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SEASONAL DYNAMICS OF GROUNDWATER MINERAL COMPOSITION AT THE TERRITORY OF THE CRIMEAN PALEOVOLCANO

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Seasonal dynamics of 25 elements concentrations in Karadag groundwater was evaluated. Increased levels of B, Li and Se were recorded, along with negative correlations between water mineralization and both flow rate of springs and the distance from the seashore ($r = -0.840$ and $r = -0.945$), as well as high seasonal variations of P and K levels (78-130% and 80-118% respectively). Positive correlations were found between Ca, Mg, Sr ($r = 0.82$-0.96); Li, B, Na ($r = 0.72$-0.90); Li, Na, mineralization ($r = 0.80$-0.90) and Se, Na ($r = 0.551$). The highest concentrations of P, K, Si, Na were registered in spring, B, Zn, Fe, Se, F in autumn; Ca, Se, F, Cl, I in winter, and Sr in spring and autumn. Ca, K, Mg, Na, B, Fe, Li, mineralization and water hardness of Bio-station well water demonstrated high seasonal variations and maximum permissible concentrations excess.

Key words: *groundwater; mineral composition; seasonal variations; paleovolcano*

Introduction

Groundwater is considered one of the most important components of terrestrial ecosystems, participating in sedimentation, dissolution, and transport of macro- and micro-elements. Chemical and mineral composition of groundwater is connected to the biogeochemical peculiarities of the territory, the intensity of macro- and micro-elements transport from the surface of the sea and oceans, long-term consequences of the volcanic activity and anthropogenic pollution [1, 5]. Many works are devoted to the patterns of spring mineral composition dynamics at ecological risk areas with high environmental pollution [5], and mineral composition of plants growing in the near vicinity of volcanoes [1]. Seasonal dynamics of groundwater chemical composition at the territories of Nature Reserves with lack of anthropogenic uptake remains scantly studied. Such information may be especially valuable for establishing the peculiarities of interaction processes regarding water/rocks, dissolution/precipitations of minerals, sorption/desorption, ion-exchange with clays, redox reactions, marine water penetration, weathering of bedrock, effect of plants on groundwater composition.

Among different Nature Reserves, Karadag is of special interest as it occupies the territory of an ancient mountain-volcanic massif in the close proximity of the Black Sea shore. The Reserve is characterized by extremely high variety of parent rocks – products of destruction of limestones, shales and volcanic rocks. It is located among sedimentary strata of the Middle Jurassic age and is distinguished by the variegation of soil-forming rocks, indicating complex geological structure, where volcanic processes were multiphase in nature and were stretched in time for several tens of millions of years.

Karadag mountains are situated near the Northern border of Subtropical zone of the Northern Chemosphere. The climate is highly dry and hot with very mild winter and is considered intermediate between sub-Mediterranean, typical of the Western part of the Crimean Southern shore, and temperate continental, temperate dry hot, typical of the steppe part of the peninsula.

The hydrosphere of the Reserve is represented by few springs feeding on precipitation and fissure-karst waters. Due to low precipitation levels the territory is poor in springs, and in dry years some of them dry up. Stationary study of Karadag groundwater has been carried out constantly [13], but they do not include chemical and elemental analysis. Dynamics of water discharge of the most popular spring of mountainous Karadag – Gyaur-Cheshme – revealed a decrease of the parameter from 4.5 times during 2000-2010 to 4.8 times in a period of 2011-2015. Significant 1.3 times decrease of atmospheric moisture during this period (by 108.2 mm) and increase of mean annual temperature by 0.4°C are important factors of possible climate change effect on the Reserve hydrological regime [13]. Furthermore, a direct relationship during this period was revealed between dynamics of atmospheric moisture and water discharge value of another spring that feeds exclusively based on atmospheric water condensate.

Only scant data are available on the chemical and mineral composition of Karadag springs: the first investigation of water hardness and mineralization level in two springs was achieved in 1987 [12] and the second study dealt with mineral content in water of four Karadag springs - in summer 2018 [8]. During this period (1987-2018) water mineralization value increased dramatically, which was in accordance with climate changes. Both works gave no information about the dynamics of seasonal changes in chemical and mineral composition of paleovolcano springs, which prevented from making any conclusions about the mechanism of hydrosphere regulation at the territory affected by volcanic activity and minerals transfer from the sea surface.

The present work was aimed to evaluate the seasonal dynamics in chemical and mineral composition of springs situated at the territory of paleovolcano in the near vicinity of the seashore.

