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REVIEW OF DIFFERENT TYPES OF MOUNTAIN SPRING AND MINERAL WATERS FROM BULGARIA BASED ON THEIR NATURAL ORIGIN AND HEALTH BENEFIT

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Abstract. Review of different types of mountain springs and mineral waters from Bulgaria based on their natural origin and health benefits. Ignatov I. *Mineral water has been renowned for its health benefits for over two millennia, with historical records indicating its use for rapid recovery and wound healing, especially among soldiers engaged in military activities. Over time, baths with mineral water became popular for therapeutic purposes. In the 19th century, analyses revealed that regions with mountains boasted many long-lived individuals and centenarians, with factors such as pure mountain water, fresh air, and quality food potentially contributing to longevity. This publication comprehensively reviews selected natural waters, including mineral and mountain waters. The author conducted extensive studies in Bulgaria from 2012 to 2019 involving 477 long-lived individuals and their brothers and sisters living in mountain and field areas. The investigation assessed their heredity, body weight, health, psychological status, tobacco smoking, physical activity, food, and water consumption. Emphasizing the importance of medical prevention and care, the study sheds light on essential aspects of longevity today. One significant conclusion drawn from this research is the crucial role of balancing certain minerals in both water and food for human health and longevity. These minerals include Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^{+}), Potassium (K^{+}), Zinc (Zn^{2+}), and Manganese (Mn^{2+}). Furthermore, a detailed analysis of the physicochemical properties of water in longevity zones reveals lower calcium ions (Ca^{2+}) levels compared to other regions, ranging from 6 to 20 mg.L^{-1}. Notably, regions like Nova Scotia, Canada, known for supercentenarians for over 110 years, have water with such calcium levels. Similarly, longevity is observed in areas of Greece characterized by Mediterranean cuisine and mountain water. Water's physicochemical composition is significantly influenced by its natural filtration through rocks, which imbues it with beneficial minerals.*

Реферат. Огляд різних типів гірських джерел та мінеральних вод з Болгарії на основі їх природного походження та користі для здоров'я. Ігнатов І. *Мінеральна вода відома своїми корисними властивостями для здоров'я вже понад два тисячоліття, й історичні джерела свідчать про її використання з метою швидкого відновлення та загоєння ран, особливо серед солдатів, які брали участь у воєнних діях. Згодом використання ванн з мінеральною водою стало популярним з терапевтичними цілями. Проведені в XIX столітті дослідження показали, що в гірських регіонах було багато довгожителів та супердовгожителів, причому фактори, такі як чиста гірська вода, свіже повітря та якісна їжа, могли сприяти довголіттю. У цій публікації всебічно розглядаються різні типи природних вод, включаючи мінеральну, гірську та льодовикову воду. Автор провів широке дослідження з 2012 по 2019 рік, що включало 477 довгожителів разом з їхніми братами та сестрами, мешканцями Болгарії, які проживають у гірських та польових районах. У ході дослідження було оцінено їхню спадковість, вагу тіла, здоров'я, психологічний статус, куріння тютюну, фізичну активність, харчування та споживання води. Дослідження наголошує на важливості медичної профілактики та догляду і висвітлює важливі аспекти довголіття в сучасному суспільстві. Одним із суттєвих висновків, зроблених у ході цього дослідження, є ключова роль балансування певних мінералів у воді та їжі для здоров'я та довголіття людини. До таких мінералів відносяться: кальцій (Ca^{2+}), магній (Mg^{2+}), натрій (Na^{+}), калій (K^{+}), цинк (Zn^{2+}) та марганець (Mn^{2+}). Крім того, детальний аналіз фізико-хімічних властивостей води в зонах довголіття показує нижчі рівні іонів кальцію (Ca^{2+}) порівняно з іншими регіонами від 6 до 20 мг/л. Визначено, що такі регіони, як Нова Шотландія, Канада, відомі своїми супердовгожителями, що мешкають понад 110 років, мають воду з таким вмістом кальцію. Так само довголіття спостерігається в районах Греції з характерною середземноморською кухнею та гірською водою. Фізико-хімічний склад води значно залежить від природної фільтрації через гірські породи, що збагачують її корисними мінералами.*

Water is nature's the most valuable chemical compound, without which life is unthinkable. Spring mountain and glacier waters and mineral water contain helpful ingredients. In nature, water is filtered through the rocks and gets saturated with beneficial minerals. This filtration determines its physicochemical composition. In the depths of the earth, near the mineral springs, there are layers with a significant difference in the electrode potentials, which act as an anode and cathode in an underground electrolyzer. In this way, the earth's crust naturally produces activated ingredients.

