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Investigation of some snow probes from Rila mountain and its energy spectra

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Abstract

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In this paper, we study snow water (Eisenberg & Kauzmann, 1969) samples from Rila Mountain. For this purpose, the method of differential energy spectra was used. A set of natural waters was taken from different places in the high parts of the mountain, where anthropomorphic activity is insignificant or minimal. New interconnections were found between properties of snow samples (Ē, δ-factor and their correlations etc.) and those from glacial lakes.Based on them, we have obtained additional classifications of the studied Rila snows and lakes. Two decreasing gradations (a – by Ē, δ-factor) and (b – according to correlation analysis), and grouping the studied objects into two groups: three objects in each (see conclusions). Waters from high mountain areas and those from industrial areas were examined and discussed, which ones were used for drinking, or for domestic, or business purposes.

Keywords: environment; snow water; energy spectrum words

Introduction

As a result of intensive development and industrialization in recent decades, there has been an increase in environmental pollution, which in turn affects the quality of life on a global scale. This dictates the need for a more thorough and comprehensive study of pollution mechanisms, the development of appropriate monitoring methods and the implementation of measures, where possible, to mitigate negative consequences. As a result, various methods and approaches to environmental research have been developed, an important part of which is monitoring the purity of natural waters.

Material and Methods

The work uses the method of nonequilibrium energy spectra (Antonov et al.,1995; Antonov, 1996), based on the study of water droplet evaporation (Todorov, 2002) from a solid carrier, in the case of Hostaphan. It is sensitive to the complex effect of chemical and physical factors on water. Contact angles are measured at 4-minute intervals with an accuracy of 0.5 degrees. The measurements were carried out using an optical microscope. Evaporation is monitored at a constant temperature, pressure and air flow rate. The used method is based on the existence of hydrogen bonds between water molecules. There is a relationship between the contact angle θ and the binding energy E (Antonov &Yuscesselieva,1983; Antonov,1984), which is given by the formula:

$$(1)\ \theta = \arccos[-1-bE],$$

where b is a constant depending on the liquid and approximately equal to 14.33 for water samples.

In this method we measure the dark ring of thickness a, which is precessed under the droplet, as a result of the refraction of a light beam (white light) passing through the droplet perpendicularly (Todorov & Damianova, 2015; Popova & Todorov, 2018).

Small water droplets of the studied sample (1) weighing 1–10 mg and a wetting angle of θ, placed on a hydrophobic substrate (2) were used. The hydrophobic substrate is placed on a glass plate (3) of thickness d (Fig. 1). Measuring the angle θ, in the process of evaporation of the studied droplet, we manage to construct the distribution function $f = f(\theta)$.

We introduce the notion of nonequilibrium energy spectrum f(E), where:

$$(1)\ f(E) = bf(\theta)/(1 - (1 + bE)^2)^{-1/2}) \text{ and } b = I(1 + \cos\theta_0)/\gamma.$$

Here γ is the drop's surface tension, $I = 5.03.10^{18}\ m^{-2}$ is the density of water molecules in the surface layer, θ_0 – the initial contact angle of the drop.

Constructing the spectrum f(θ) through the above measurements, we conveniently calculate f(E) – called non-equilibrium energy spectrum, (Antonov et al.,1996; Antonov et al.,1997) through the above formulas (1).

As experiments show, the hydrogen bond energy of water molecules is contained in the interval of variation of the variable E.

Furthermore, along with the nonequilibrium energy spectrum of the sample $f(E)_p$, it is convenient to construct the nonequilibrium energy spectrum of a control sample of deionized water (called the "control") – $f(E)_k$.We form the arithmetic difference between the non-equilibrium energy spectrum of the sample and that of the control, and thus introduce the so-called differential energy spectrum: $df(E) = f(E)_p - f(E)_k$

Since the side factors (pressure, solar radiation, etc. factors that do not interest us at the moment) act in the measurement process on both $f(E)_p$ and $f(E)_k$, we believe that with the df(E) constructed in this way the difference between its two elements eliminates the impact of these side factors on the thus constructed differential energy spectrum df(E).