Materials and Methods

Six springs of the Karadag Nature Reserve (44°56′10″NW 35°14′00″EL.), situated at the South-Eastern Crimean shore were investigated: (1) well of Biostation; (2) Levinson-Lessing spring situated at the sea shore at the foot of the eponymous rock, composed from volcanic tuff, 1 km to the east from the Karadag Biostation; (3) spring "Valley of Roses", situated between Livadia and Graviinaya bays; (4) Gyaur-Cheshme spring at the South-Western slope of Saint mountain, 2.75 km from the Biostation; (5) Choban-Chokrak spring at the foot of the mountain range Suru-Kaya; and (6) spring "Frog" at the Northern part of the Reserve (fig. 1).

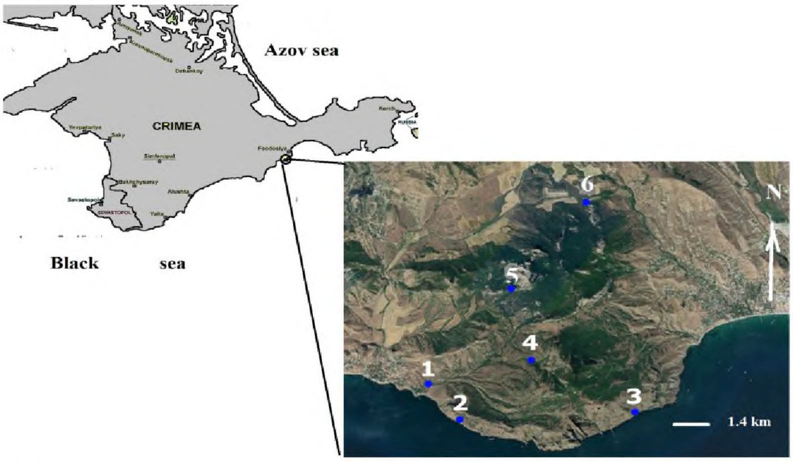


Fig. 1 Places of water sampling at the territory of the Karadag Nature Reserve

Water sampling places in the Karadag Nature Reserve (decoding of numbers are given in table 1). The territory is characterized by significant solar radiation with relatively little cloudiness. Mean annual temperature reaches 12.1°C. Mean temperature of the coldest month (February) reaches 1.5°C. The distribution of precipitation shows two not sharply expressed seasonal maxima: autumn-winter (November-December) and summer (June-July), though seasonal differences are relatively smoothed out compared to other regions.

Water samples were gathered into clean sterile plastic 1 L bottles in June and November in 2018, and in December and April 2019, twice per week during two weeks. Water samples were stored at 4°C before the beginning of the analysis.

Table 1

Characteristics of Karadag groundwater

Number on the map	Type of groundwater	Geographical coordinates	Distance from the seashore
1	Well of Biostation*	N 44°92′7205 E 35°20′4668	400 m
2	Levinson-Lessing spring	N 44°91′2197 E 35°.22′1550	5 m
3	Spring in the ′Valley of roses′	N 44°93′1718, E 35°.24′7515	300 m
4	Gyaur-Cheshme spring	N 44°55'52.1",E 35°13'12.3"	3000 m
5	Choban-Chokrak spring	N 44°56'08.4", E 35°12'41.5"	5000 m
6	′Frog′ spring	N 44° 96′0247, E 35° 20′0531	8000 m

*the depth is more than 12 m; water column is more than 7 m

Cl and F ion concentrations were determined using ion selective electrodes of ionomer Expert-001 (Econix corp., Moscow, Russia). Total mineralization level was assessed using a portable conductometer TDS-3A. Water hardness was determined according to GOST 31954-2012. Al, As, Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, I, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Si, Sn, Sr, V, and Zn contents in water samples were assessed using ICP-MS on quadruple mass-spectrometer Nexion 300D (Perkin Elmer Inc., Shelton, CT, USA), at the Biotic Medicine Center (Moscow, Russia). Taking into account the trace amounts of Ag, As, Hg, Pb, Cd, Ni and Sn in the samples investigated, these data were not included in the text.

Statistical analysis Data were processed by two-way analysis of variance and mean separations were performed through the Duncan′s multiple range test, with reference to 0.05 probability level, using SPSS software version 21. Data expressed as percentage were subjected to angular transformation before processing.

Results and Discussion

Hydrosphere of the Karadag Nature Reserve is affected by several factors including climate changes, seasonal fluctuations of temperature and humidity, geochemical peculiarities of the territory connected with the existence of paleovolcano of the Jurassic period, active transport of macro- and microelements from the sea surface and local anthropogenic influence in places close to residential buildings. The hydrosphere of the territory is presented by 5 springs, and one well situated at different distances from the Black Sea shore, from 5 m (Levinson-Lessing spring; №2) to 8 km (′Frog′ spring; №6).