The Balkan Peninsula is rich in minerals and mountain spring waters. Interestingly, there are mineral sources located over 800 m above sea level in the mountains. In the mountains, the tap water is from the mountain sources. In Sofia, the tap water is from dam Iskar, Rila Mountain. Hristov and co-authors published a review of mineral water in Bulgaria [1]. Bulgaria has one geyser – Sapareva banya [2]. Oreshova and Bojilova analyzed mountain water karst springs in Bulgaria [3].

The present article reviewed the parameters of different types of water intended for drinking purposes. The first two types are natural – mineral, mountain springs, and glacier waters.

The indicated drinking waters were examined according to Ordinance No. 9/2001 and are beneficial for human health. Decree No. 178/23.07.2004 is connected with the regulation on requirements for bottled natural mineral, spring, and table waters intended for drinking purposes.

The article aims to systematize different waters depending on their natural origin and filtering of natural waters. The current publication contains main parameters such as physicochemical composition and data from the physicochemical analyses. All waters in the publication are with microbiological parameters in the norm.

MATERIALS AND METHODS OF RESEARCH

The methods for the research of waters are included in Ordinance No. 9/2001, Official State Gazette, issue 30, about the quality of water intended for drinking purposes [4], and Decree No. 178/23.07. 2004 adopted the Regulation on requirements for bottled natural mineral, spring, and table waters for drinking purposes [5]. The methods were included in [6, 7, 8].

Devices for research of physicochemical composition of water

Studies on the physicochemical composition of water were performed in the licensed laboratory Eurotest Control and the Scientific Research Center of Medical Biophysics laboratory, Sofia, Bulgaria. The Bulgarian state standards (BSS) and ISO standards are in Table 1.

1. For research of pH – technical device pH meter type UB10 ID NoUB10128148;

2. Device for the measurement of electro-conductivity

3. Method for determination of Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Na^{+}, K^{+}, Fe^{2+}, SO_4^{2-}, Cl^{-}, HCO_3^{-}, CO_3^{2-} spectrophotometer "NOVA 60 A";

Methods and parameters for physicochemical analysis

Table 1 illustrates the parameters in our studies concerning physicochemical analysis in Bulgarian state standard (BSS), ISO, Ordinance No. 9/2001, and additional parameters not included in Ordinance No. 9/2001.

Table 1

Parameters of physicochemical analysis in Bulgarian state standard (BSS), ISO, Ordinance No. 9/2001, and additional parameters, which are not included in Ordinance No. 9/2001

Parameter	Standard	Measuring unit	Maximum Limit Value
pH	BSS EN ISO 10523: 2012	pH values	≥ 6,5 and ≤ 9,5
Electrical conductivity	BSS EN 27888: 2000	$\mu S.cm^{-1}$	2000
Calcium (Ca^{2+})	BSS ISO 9964-3 2002	$mg.L^{-1}$	150
Sodium (Na^{+})	BSS ISO 9964-3: 2002	$mg.L^{-1}$	200
Zinc (Zn^{2+})	BSS EN ISO 11885-2009	$mg.L^{-1}$	4
Manganese (Mn^{2+})	BSS EN ISO 11885 2009 (item 9.5.3)	$\mu g.L^{-1}$	50
Iron (Fe^{2+})	BSS EN ISO 11885-2009	$\mu g.L^{-1}$	200
Sulfates (SO_4^{2-})	BSS EN ISO10304-1:2009	$mg.L^{-1}$	250
Chlorides (Cl^{-1})	BSS EN ISO10304-1:2009	$mg.L^{-1}$	250
Additional parameters			
Potassium (K^{+})	BSS ISO 9964-3: 2002	$mg.L^{-1}$	-
Hydrogen carbonates (HCO_3^{-})	BSS EN ISO 9963-1:2000	$mg.L^{-1}$	-
Carbonates (CO_3^{2-})	BSS EN ISO 9963-1:2000	$mg.L^{-1}$	-
Sulfur (S^{2-})	BSS EN ISO 11885-2009	$mg.L^{-1}$	-

The studies of physicochemical indicators were performed in licensed laboratories according to Bulgarian and EU standards.