(Therein lies the advantage of df(E) over f(E).)

The average value of the energy $\bar{E}$,the proportionality of the hydrogen bond energy in the energy interval (A, B) is determined by the formula:

$$\bar{E} = \Delta E \sum_{i=A}^{B} E_i f(E_i)$$

discretizing expression

$$\bar{E} = \int_A^B E f(E) dE,$$

where ΔE is the discretization step.

We also introduce the concept of compensation factor δ,which we will use below. Let $\bar{E}_p$ denote an energy proportional to the average energy of the hydrogen bond of the studied sample, with $\bar{E}c$ – energy proportional to the average hydrogen bond energy of the corresponding it's control. Let $\bar{E}eq$ be an average of the various $\bar{E}c$, over a long period of time and then we enter $\delta = \bar{E} - \bar{E}eq$.

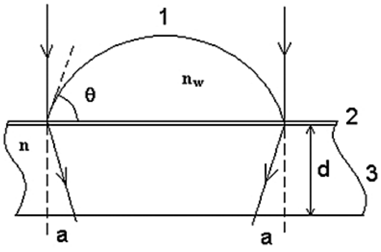

Fig. 1. Schematic diagram of the setup for determining the contact angle *θ* of a droplet during its evaporation using a microscope

Results and Discussion

The obtained differential energy spectra (Fig. 2 – Fig. 4) of the studied samples show a characteristic minimum of about 0.09–0.10 eV for all pure lake and snow waters.

(Many other graphs of snow samples confirm the above statement.)

In Table 1, we have snow waters and lakes waters (Ignatov and Valcheva, 2023) (see bellow):

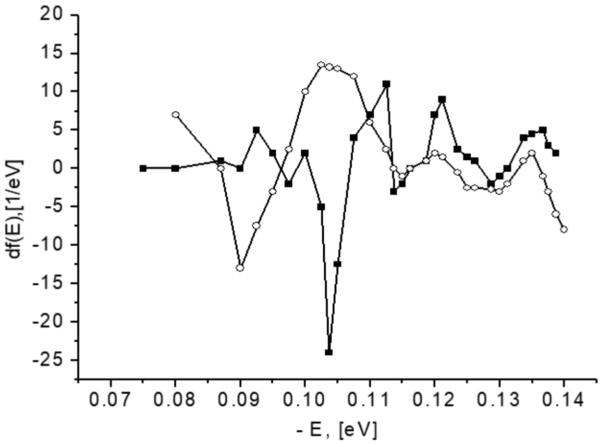

Fig. 2. Differential energy spectra of a sample from the Musala Peak region taken from the surface (squares) and from 1 cm depth (other place from the Musala Peak) (circles)

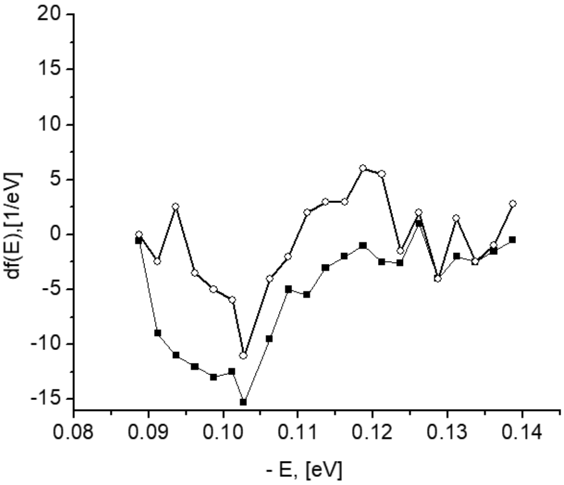

Fig. 3. Differential energy spectra of Ledeno Lake (circles), Mousala Lake (squares)