Macro-elements are usually present in groundwater at concentrations from 10 to 1000 mg L^{-1}. An integral parameter of their content is the mineralization level with MPC (Maximum Permissible Concentration) value for drinking water equal to 1000 mg L^{-1}. Water of all Karadag springs demonstrated mineralization values and water hardness lower than both MPC data and values recorded in the water of Bio-Station well (table 2).

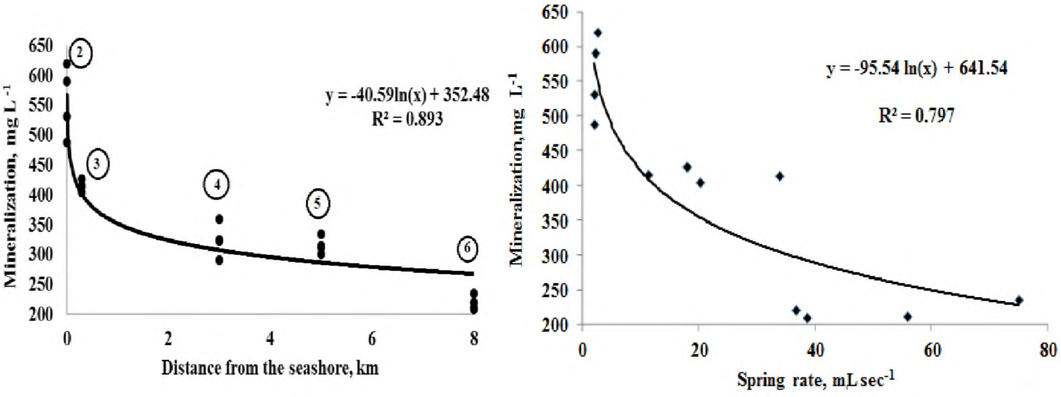
Table 2

Seasonal changes in water mineralization, hardness and Ca, K, Mg, Na, P and Si content

Parameter, MPC	*	Summer	Autumn	Winter	Spring	M±SD	CV (%)
Mineralization mg L^{-1} 1000**	1	735b	989a	976a	721b	855±127	14.9
	2	531cd	488de	620bc	590c	557±48	8.6
	3	415ef	427e	414ef	405ef	415±8	1.9
	4	325g	360fg	323g	292g	325±17	5.2
	5	312g	334g	315g	301g	316±9	2.9
	6	209h	220h	235h	212h	219±8	3.7
Hardness Mg-eq dm^{-3} 7**	1	12.7a	10.9a	8.4b	7.5b	9.9±1.9	19.2
	2	2.9d	2.4	3.7c	3.8c	3.2±0.6	18.8
	3	2.3ef	2.5e	2.1efg	2.3ef	2.3±0.1	4.3
	4	3.4cd	3.4cd	3.1cd	3.5c	3.3±0.1	3.0
	5	2.0fg	2.3ef	2.3ef	2.4ef	2.2±0.1	4.5
	6	1.9g	3.4cd	3.0cd	2.8d	2.8±0.4	14.3
Ca, mg L^{-1} 100^{***}	1	200.0a	231.0a	241.0a	91.0de	191±50	26.2
	2	40.2km	56.5h	65.8gh	67.5f	57.5±9.1	15.8
	3	104.0cd	80.8ef	150.0b	111.0c	104.0±26.5	25.5
	4	48.8jk	70.1fg	49.0jk	56.0hj	53.7±9.3	17.3
	5	29.1p	33.5mp	38.4m	33.5m	33.6±2.4	7.1
	6	107.0cd	143.0b	118.0c	86.4e	114.0±16.9	14.8
K, mg L^{-1} 12^{***}	1	29.6a	6.5d	4.9e	3.9f	11.2±9.2	82.1
	2	5.1e	0.6n	0.3m	0.8k	1.7±1.7	100
	3	9.0c	1.6h	1.1j	2.1g	3.5±2.8	80
	4	8.5c	0.3m	0.7kn	1.5h	2.7±2.8	104
	5	3.8f	1.0j	0.1	0.8k	1.4±1.2	85.7
	6	14.9b	0.9jk	0.7kn	1.1j	4.4±5.2	118
Mg, mg L^{-1} 50^{**}	1	103.0a	111.0a	111.0a	59.8b	96.2±18.2	18.9
	2	3.3m	3.0m	4.4kn	5.2j	4.0±0.8	20
	3	11.8d	14.2c	10.6d	12.8cd	12.4±1.1	9.3
	4	8.3f	10.1de	7.2gh	9.0ef	8.7±0.9	10.3
	5	4.0n	4.8k	5.3jk	5.9j	5.0±0.6	12.4
	6	8.1f	9.5de	6.6hj	8.1fg	8.1±0.8	9.3
Na, mg L^{-1} 200^{**}	1	246.0ab	251.0a	212.0bc	151.0d	215.0±33.5	15.6
	2	186.0c	183.0c	191.0c	205.0bc	191.0±6.9	3.6
	3	23.0h	30.2g	12.0j	21.2h	21.6±5.0	23.1
	4	97.0e	94.9e	85.5e	87.7e	91.0±4.7	5.2
	5	63.6f	61.3fe	50.9e	51.9e	56.9±5.5	9.7
	6	12.5j	12.8j	7.1m	10.1k	10.6±2.0	18.9
P, µg L^{-1} 100^{**}	1	900e	1630d	45k	45k	655±610	93.1
	2	900e	310g	45k	2030bc	821±644	78.4
	3	600f	140h	45k	900e	421±329	78.1
	4	3420a	280g	45k	4260a	2001±1839	91.9
	5	1820cd	130h	45k	56jk	513±654	127
	6	2270b	150h	60j	45k	631±819	130
Si, µg L^{-1} 10000^{**}	1	1870a	840cd	870cd	870cd	1113±379	34.0
	2	1230b	770e	1000bc	940c	985±130	13.2
	3	1000bc	820cd	940c	920c	920±50	5.4
	4	1020b	670e	750e	850cd	823±113	13.7
	5	1020b	730e	830cd	850cd	858±81	9.4
	6	1110b	790de	1000bc	770e	918±138	15.0

