 18	Jun.18	Jul.18
t (° C)	6.5	7.7	2	2.3	-0.1	3.8	3.9	3.7	2.03	14.1	6.6	7.6
pH	6.766	7.553	8.164	5.705	6.246	6.000	7.648	8.101	7.427	7.543	8.933	9.437
U (mV)	-16.87	-30.65	-66.27	-69.5	-41.07	-0,333	-37.433	-61.47	-35.20	-40.23	-109.93	-109.93
Concent. O_2 (mg/l)	10.22	8.31	8.59	9.25	11.99	10.54	10.81	10.93	11.05	9.38	10.30	10.11
O_2 (mbar)	179.37	166.90	165.67	155.10	172.97	168.233	172.43	176.40	167.93	193.10	176.86	175.30
Sat. O_2 (%)	102.50	94.80	89.63	88.33	99.27	96.66	100.13	101.63	94.60	110.47	101.06	101.23
Conductivity (µS/cm)	10.23	9.55	15.27	9.03	14.23	23.267	26.567	27.23	10.87	15.30	12.53	7.70
TDS (mg/l)	9.5	9.5	15.33	9	14.33	23	28	26.67	11	13	13	8
p (kΩ*cm)	98	103.55	65.77	111.03	69.97	43.233	38.467	37.27	91.17	79.6	78.86	130.2
COD (ml)	6.25	4.7	2.79	10.59	3.27	0.93	0.92	2.18	2.85	1.8	3.41	0.82
Cl - (mg/l)	6.4	0.63	0.9	22.2	0.9	17	3.2	21.5	11.16	1.43	4.2	0.5
NaCl (mg/l)	10.2	1.23	1.5	36.7	1.5	28	15.8	35	18.5	2.1	6.9	0.8
chlorides $CaCO_3$ (mg/l)	8.7	18.33	1.3	31.3	1.3	24	4.53	30	15.66	1.8	5.9	0.7
tot. hardness $CaCO_3$ (mg/l)	10	0.9	6.6	40	1.7	30	10	Det limit	11.6	20	15	5
SO_4^{2-} (mg/l)	83.3	6.66	4	18.6	8	4	9	10.6	3	0	3	0
S (mg/l)	28.3	2.66	1	6	3	1	3	3.6	1	0	1	0
ammonia N (mg/l)	Det limit	Det limit	Det limit	0.49	0.23	0.15	0,02	0.01	0.66	0.04	0.72	0.15
PO_4^{3-} (mg/l)	Det limit	Det limit	0.16	0.17	0.05	0.26	0.09	0.11	0.06	0.03	0.34	0.01
P (mg/l)	Det limit	Det limit	0.05	0.05	0.02	0.09	0.03	0.04	0.02	0.01	0.11	0.0
S (ppm)	76 ± 64	Det limit ±62	59 ± 48	96 ±67	93 ± 34	Det limit ±56	Det limit ±57	Det limit ±63	196 ±145	Det limit ±138	187 ±144	Det limit ±137
Cl (ppm)	300 ± 31	266 ± 29	312 ± 24	338 ±33	347 ± 32	273 ±27	324 ±28	296 ± 31	184 ± 19	206 ±19	192 ±19	159 ±18
K (ppm)	187 ± 12	196 ± 12	210 ± 10	252 ±15	193 ± 13	203 ±11	215 ±12	187 ± 13	134 ± 9	152 ±9	133 ±8	137 ±8
Ti (ppm)	Det limit ±10	Det limit ±10	Det limit ±7	10 ±10	Det limit ±10	9 ± 9	9 ±9	Det limit ±10	Det limit ±10	Det limit ±10	Det limit ±10	Det limit ±10
Rb (ppm)	1.6 ± 0.6	1.6 ±1.1	1.2 ± 0.8	1.5 ±0.5	1.5 ± 0.6	1 ± 1	1.2 ±0.5	Det limit ±1.1	Det limit ±0.4	1.3 ±0.2	1 ± 0.4	Det limit ±0.4
Mo (ppm)	1.3 ± 0.5	1.1 ±1	1.1 ± 0.8	1.1 ±1	Det limit ±1	1.3 ±0.9	1.3 ±0.4	Det limit ±1	Det limit ±0.1	Det limit ±0.1	Det limit ±0.1	Det limit ±0.1
Sn (ppm)	Det limit ±9	12 ±9	Det limit ±7	9 ±4	Det limit ±9	11 ±4	Det limit ±8	Det limit ±9	9 ±9	9 ±9	12 ± 4	Det limit ±9
Sb (ppm)	9 ± 3	11 ±3	6 ± 3	7 ±3	7 ± 3	9 ± 6	Det limit ±6	9 ± 3	7 ±3	12 ±3	9 ± 3	10 ±3

Appendix 2. Correlation coefficients of selected physical and chemical variables. Only significant values ($P<0.05$) are listed.

	Physical variables										Chemical variables							
	t (° C)		**pH**		**U (mV)**		**O_2 (mbar)**		**p (kohm*cm)**		**S (ppm)**		**Cl (ppm)**		**K (ppm)**		**Ti (ppm)**	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
U (mV)			-0.719	0.0084														
O_2 (mbar)	0.7197	0.0083																
Sat.O_2 (%)	0.6945	0.0122					0.9637	0										
Conductivity (μS/cm)									-0.9437	0								
TDS (mg/l)									-0.9363	0.00001								
NaCl (mg/l)																	0.6632	0.0187
tot. hardness $CaCO_3$ (mg/l)																	0.7978	0.0019
ammonia N											0.884	0.0001						
Cl (ppm)			-0.638	0.0256														
K (ppm)			-0.650	0.0221			-0.5998	0.0392					0.8936	0.00009				
Ti (ppm)			-0.588	0.0446			-0.5942	0.0416					0.7098	0.0097	0.7098	0.0097		
Mo (ppm)					0.5892	0.0438												
Sb (ppm)	0.819	0.0011																