Statistical analyses

The statistical processing of the results was performed according to the classical method of Student-Fisher with a t-test. Microsoft® Office Professional Plus Excel 2013 (15.0.4569.15060) was used for the calculations, with rights from the Scientific Research Center of Medical Biophysics, Sofia, Bulgaria. The average values and their standard deviations were calculated. Student's t-test analysis for independent samples was applied to determine the statistical dependence and reliability of the results. The Student's t-test was counted for five results in each parameter of physicochemical composition. The significance of the differences was defined at significance levels of $p<0.01$.

RESULTS AND DISCUSSION

Mineral and mountain spring waters

The incoming amounts of water are formed by precipitation. Water usage is related to evaporation, retained water in a given area, and run-off flows. Run-off drainage includes surface and underground flows. The underground run-off in the mountains forms the mountain springs. The water penetrating in-depth warms up, forming mineral springs. The chemical composition of the water depends on the dissolved substances during its passage through the earth's crust. We also have reservoirs with shallower groundwater and deeper artesian water.

Figure shows a mountain cavity surrounded by impermeable layers. Two sources are indicated. The first is at a higher altitude and may be the source of a river. The second may be a mountain spring.

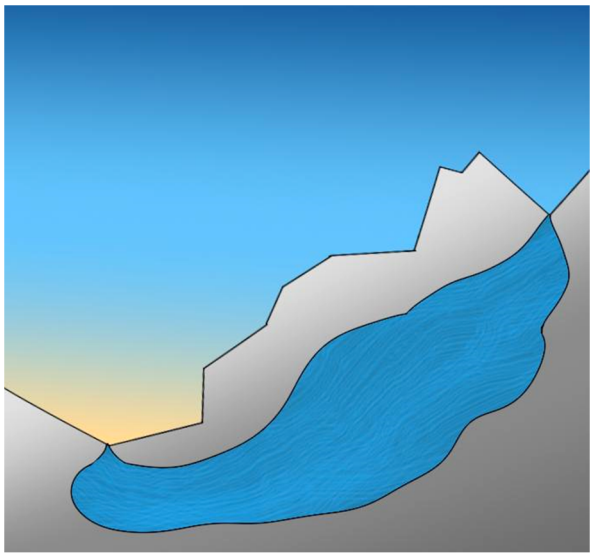
Mineral waters

Bulgaria has the second largest mineral resources in Europe after Iceland. It has 225 springs with over 5000 litters flow rate per second. In southern Bulgaria, there are 148, and in northern Bulgaria – 77.

Depending on their temperature, the mineral springs can be cold (up to 37°C), warm (from 37 to 60°C), and hot (above 60°C). Sapareva Banya spring has a temperature of 103°C. It is the only geyser in continental Europe.

Depending on the chemical composition, mineral waters are classified as weak (up to 2 $g.L^{-1}$), moderate (from 2 to 15 $g.L^{-1}$), and highly mineralized (from 15

to 30 g.L^{-1}). When the mineralization of the water is from 30 to 60 g.L^{-1}, it is saline, and water over 60 g.L^{-1} is highly saline.



Mountain cavity surrounded by impermeable layers

Regarding gas composition, the mineral waters are selected as sulfide, radon, sulfate, hydrogen carbonate, chloride, and carbonated acidic waters.

Eight of the most popular mineral springs in the Bulgarian mountains have been selected. The average water temperatures resulting from annual measurements are shown in Table 2. Table 2 gives the changes in water temperature in Bulgarian mineral springs in Celsius degrees per 100 m. To access the temperature change of the mineral water per 100 m, the accepted average surface water temperature of 15˚C is subtracted. Table 2 also illustrates that in Bulgaria, the water temperature varies from 1.8 to 6.2˚C per 100 m of depth for the mineral sources in mountain areas. The average result is 4.5˚C.

Statistical analysis with t-test of Student showed that water temperature (˚C) depends on the spring's depth in m result $p<0.01$. The correlation coefficient is $r=0.86$.

The results show that in an aquifer from 270 to 1200 m, there is a reliable change of mineral water temperature every 100 m by 4.5˚C.