*-number on the map (Fig.1).** SanPiN 2.1.4.1074-01; ***WHO (Guidelines for drinking-water quality, 3^d ed., 2003; http://who.int/water_sanitation_health /dwq/guidelines 3rd/en); CV- coefficient of variation; Within each column and parameter, values with the same letter do not differ statistically according to Duncan test at $p<0.05$.

In general, a close relationship between water mineralization levels and the distance from the seashore was recorded at the Karadag Nature Reserve ($r = -0.945$; $R^2=0.893$; $p<0.001$) (fig. 2). The predominance of the effect of aerosol transfer from the sea surface on mineralization values may be explained by low precipitation levels at the paleovolcano territory.



(a) (b)

Fig. 2 Relationship between spring water mineralization levels and (a) the distance from the seashore and (b) spring rate. 2-Levinson-Lessing spring; 3- spring in the 'Valley of roses'; 4-Gyaur-Cheshme spring; 5-Choban-Chokrak spring; 6- 'Frog' spring

The data indicate a rather low seasonal variability of this parameter for all springs investigated, except for Biostation well where significant seasonal fluctuations were revealed, with mineralization level approaching MPC in autumn-winter period. Compared to 1987 data [12], water mineralization levels in Gyaur-Cheshme (№ 4) and Levinson-Lessing (№ 2) springs increased significantly: 1.3 and 1.9 times respectively, which may relate to significant changes of climate during this period: rainfall decrease and increase of air temperature [13].

Seasonal variations in precipitation levels are known to affect both water quality and flow rate of springs. The latter parameter, indirectly reflecting the duration of water contact with environmental minerals, may serve as an important indicator directly related to mineralization levels. Indeed, a negative correlation between mineralization and flow rate of springs was recorded ($r = -0.840$; $R^2=0.797$; $p<0.01$).

Among the macro-elements tested, only K and P demonstrated valuable seasonal fluctuations, mostly closely related to biosphere influence, which were the highest (up to 130%) in summer and spring for all groundwater samples. In particular, the highest P concentrations were demonstrated in spring-summer, and K in summer, the periods of the highest plants activity. MPC excess of P was recorded in water of spring situated in the Valley of roses (№ 3). In this respect, it seems significant that lichen *Dermatocarpon miniatum* (L.) W. Mann.B, grown in the close vicinity of this spring accumulated anomalously high levels of P [7]. Lack of anthropogenic pollution in this area indicates that the phenomenon reflects natural fluctuation of P in the environment, 5-8 times higher than the values detected in Minnesota groundwater [3]. Interestingly, seasonal variations of P content are connected also with springs rate and temperature, while the absolute concentration is governed by the previous precipitation: intensive P level increase takes place with the temperature increase after a significant precipitation period, which is consistent with the published data [3]. Literature data indicate that higher levels of P in groundwater are typical for a high precipitation season. On the contrary, the highest groundwater P content in Karadag takes place in spring-summer (CV=90-100%), while the highest seasonal variations are recorded in autumn and spring, and the lowest in winter (CV = 8%).

