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Monitoring of chemical and elemental substances in snow over two years (2022/2023) in Malá Fatra

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Abstract. Data on chemical parameters and heavy metals in snow collected and processed during March 2022 and 2023 from two localities in Malá Fatra (Lúčanská Malá Fatra and Krivánska Malá Fatra at various altitudes; Slovakia). The analysis of chemical parameters ($CaCO_3$, P, PO_4^{3-}, N, NO_3, N, NH_3, NH_4, Cl, NaCl) was performed by direct-read photometers with the use of chemical reagents. Afterwards, analysis of P, S, Cl, K, Ca, Rb, Zn, Mn, Mb, Fe, Ti, Sn, Co, Ni, Cu, As, Se, Pb, Sb, Ba, Hg, Cr, Ag, Cd by XRF spectrophotometer was performed. Only the elements that were detected are listed in the results. Some variables were significantly different between years and two study sites. And some were significantly different within one year at both sites.

Key words: snow, contamination, annual comparison, Malá Fatra

Characteristics of the site

Malá Fatra is a core mountain range in the north of Slovakia in the Žilina region (Fig. 1). It is a part of the Fatransko-Tatranský region, which forms part of the Western Carpathians. The Malá Fatra Mountains are bordered by the Strážovské Hills, the Orava Magura and Veľká Fatra in the south. Malá-Fatra is divided into two geomorphological units by the Váh River (www.terchova.eu 2023; www.sk.wikipedia.org 2023):

1. Krivánska Malá Fatra – towards the north and the area is classified as the Malá Fatra National Park. The sampling took place on the way to the peaks of Veľký Kriváň (1708.7 m a.s.l.) and Chleb (1670.9 m a.s.l.). The bedrock of this part of the mountain range is formed by Mesozoic sediments (Middle Triassic) consisting of gutenstein limestones with ramsau dolomites (ŠGÚDŠ 2023).

2. Lúčanská Malá Fatra – southwards, the Lúčanská Mala Fatra mountains are surrounded by the Strážovské vrchy, Turčianská basin, the Rajčanka river and the Váh river in the north. The highest peak of Lúčanská Malá Fatra is Veľká Lúka, the second is Krížava. Snow samples were taken from both places. The bedrock is Quaternary sediments (organic and deluvial) on Crystaline core (Hercinian granites).

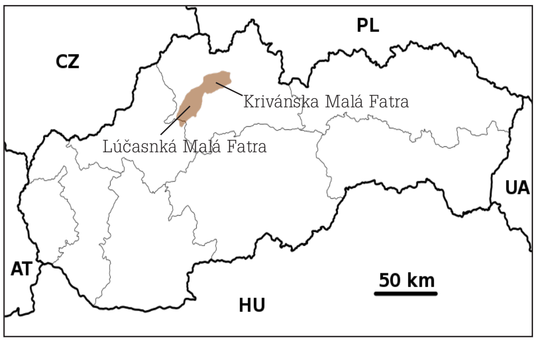

Fig. 1. The territory of the Malá Fatra National Park.

The whole area is divided into several smaller protected areas, nature reserves and natural monuments. The geological subsoil, the rugged relief and the broad range of altitudes have conditioned the diversity of vegetation. Protected plants such as the late carnation (*Dianthus serotinus*), Alpine aster (*Aster alpinus*), and the Slovak Pasque flower (*Pulsatilla slavica*) occur here. The mountains are also home to protected animals such as the lynx (*Lynx lynx*), the grey wolf (*Canis lupus*), the golden eagle (*Aquila chrysaetos*), and the Eurasian hobby (*Falco subbuteo*) (www.terchova.eu 2023). The mountains are densely forested except for the ridges. All vegetation stages are preserved with the addition of rock communities and alpine meadows