Table 2

Alterations of water temperatures in Bulgarian mineral springs in Celsius degrees per 100 m. The mineral water temperature is subtracted from 15˚C for the accepted surface average water temperature

Spring	Annual average temperature (˚C)	Temperature change – 15 degrees for groundwater (˚C)	Depth (m) ofthe mineral source	Change of temperature per100 m (˚C)
Velingrad	37	22	1200	1.8
Devin	44	29	700	4.1
Belchinski bani	41	26	418	6.2
Chiflik	51	36	1000	3.6
Jeleznitsa	33	18	600	3.0
Banya, Razlog	57	42	790	5.3
Nevestino	30	15	270	5.6
Gorna Banya	42	27	492	5.5

There is a tendency for higher water temperature at greater depths of the spring. The correlation coefficient shows a strong positive correlation between the depth of the spring and the water temperature (correlation coefficient $r=0.86$, $p<0.01$). This provides insight into the relationship between the depth from which the spring draws water and the water temperature, emphasizing the importance of studying mineral water sources (Table 3).

Table 3 shows that for the temperature more than 30˚C, the sodium (Na^+) predominates over calcium (Ca^{2+}) ions in mineral waters.

In Bulgaria, the mineral waters assume more Na-Cl composition. The warm and hot mineral waters are

generated within the deep aquifer strata, consisting of Paleogene clayey-sandy deposits and carbonates and carbonate rocks spanning the Triassic, Jurassic, and Cretaceous periods. The Upper Jurassic-Lower Aquifer is notably significant in Northern Bulgaria [9].

The alkalinity of the mineral waters in Bulgaria

Dissolved sodium compounds with chloride and carbonate ions primarily determine the alkalinity of mineral waters in Bulgaria. Due to the higher temperature, carbonate ions are also present in the water.

Table 3

The results of mineral sources of calcium (Ca^{2+}), sodium (Na^{+}) and pH

Spring	Annual average temperature (˚C)	Depth (m) ofthe mineral source	Calcium (Ca^{2+})	Sodium (Na^{+})	pH
Velingrad	37	1200	3.3	42.9	9.15
Devin	44	700	1.6	65.5	9.44
Belchinski bani	41	418	2.0	52.0	9.78
Chiflik	51	1000	24.1	42.7	8.22
Jeleznitsa	33	600	1.8	49.9	9.73
Banya, Razlog	57	790	2.0	75.5	9.31
Nevestino	30	267	1.8	229.3	9.50
Gorna Banya	42	492	2.3	33.3	9.80

Mountain spring waters

Mountain spring waters originate from springs in the hilly and mountainous parts of Bulgaria. In Bulgaria, in the Rhodope Mountains, there are areas in which the water is filtrated through zeolite layers [10, 11]. Unlike mineral waters, they have a temperature of up to 20˚C. Calcium (Ca^{2+}) predominates over sodium (Na^{+}) ions in mountain spring waters. No presence of sulfur (S^{2-}) is observed.

Since 2010, the Municipality of Teteven, Lovech region, Bulgaria, has organized the "Days of Mountain Water" event. The organization is a joint activity between the Municipality of Teteven and Prof. Ignat Ignatov [12].

Table 4 illustrates the chemical composition of spring mountain waters from Zlatishko-Tetevenska and Vasiliovska mountains, Municipality of Teteven, Bulgaria.

Table 4

Chemical composition of spring mountain waters from Zlatishko-Tetevenska and Vasiliovska mountains, Municipality of Teteven, Bulgaria

Spring	Calcium (Ca^{2+})	Sodium (Na^{+})	Hydrogen carbonate (HCO_3^{-})	pH
Klindiovo	89.9	4.1	265	8.03
Dolnata Cheshma	94.4	2.5	184	7.91
Gornata Cheshma	103.6	4.2	148	7.34
Sondata	113.6	7.3	271	7.32
Vejnitsa	133.0	2.3	408	7.28
Borisova Cheshma	65.0	2.6	214	7.54
Babintis	54.0	0.5	154	8.04
Gechovoto	66.6	1.5	118	7.94

In the Municipality of Teteven, dolomite and limestone-dolomite with calcium (Ca^{2+}) are in the composition [13].