Seasonal fluctuations of Si were most pronounced in water of Biostation well and the lowest variations were recorded at Gyaur-Cheshme spring (№ 3). The main sources of water Si are silicate rocks and anthropogenic loading [11]. The latter explains the anomalous Si fluctuations in Biostation well water. On the other hand, Table 2 data indicate that the highest absolute Si concentrations in groundwater of the paleovolcano territory were typical for the hottest period, i.e., summer when high temperature stimulates Si dissolution by water-rock interaction. Despite the Si groundwater levels are considered the most stable parameters in different geographical and seasonal conditions, this element demonstrates a positive correlation with K levels ($r = 0.871$; $p<0.01$) that may reflect the long-term consequences of volcano activity, known to increase K and Si content (among other elements) in the environment [1].

Sr is eluted to water mainly from limestone of igneous and metamorphic rocks, including granites and sedimentary rocks, through leaching. Usually, groundwater of volcanic areas has low Sr concentrations [1]. The highest Sr levels were detected in water of Biostation well, reaching 2120-2140 µg L^{1} in summer, autumn and winter and decreasing in spring up to 1130 µg L^{-1}. These levels are much lower than Sr MPC value (7000 µg L^{-1}). More specific fluctuations of Sr in groundwater were recorded in other samples (fig. 3). Two distinct periods of low and high Sr levels were: 1) summer and winter; and 2) autumn and spring, respectively.

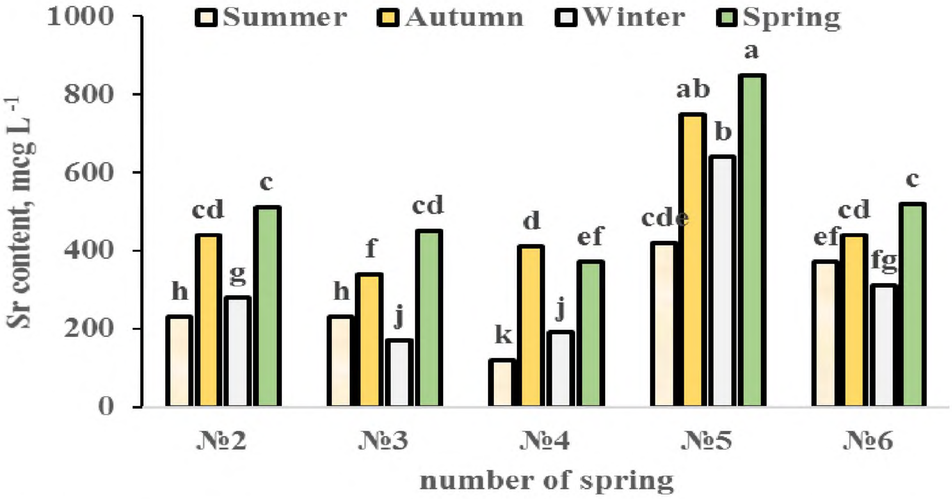
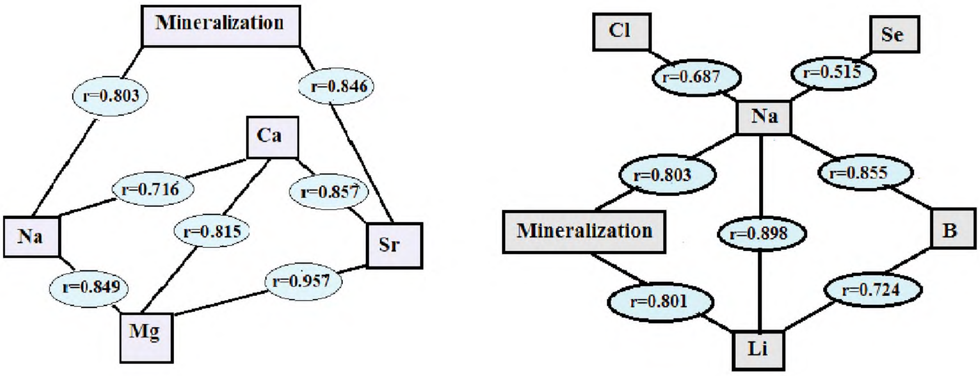