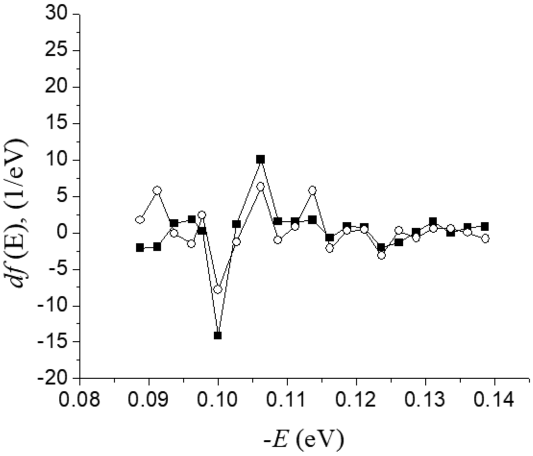

Fig. 4. Differential energy spectra of Gorno Marichino Lake (squares), Dolno Marichino Lake (circles)

Snow waters:

Snow water from peak Mussala: N_1 is a from 1st layer: 1 cm below the surface, N_1^* – from 2nd layer 7 cm below the surface. (Snow probes are taken from едно и също place from peak Mussala.)

Snow water near Beli Iskar River: N_2 – taken from 1st layer: 1 cm below the surface, N^*_2 – from 2nd layer: 6 cm below the surface, N_2^{**} – from 3rd layer: 12 cm below the surface. (Snow probes are taken from едно и също place near Beli Iskar River.)

Lakes waters:

N_3 – water probe from Ledeno Lake, N_4 – water probe from Musalensko (Bezimenno) Lake, N_5 – water probe from Alekovo Lake, N_6 – water probe from Gorno Marichino Lake and N_7 – water probe from Dolno Marichino Lake.

1. Dependences in the snow samples

From Table 1, it can be seen that the more the snow sample is dug down, the more its average energy Ē per module increases. (this applies to the snow samples taken as from peak Mussala: N_1, N_1^* – so also from Beli Iskar River – N_2,N_2^*,N_2^{**}).

A similar dependence is also observed with compensation factor δ for snow waters – again Table 1.

In the upper layers $\delta > 0$: (N_1, – peak Mussala), (N_2, N_2^* – Beli Iskar River).

In the last layer $\delta < 0$ (N_1^* – peak Mussala), ((N^{**}_2 – Beli Iskar River). (The deeper the layer of snow, we assume that the sample is cleaner and the temperature is lower). The longer the sample has been on the surface, the greater the probability that contamination will penetrate it. For now, we have not investigated whether the pressure of the upper layers affects the given results in any way, or whether the reasons are different.

2. Dependencies at the lakes

A) The first two musalen lakes

A similar dependence – the lakes near Mussala peak: On the northern side of Musala are the Musalen lakes, which are glacial lakes. They are fed mainly by snow and melted snow water.

The closest to the summit are Ledeno Lake and after it Musalensko Gorno (Bezimenno) Lake. Ledeno Lake is not frozen only from July to November and underwater feeds Musalensko (Bezimenno) Lake.

These characteristics make them similar to the corresponding snow samples from Table 1. See N_3 and N_4 in Table 1.

There, for Mean energies Ē**,** we have $N_3 = 0.1073$ (Ledeno Lake), which is located by module for Ē between 1st and 2nd layer for the snow samples taken from peak Mussala, and is located modulo between layer 2nd and 3rd for the snow samples taken from place near Beli Iskar River.

Table 1. Mean energies Ē of snow and lake water probes and their compensation factor δ

	N_1	N^*_1	N_2	N^*_2	N^{**}_2	N_3	N_4	N_5	N_6	N_7
-Ē eV	0.1041	0.1112	0.1050	0.1051	0.1110	0.1073	0.1101	0.1031	0.1027	0.0991
δ, eV	> 0	< 0	> 0	> 0	< 0	< 0	< 0	< 0	< 0	> 0

Absolutely the same (literally) applies to the second-Musalensko Gorno (Bezimenno) Lake. (Above only need to replace Ledeno Lake with Musalensko (Bezimenno) Lake. and repeat the reasoning).When considering the compensation factor δ for Ledeno Lake and for Musalensko (Bezimenno) Lake, we notice that for both places $\delta < 0$.

This corresponds ($\bar{E}$ and δ for Mus. lakes) to the deepest layers of the snow samples taken from both places (points). That is, places where there is a possibility of heavy snowfall or not so heavy, the lower layers of 7–12 cm to keep intact caused by pollution, melting, etc. restructuring of the snow (surface phenomena).