The main chemical reaction for pH in mountain water is:

$$CO_3^- + H_2O = HCO_3^- + OH^-$$

Water as a factor of health and longevity

One of the secrets of humanity is longevity. There are areas where centenarians (over 100 years old) live, and even supercentenarians (over the age of 110). These are Nova Scotia (Canada) [14], Greece [15], and Japan [16]. In Nova Scotia, there are 210 centenarians per million. In Switzerland, there are 208 centenarians per million. Switzerland is a mountain country with mountain and glacier water and excellent social standards.

Researchers show interdependence between the properties and the physicochemical composition of water. Most often it is mountain or glacier water from melting snow and ice.

In Bulgaria, most centenarians have lived in Smolyan municipality in the 20th century. In 1985, there were 55 of 49 200 people in the Smolyan region, or 350 centenarians per million.

The altitude above sea level in the villages and towns in the Smolyan region is between 800-1200 m. s. l. Research on water and medicinal plants has been published [17]. In the 1980s, Hadjihristev conducted medical research on 55 centenarians. The studies involved clinical tests of blood and urine, as well as hormonal analyses. Examinations of the internal organs and nervous system were performed. The research shows that the parameters of centenarians are similar to those of 60-70-year-olds.

The difference between Smolyan municipality and nearby regions Plovdiv and Pazardzhik is in the altitude and mountain water.

Aliberti et al. show the quantity of Na^+ ions in the water consumed by the centenarians in Cilento, Italy, is 19 $mg.L^{-1}$, and the dependence is at level $p<0.05$ [18].

The author shows that the optimal amounts of the water and food as factors of health and longevity of the following minerals – Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Potassium (K^+), Sodium (Na^+), Manganese (Mn^{2+}), and Zinc (Zn^{2+}) are helpful for the health [6].

The results of the effects of Ca^{2+}, Mg^{2+}, K^+, Na^+, Mn^{2+}, and Zn^{2+} ions on human health as a factor of longevity were achieved for different countries. The results of this direction were published in [19, 20, 21, 22].

Water hydration in sports performance

In the last 30 years, more and more results with hydration have been obtained in athletes depending on the water quality. Results of measurement of cardio-vascular and respiratory parameters were obtained in the state of dehydration and optimal hydration. These parameters are – heart rate or HR bpm, HR recovery, RF breathing, maximal oxygen consumption per minute, or VO_2/max [23, 24, 25].

The study's findings indicate that ingesting high-mineral alkaline water for three days does not affect reaction time. However, some evidence suggests alkaline water could enhance anaerobic performance [26].

The hydration of climbers climbing peaks above 5000 m with glacier water has been analyzed [27].

CONCLUSIONS

1. In Bulgaria, the peculiar features of specific underground layers and rock formations significantly influence the composition of sodium and calcium in the mountain water. Analises presented in the publication focuses on the natural waters from the mountainous regions. The majority of mineral waters contain more Sodium than Calcium ions. The majority of the spring mountain waters contain more Calcium than Sodium ions.
2. Long-lived and centenarians in Bulgaria primarily consume mountain spring waters as one of the health and longevity factors. An analysis of the preference ratio between mineral and mountain spring waters for modern-day consumption has been conducted.
3. The article shows the data on the positive effect of water quality and hydration.
4. The analyses demonstrate a 4.5˚C increase in mineral water temperature for every 100-meter shift within the 270 to 1200 meters range. Notably, deeper springs tend to exhibit higher water temperatures. The correlation analysis highlights a robust positive relationship between spring depth and water temperature.
5. The publication presents the properties of mineral and spring mountain waters from Bulgaria. Geological studies indicate that due to the structure of the earth's layers, among 30 bottled mineral waters from 24 sources described by Hristov et al., the quantity of Na+ ions is greater than that of Ca2+ ions. In the case of the mountain spring waters in Bulgaria, the dominant are the Ca2+ ions.
6. Consumption of both types of water is necessary to achieve a healthy balance between Na+ and Ca2+ ions. A recent study by Aliberti et al. demonstrates results with a Student's t-test yielding $p<0.05$ for the quantity of Na+ ions in the water consumed by the centenarians in Cilento, Italy, which is 19 mg.L-1.
7. The results indicate that consuming 0.5-0.75 L of mineral water and the remaining 1.5-2.25 L volume from mountain spring water is optimal. The optimal amount of water is 30 mL per kg of body weight.

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