Fig. 3 Seasonal changes of Sr content in Karadag springs. Values with the same letters do not differ statistically according to Duncan test at $p\leq 0.05$

Taking into account the above mentioned, data the existence of strong Ca, Mg, Sr, Na and mineralization with Na, Li relationship should be highlighted. Fluorine content in groundwater depends on geological, physical, and chemical characteristics of aquafer, porosity and acidity of soil and rocks, temperature and aquafer depth, groundwater age, hydrological conditions and geological structure. Among factors favoring groundwater enrichment with F, the high degree of evaporation and anthropogenic factors should be mentioned. High concentrations of HCO_3, Na^{+} and high pH favor F emission from aquafer into groundwater [10]. Usually, F concentrations in groundwater correlate with the degree of interaction water-rocks, as the main F source is the bedrock. The concentration of F in water of Karadag springs was significantly lower than MPC (1.5 mg L^{-1}) for all samples investigated and increased by autumn and winter, contrary to the data for Nigeria springs, where F level was elevated in dry season [10]. Such differences may be connected both with higher F levels in Nigeria environment compared to Karadag area and with remote consequences of the Karadag volcanic activity. Interestingly, despite volcanic activity usually causes the increase of F content in hydrosphere [10], the concentrations of this element in Karadag groundwater were relatively low (fig. 4a, b).



a b

Fig. 4 Relationship between elements

Among halogens, I and Cl are closely connected with elements transfer from the sea surface, whereas F reflects mostly geological peculiarities of the environment. The highest seasonal fluctuations of Cl ions (40-50%) were recorded in springs situated in the near vicinity of the seashore (№ 2, 3), while Na fluctuations in these conditions were the lowest (table 3).

Table 3

Seasonal changes in water Cl^-. F^- and I^- ions content of Karadag springs

Parameter, MPC	*	Summer	Autumn	Winter	Spring	M±SD	CV (%)
F mg L^{-1} 1.5**	1	0.2e	0.6a	0.5b	0.4c	0.4±0.1	23.8
	2	0.2e	0.3d	0.4c	0.3d	0.3±0,1	16.7
	3	0.3d	0.5b	0.5b	0.4c	0.4±0.1	23.3
	4	0.2e	0.5b	0.6ab	0.2e	0.4±0.2	51.4
	5	0.3d	0.7a	0.5b	0.3d	0.4±0.1	36.4
	6	0.2e	0.4c	0.4c	0.3d	0.3±0.1	26.7
Cl mg L^{-1} 350**	1	408a	110d	159bc	140c	204±102	50.0
	2	25k	91de	159bc	170b	111±53	48.0
	3	33h	38gh	65f	65f	50±15	29.4
	4	21k	38gh	80e	60f	50±20	40.6
	5	35hj	44g	65f	58f	51±11	21.8
	6	11m	30j	45g	41g	32±11	35.2
I µg L^{-1} 10-125**	1	10d	10d	10d	5g	9±2	21.5
	2	10d	10d	20c	6fg	12±4	37.4
	3	30b	40a	30b	30b	33±4	11.7
	4	8de	7ef	30b	8de	13±8	63.2
	5	20c	20c	30b	10d	20±5	25.0
	6	10d	10d	20c	10d	13±4	47.5

*number of spring. ** SanPiN 1.2.3685-21. Along each line, values with the same letters do not differ statistically according to Duncan test at $p \leq 0.05$.

The phenomenon may relate to the possibility of Cl ions penetration not only with aerosols from the sea surface, but also from sedimentary and igneous rocks. It is necessary to indicate also that statistically non significant correlations between Cl, F and I were revealed: $p>0.05$: r (F-Cl) = - 0.041; r (F-I) = 0.422; r (Cl-I) = - 0.221.

Levels of Cl ions in Karadag groundwater are low, being in the range of 11-80 mg L^{-1} and taking into accounts the MPC value of 250 mg L^{-1} Levinson-Lessing spring (№ 2), situated in the near vicinity of the seashore, and Biostation well are the exception due to wide concentration range of 25-170 mg L^{-1} and 110-408 mg L^{-1} respectively. It may be supposed that high Cl levels in well water relate to anthropogenic uptake, highly expressed in summer. For other springs, a tendency of Cl concentration increase in winter and spring, took place indirectly suggesting the intensification of Cl transition from the sea surface through aerosols.