Studies examining contaminants in snow are often helpful in environmental decisions to reduce pollution for a given area, with an emphasis on potential producers of contamination. Depending on the sources of pollution, the transmission path, and the time pollutants remain in the air, different regions show different pollution levels (Adachi and Tainosho 2004; Dong *et al.* 2015; Singh *et al.* 2007). Therefore, the following study is also aimed at a closer analysis and comparison of heavy metals and other elements and compounds present in snow from the Lúčanská Malá Fatra and Krivánska Malá Fatra sites. Snow sampling and chemical analysis of this type of sample is one of the oldest and most widespread methods for assessing environmental pollution at high altitudes (Vasilenko *et al.* 1985). This method was already in use by Nordenskiöld, who applied it to research in Antarctica (Nordenskiöld 1875). In recent decades, there has been a growing interest in heavy metals and other pollutants (Thomas and Merian 1991) found in atmospheric deposition and their potential environmental impacts. In terms of deposition of contaminants and heavy metals, a distinction is made between dry or wet deposition, where in the case of wet deposition, compounds (contaminants) and metals bind to water and fall to the Earth in the form of snow or rain (Holoubek 2000; Osada *et al.* 2010). The atmospheric wet deposition pathway of many heavy metals can pose a potential risk to humans and other organisms and is also of significant importance to many ecosystems (Veysseyre *et al.* 2001). As several sources report, one of the pathways for heavy metals to enter the environment is natural sources such as volcanic eruptions and sandstorms, the other is anthropogenic sources such as biomass, fossil fuel combustion, traffic exhaust, and others (Taylor and McLennan 1995; Kim *et al.* 2012; Liu *et al.* 2013). Due to the process of wind circulation, contaminants in the atmosphere are transported over long distances and deposited on glaciers and in remote high mountains (Tripathee *et al.* 2014). Therefore, the function of snow and ice in high mountain areas is not only as a reservoir of suspended particles in the atmosphere but may also reflect the extent of the impact of atmospheric pollution from human activities (Jiao et *al.* 2021). During occasional snowmelt, pollutants are released further into the environment, but during rapid warming when melt rates are high, they are released into the environment at higher concentrations (Meyer *et al.* 2009). Heavy metals released into the environment do not decompose but are classified as either soluble or as particle-bound fractions (Glenn and Sansalone 2002). This makes data on heavy metal concentrations in snow

		All sites		Malá Fatra Lúčanská		Mala Fatra Krivánska		
Variables	**Year**	**N**	**Mean (SE)**	**N**	**Mean (SE)**	**N**	**Mean (SE)**	
Elevation	2022	48	1522.33 (12.12)	24	1445.11 (1.59)	24	1599.55 (8.92)	b
	2023	42	1509.01 (13.10)	22	1442.56 (2.42)	20	1582.10 (15.28)	b
Cl	2022	48	5.44 (1.28)	24	5.19 (1.80)	24	5.70 (1.86)	
	2023	41	5.66 (1.27)	22	3.07 (0.48)	19	8.66 (2.55)	
NaCl	2022	48	8.97 (2.11)	24	8.51 (2.93)	24	9.43 (3.09)	
	2023	41	9.20 (2.10)	22	4.98 (0.79)	19	14.08 (4.23)	
$CaCO_3$	2022	48	7.68 (1.80)	24	7.28 (2.51)	24	8.08 (2.64)	
	2023	41	7.95 (1.80)	22	4.27 (0.68)	19	12.21 (3.61)	
Hardness $CaCO_3$	2022	48	**23.54 (2.22)**	24	21.88 (3.05)	24	**25.21 (3.25)**	
	2023	41	**13.54 (2.43)**	22	17.96 (3.86)	19	**8.42 (2.33)**	b
S	2022	48	3.81 (0.39)	24	4.17 (0.61)	24	3.46 (0.49)	
	2023	41	5.95 (1.76)	22	5.55 (2.04)	19	6.42 (3.02)	
SO_4^{-2}	2022	48	11.23 (1.16)	24	12.25 (1.87)	24	10.21 (1.38)	
	2023	41	17.93 (5.19)	22	16.91 (6.13)	19	19.11 (8.85)	
Ammonia - N	2022	48	**0.47 (0.04)**	24	0.42 (0.06)	24	**0.51 (0.05)**	
	2023	41	**0.66 (0.06)**	22	0.43 (0.08)	19	**0.92 (0.04)**	b
$N\text{-}NH_3$	2022	48	**0.56 (0.05)**	24	0.50 (0.07)	24	**0.62 (0.06)**	
	2023	41	**0.80 (0.07)**	22	0.54 (0.09)	19	**1.11 (0.05)**	b
NH_4	2022	48	**0.60 (0.05)**	24	0.54 (0.07)	24	**0.66 (0.06)**	
	2023	41	**0.86 (0.08)**	22	0.57 (0.10)	19	**1.19 (0.06)**	b
Nitrate - N	2022	48	**1.29 (0.57)**	24	**1.19 (0.82)**	24	**1.40 (0.81)**	b
	2023	40	**0.23 (0.02)**	22	**0.23 (0.03)**	18	**0.24 (0.02)**	
NO_{3-}	2022	48	**2.81 (0.54)**	24	**2.39 (0.78)**	24	**3.22 (0.76)**	b
	2023	40	**0.99 (0.07)**	22	**0.92 (0.09)**	18	**1.07 (0.11)**	
P	2022	48	0.05 (0.01)	24	**0.05 (0.01)**	24	0.05 (0.01)	
	2023	40	0.06 (0.02)	21	**0.05 (0.02)**	19	0.06 (0.02)	
PO_4^{3-}	2022	48	0.15 (0.02)	24	**0.14 (0.02)**	24	0.15 (0.03)	
	2023	40	0.16 (0.04)	21	**0.15 (0.07)**	19	0.18 (0.05)	