B) Upper and lower (Gorno and Dolno) Marichini lakes

On the other side of peak Mussala, (this source of snow and cold for Bulgaria) the southern one, where the four Marichini lakes are located.

The distance from Mussala peak to them is approximately 2–5 times further than from peak Mussala to the first two Musalen lakes.

In this work, we consider only two Marichini lakes, second and third, called Gorno and Dolno, because the other two they dry up in the summer.

When comparing the characteristics $\bar{E}$ and δ from Table 1 with the snow samples and the samples from Gorno and Dolno Marichini Lakes, we do not observe the picture that is at the lakes near Mussala peak.

Possibly for the reasons stated above: Gorno and Dolno Marichini Lakes, are geometrically 2–4 times farther than first two Musalen Lakes from Musala Peak and are on its southern side unlike the last two.

When examining the energies: $\bar{E}(N_6)$ for (Gorno Marichino) and (Dolno Marichino), they do not find a place in Table 1., as do the first two Musalen Lakes (compare N_1, N_2, N_1^*, N_2^*, $N_3^*$with N_6 and N_7, and repeat the reasoning for the two Musalen lakes discussed above.)

When considering the energies: $\bar{E}(N_6)$ for Gorno Marichino Lake, we observe:

$\bar{E}(N_6) < \bar{E}(N_1) < \bar{E}(N_1^*)$, for (Mussala snow probes)

$\bar{E}(N_6) < \bar{E}(N_2) < \bar{E}(N_2^*) < \bar{E}(N_2^{**})$, for (Beli Iskar snow probes)

From Dolno Marichino Lake- $\bar{E}(N_7)$, the reasoning from the above Gorno Marichino Lake is repeated.

For $\delta(N_6)$ it is < 0 (Gorno Marichino), as it is for Ledeno Lake and for Musalensko (Bezimenno) Lake, i.e. corresponds to δ for the deepest layers of a layer for the snow samples.

While for $\delta(N_7)$ it is > 0 (Dolno Marichino), it does not correspond to δ for the deepest layers of a layer for the snow samples.

The reason seems to be that it is much more distant from Mussala than Gorno Marichino and has less contact with snow waters.

C) Third Musalensko (Alekovo) lake

After the first two Mus. Lakes, the third Alekovo Lake is geometrically located in third place.

The reasoning about Maricini Lakes applies to him and in particular, literally for Gorno Marichino. It is possible that it is due to a certain greater distance from Musala compared to the first two Musalen Lakes. According Table 1, we have the following energy order:

$\underline{N_1^*: N^{**}_2: N_4: N_3: N_5: N_6: N_7:}$

1. snow Mussala II layer (N_1^*): $\bar{E} = \bar{E}_{max}$ the highest quality snow with $\bar{E}_{max}$ of all snow and lake samples shown here,(in this work).
2. snow Beli Iskar III layer (N^{**}_2)
3. water probe from Gorno Musalensko (Bezimenno) Lake – (N_4)
4. water probe from Ledeno Lake – (N_3)

We have an exchange of (N_3) with (N_4), but in general, the first 2 lakes are „in the lead“.

After that in order of numbers and distance from Musala are:

5. water probe from Aleko Lake – (N_5)
6. water probe from Gorno Marichino Lake – (N_6)
7. water probe from Dolno Marichino Lake – (N_7)

Table 1:

According Table 2, we have a similar arrangement:

$\underline{N_1^*: N_3: N_4: N_6: N_5: N_7 :}$

1. snow Mussala- (N_1^*)
2. water probe from Ledeno Lake – (N_3)
3. water probe from Gorno Musalensko (Bezimenno) Lake-(N_4)
4. water probe from Gorno Marichino Lake – (N_6)
5. water probe from Aleko Lake – (N_5)
6. water probe from Dolno Marichino Lake – (N_7)

As with the conclusions from Table 1., the two groups – „snowy“ and „other“ remain the same, but in contrast to Table 1 in Table 3, in the first group, 2 and 3 changes their places, so also in the second group, 4 and 5, analogously.