As far as iodine is concerned, Table 3 indicates significantly higher levels of the element both in water of Choban-Chokrak spring (№ 5) and spring situated at the Valley of roses (№ 3). This may be connected with intensive iodine transfer in spring №3 from plant organic residues and to a lesser extent in spring № 5, with predominant accumulation of the element in sedimentary rocks compared to volcanic ones. On the other hand, these springs may become important sources of iodine to humans: 2 L of water from these springs may provide from 17 to 34% of the daily iodine requirement (120 μg).

Furthermore, Table 3 indicates that the highest iodine concentration in Karadag springs was recorded in winter, the wettest season. This peculiarity is typical of all halogens investigated (Cl, F, I). Furthermore, according to Korobova et al. [9], the highest iodine level in groundwater of European Russia occurs at the end of vegetation period (autumn), characterized by intensive leaching of this element from organic residues due to intensive precipitation. For Karadag, the highest level of precipitation recorded in winter promotes iodine leaching.

Among microelements in the groundwater at the territory of paleovolcano, B Li and Se are of special interest, known to be strongly emitted in the environment during volcanic activity [2, 14]. Increased B and Li concentrations in regions of ancient volcanoes are considered as a potential ability to industrial production of these elements [2]. Natural weathering (chemical and mechanical) is considered the main source of B for hydrosphere, though the amount of B emitted to water ecosystems may vary significantly depending on the geology of the environment.

Significant amount of B, Li and Se penetrating groundwater, soil and plants is also connected with transfer of these elements from the sea surface. Valuable sources of Se are also di- and tri-selenides emitted during livelihood of phytoplankton, soil microorganisms and plants [14]. Se content in groundwater depends on many factors, including the size and groundwater depth, chemical composition of parent rock and soil, through which water seeps out after rainfall. This element usually accumulates in marine sediments [14]. Though no MPC excess was recorded for Se, its concentration in springs near the seashore was significantly higher than in other resources.

The comparison of the aforementioned parameters with the results of our investigations indicates both high levels of these elements at the territory of paleovolcano and the mosaic pattern of their distribution. A similar situation was reported in our previous investigation regarding the Se accumulation levels in Karadag herbs [6].

As far as B is concerned, its MPC excess was indicated in water of Biostation well, springs situated near the seashore (№ 2, № 3) and Gyaur-Cheshme spring (№ 4). The concentration of Li in groundwater reached the MPC value in water of Biostation well and Levinson-Lessing spring (№ 2).

Overall, the results indicate a positive correlation between B, Li and Se, and the groundwater salinization level (mineralization value), and particularly with Na concentration, which confirms a powerful effect of these elements transport from the sea surface on B, Li and Se accumulation in groundwater of the Reserve (fig. 4b).

The results are consistent with the known data, regarding the positive relationship between B content and groundwater mineralization level. The weaker correlation between Se and Na compared to B and Li data possibly reflects the participation of living organisms in Se circulation, due to the ability to synthetize volatile methylated forms [14]. Furthermore, the relationship between Se and springs flow rate is weaker than that between mineralization level and spring flow rate (r = - 0.620 compared to r = - 0.840). These relationships were revealed for the first time and may be considered as important characteristics of Karadag springs.

The highest levels of Li, B, Na concentrations in Karadag groundwater occur in dry summer season, which may relate to concentration processes. At the same time, the highest concentration of Se was recorded in the wettest autumn-winter period, which supposes significant contribution of Se transport from the sea surface and erosion of this element from dead plants. In this respect, Se significantly repeats iodine behavior, also forming volatile derivatives providing intensive transfer of the elements from the sea surface and increase of the element concentration in groundwater during wet season (table 4).

Table 4

Seasonal dynamics of B, Fe, Zn, Se and Li accumulation in springs of paleovolcano