Table 1. Load (in ppm) of selected chemical compounds in snow samples collected in the Malá Fatra mountains. Significant differences ($p < 0.05$) between years (2022, 2023) are in bold. Letter b indicates significant differences between two sites (Malá Fatra Lúčanská and Krivánska) in one year – chemical parameters.

		All sites		Malá Fatra Lúčanská		Malá Fatra Krivánska		
Variables	**Year**	**N**	**Mean (SE)**	**N**	**Mean (SE)**	**N**	**Mean (SE)**	
S	2022	32	84.64 (2.41)	18	87.92 (3.22)	14	**80.43 (3.45)**	
	2023	15	92.47 (4.82)	11	88.00 (5.49)	4	**104.75 (7.79)**	
Cl	2022	48	**313.19 (3.65)**	24	**313.68 (5.17)**	24	**312.71 (5.26)**	
	2023	41	**351.98 (5.97)**	22	**351.91 (7.74)**	19	**352.05 (9.48)**	
K	2022	48	**215.49 (4.04)**	24	**210.00 (6.23)**	24	**220.98 (5.02)**	
	2023	42	**178.53 (4.72)**	22	**194.28 (4.15)**	20	**161.20 (7.05)**	b
Ca	2022	22	66.95 (22.75)	14	90.77 (34.48)	8	25.25 (3.80)	
	2023	30	61.13 (8.56)	19	78.58 (11.54)	11	31.00 (4.64)	b
Ti	2022	3	**22.67 (4.18)**	1	18.00 (0.00)	2	**25.00 (6.00)**	
	2023	22	**16.41 (0.63)**	7	18.64 (1.29)	15	**15.37 (0.54)**	b
Cr	2022	13	5.20 (0.83)	11	5.55 (0.95)	2	3.25 (0.35)	
	2023	12	7.13 (1.20)	7	6.51 (2.00)	5	8.00 (0.89)	
Mn	2022	10	9.04 (1.96)	10	9.04 (1.96)	0	0.00 (0.00)	
	2023	24	15.13 (2.16)	8	15.53 (3.47)	16	14.93 (2.80)	
Rb	2022	48	**5.41 (0.27)**	24	6.00 (0.47)	24	**4.83 (0.20)**	
	2023	42	**7.62 (0.28)**	22	6.86 (0.37)	20	**8.46 (0.35)**	b
Mo	2022	48	**2.91 (0.09)**	24	**3.09 (0.16)**	24	**2.73 (0.07)**	
	2023	42	**4.00 (0.13)**	22	**3.59 (0.16)**	20	**4.45 (0.15)**	b
Cd	2022	8	7.38 (0.32)	5	**7.80 (0.37)**	3	6.67 (0.33)	
	2023	3	6.67 (0.67)	2	**6.00 (0.00)**	1	8.00 (0.00)	
Sn	2022	34	11.05 (0.28)	17	11.25 (0.47)	17	10.85 (0.29)	
	2023	6	11.83 (0.85)	6	11.83 (0.85)	0	0.00 (0.00)	
Sb	2022	48	**9.82 (0.19)**	24	9.78 (0.25)	24	**9.85 (0.28)**	
	2023	32	**12.42 (0.48)**	19	10.90 (0.46)	13	**14.65 (0.58)**	b
Ba	2022	21	14.29 (1.55)	15	16.07 (1.99)	6	9.83 (0.40)	
	2023	11	19.11 (3.70)	11	19.11 (3.70)	0	0.00 (0.00)	
Pb	2022	44	**5.60 (0.31)**	22	6.69 (0.48)	22	**4.51 (0.19)**	b
	2023	42	**8.25 (0.42)**	22	6.95 (0.52)	20	**9.68 (0.51)**	b