(This can be seen from the first column of Table 3.)

From the last two columns, we observe that Musalensko (Bezimenno) and Ledeno Lake correlate more with the Mus-

Table 2. Correlation coefficients of the differential energy spectra for the snow and lake's waters

	Mussala peak snow water (N_1^*)	Aleko Lake (N_5)	Gorno Marichino Lake (N_6)	Dolno Marichino Lake (N_7)	Musalensko Lake (N_4)	Ledeno Lake (N_4)
Mussala peak snow water (N_1^*)	1	0.323	0.369	0.059	0.480	0.521
AlekoLake (N_5)	0.323	1	0.782	0.437	0.043	0.277
Gorno Marichino Lake (N_6)	0.369	0.782	1	0.698	-0.174	0.164
Dolno Marichino Lake (N_7)	0.059	0.437	0.698	1	-0.24	0.102
Musalensko Lake (N_4)	0.480	0.043	-0.174	-0.24	1	0.447
Ledeno Lake (N_3)	0.521	0.277	0.164	0.102	0.447	1

Table 3. Total dissolved solids (TDS)

	N_4	N_5	N_6	N_7	N_8	N_9
TDS (mg/l)	7.1	7.0	7.7	9.3	136.6	243.0

$N_{4,}$ $N_{5,}$ N_6, $N_{7,}$: see text under Table 1
N_8 – water from Iskar River near Sofia
N_9 – water from Iskar River near Dolni Lukovit

alla snow sample than between them. They then correlate more with each other than with the other lakes.

The same goes for the second group of lakes. They correlate more with each other than with the other lakes. We have the strongest correlation between Gorno Marichino Lake and Aleko Lake – 0.782. Weakest between Dolno Marichino Lake and Mussala peak snow water – 0.059 i.e. and from here it is clearly seen that the characteristics of the last lake are the least similar to those of the „snow group".

Total dissolved solids (TDS) (mg/l) are shown in Table 3. The difference between the TDS of the high mountain glacial lakes- N_4, N_5, N_6, N_7 and water from Iskar River, near Sofia, and water from Iskar River, near Dolni Lukovit.-N_8, $N_{9,}$ is clearly seen – from 20 to 30 times between the first and the second (more polluted group of rivers).

Conclusions

Snow probes graphs and these of glacial lakes they look very similar, which shows the proximity of the origin of the waters in the snow samples and those in the indicated glacial lakes.

According to $\bar{E}$ and δ from the Table 1, we have ranked Musalen snow in the 1st place (N_1^*). After him is the one from the Beli Iskar River (N_2^{**}), then there are N_3, N_4, N_5, N_6, N_7, the more the sample moves away from Musala, the more the average energy $\bar{E}$ of the hydrogen bond decreases (first for the snows, and then for the lakes) (Exception for N_3, N_4, – swap places). According to the correlation analysis, we have a similar arrangement of the examined samples, but here N_5 and N_6 are swapped.

According to Table 1 and Table 2, the given samples can be arranged into the 2 groups shown bellow: first group $\bar{E}$ and δ, and according to the correlation coefficients. According to the aggregate of these 3 indicators they are similar to the snow samples.

The second group according to $\bar{E}$ and according to the correlation coefficients, are not so similar with the snow samples, the most drastic is the situation at Dolno Marichino Lake – the farthest distance from Musala and located to the south of it. It is distinguished even from the lakes in its group by the opposite sign of the δ and the minimum correlation coefficient: 5–6 times smaller than those of Gorno Marichino Lake and Aleko Lake to Musala snow.

According to Table 3, the waters of the examined lakes seem to be excellent for drinking purposes and after some measurement they could probably be used for this**.** The water from the first, Ledeno Lake, after the necessary measurement, is used for drinking needs by our colleagues from BEO "Musala". Even the polluted waters of the Iskar River, after some purification, could probably be used for household needs, because its indicators fall within the norm, if there are no harmful substances and other dangerous pollutants.

It is interesting to continue these studies, both with water samples from the Rila mountain and from other places [8].

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