Table 2. Load (in ppm) of selected elements compounds in snow samples collected in the Malá Fatra mountains. Significant differences ($p < 0.05$) between years (2022, 2023) are in bold. Letter b indicates significant differences between two sites (Malá Fatra Lúčanská and Krivánska) in one year – element parameters.

a reliable guide for determining the degree of air pollution and thus, they can be used as a simple and effective indicator of air pollution (Elİk 2002).

The problem is not only the elevated concentrations of heavy metals present in the environment, but also acid precipitation. Elevated concentrations of SO_4, NO_3^- and NH_4 accumulate in the snowpack and, during the snowmelt period during spring, have the greatest adverse effect on water quality, lakes, and the environment (Johannessen and Henriksen 1978).

Research methodology

Ninety snow samples were collected from areas with an altitude above 1100 m a.s.l. The snow was collected from a layer of older snow, using a shovel. Snow samples were stored in the liquid state in clean 250 mL plastic sampling bottles in a refrigerator (4 ° C) until further analysis. Sampling took place at 28 - 29 March in 2022 and 2023.

Testing of basic chemical parameters was performed by direct photometry using a YSI EcoSense 9500 photometer (YSI Inc., Ohio, USA) and accessories compatible with this instrument. Total hardness ($CaCO_3$ in mg/L), phosphate (P, PO_4^{3-} in mg/L), nitrate (N, NO_3 in mg/L), ammonia (N, NH_3, NH_4 in mg/L) and chloride (Cl, NaCl in mg/L) of the samples were measured using chemical reagents (PALINTEST Ltd., Gateshead, UK). According to the instructions for use of the reagents and the measuring equipment, the measurement procedure was carried out using coloured reagents.

Water was also analyzed by XRF spectrometry using a DELTA Professional ED XRF spectrometer with XRF WorkStation (Olympus, Innov-X, USA). Identification of metalic elements using the XRF spectrophotometer is achieved based on the different characteristic wavelength of radiation emission (λ) or energy (E). The abundance of an element is detected by measuring the intensity of its characteristic wavelength energy. The elements measured were P, S, Cl, K, Ca, Rb, Zn, Mn, Mb, Fe, Ti, Sn, Co, Ni, Cu, As, Se, Pb, Sb, Ba, Hg, Cr, Ag, Cd. We found that the optimum analysis time is 30 seconds. Each measurement was run three times, and the results were then averaged.

Statistical analysis

Statistical analysis was performed using Statistica 8 software (StatSoft, USA). The data collected did not have a normal distribution according to the Shapiro-Wilk normality test. Therefore, nonparametric statistical methods, Mann-Whitney U test were used.

Preliminary results and conclusion

Only those variables that were detected are presented in the preliminary results. The concentrations of the snow chemical parameters are given in Table 1. The concentrations of the elements that were measured at each sampling site are given in Table 2. Differences between the years 2022 and 2023 (Lúčanská Malá Fatra with Krivánska Malá Fatra) were significant for total hardness ($CaCO_3$), ammonia (N; NH_3; NH_4), nitrates (N; NO_3^-) and elements as Cl, K, Ti, Rb, Mo, Sb and Pb. Separately in sites, nitrates, phosphates (P; PO_4^{3-}) and elements as Cl, K, Mo and Cd were significantly different between years at the Lučanská Malá Fatra. In the Krivánska Malá Fatra, total hardness, ammonia, nitrates and the elements as S, Cl, K, Ti, Rb, Mo, Sb and Pb were significantly different between years. Differences between sites were significant for total hardness, ammonia and elements as K, Ca, Ti, Rb, Mo, Sb and Pb in 2023, and for nitrates and Pb in 2022.

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