Parameter, MPC	*	Summer	Autumn	Winter	Spring	M±SD	CV (%)
B ($\mu g\ L^{-1}$) 300^{***}	1	570bc	720a	560bc	380d	558±89	15.9
	2	480c	580bc	490c	500bc	513±34	6.6
	3	90gh	120f	70jk	90gh	93±13.8	14.8
	4	250e	320d	210e	240e	255±33	12.9
	5	520bc	600ab	210e	310d	410±150	36.6
	6	80hj	100fg	60k	80hj	80±10	12.5
Fe ($\mu g\ L^{-1}$) 300^{**}	1	70k	890a	580b	350c	473±263	55.6
	2	70k	200f	120h	240ef	158±63	39.9
	3	100j	290de	410c	520b	330±135	40.9
	4	60k	240ef	140g	250e	173±73	42.2
	5	24n	130gh	40m	110hj	76±44	57.9
	6	24n	530b	310c	340d	301±139	46.2
Li ($\mu g\ L^{-1}$) 30^{**}	1	30b	30b	30b	20c	27.5±3.8	13.8
	2	30b	30b	30b	40a	32.5±3.8	11.7
	3	10d	10d	9de	10d	9.8±0.4	3.8
	4	6g	7fg	5h	7fg	6.25±0.75	12
	5	7fg	7fg	6gh	8ef	7±0.5	7.1
	6	5h	6gh	5h	6gh	5.5±0.5	9.1
Zn ($\mu g\ L^{-1}$) 5000^{**}	1	40d	170a	50c	20f	70±50	71.4
	2	40d	20f	10g	40d	28±13	46.4
	3	25fe	30e	10g	40d	20±13	65.0
	4	20f	80b	10g	50c	40±25	62.5
	5	19f	90b	10g	20f	35±28	80.0
	6	30e	150a	20f	20f	55±48	87.3
Se ($ng\ L^{-1}$) 10 000**	1	36k	500c	1160a	90hj	528±316	59.8
	2	34k	440c	1000a	360d	537±232	43.2
	3	98h	250e	85j	100h	133±58	43.6
	4	740b	930a	980a	40k	673±316	47.0
	5	93hj	180f	100h	96h	117±31	26.5
	6	109gh	290e	110gh	120g	157±66	42.0

*number of spring; ** SanPiN 1.2.3685-21; ***WHO (Guidelines for drinking-water quality, 3^{d} ed., 2003; http://who.int/water_sanitation_health /dwq/guidelines 3rd/en.)ю For each element, values with the same letters do not differ statistically according to Duncan's test at $p<0.05$.

Among the other elements analyzed, the most significant concentrations were recorded for Fe, which ranks the second in the Earth's crust. In water it is present in suspension or solubilized forms of 2^+ or 3^+ derivatives. The acceptable levels of Fe^{+2} and Fe^{+3} in drinking water are 0.3 mg L^{-1} and 1 mg L^{-1} respectively. The availability of Fe and Mn are connected with the processes of solubilization and weathering. Compared to concentrations of Na, Ca and Mg, Fe level in groundwater is more variable, which is in accordance with literature data [5]. Summer season was characterized by the lowest levels of Fe in Karadag springs (fig. 5).

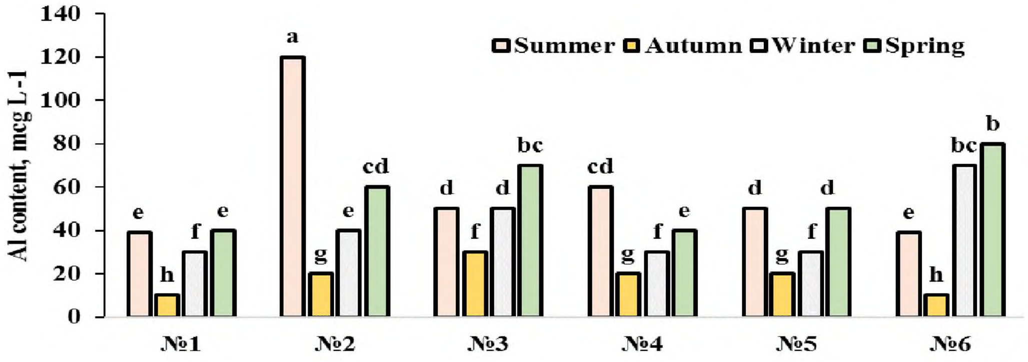


Fig. 5 Seasonal changes of Al content in Karadag springs. Values with the same letters do not differ statistically according to Duncan test at $p<0.05$

Mean concentration of Zn in groundwater reaches 10-20 µg L^{-1}, while lower levels (< 10 µg L^{-1}) are typical for the surface water. Zn is present in small amount almost in all igneous rocks. Zn levels in Karadag groundwater were rather high forming an interval from 10 to 170 µg L^{-1}. The highest Zn levels in Karadag groundwater were recorded in autumn in the remoted from the seashore springs (№ 4, 5, 6) and Biostation well (№ 1). On the contrary, the sea closeness changes this peculiarity increasing Zn levels in spring water (№ 2, 3). Therefore, air transfer of Zn from the sea surface activated by the phytoplankton development rules this element concentration in spring.

Though MPC excess of B, Li, Ca, Na, and Fe were recorded in all Karadag springs (Tables 1,3), these situations reflect only peculiarities of the Reserve hydrology and cannot be considered as factors threatening human health (fig. 6).

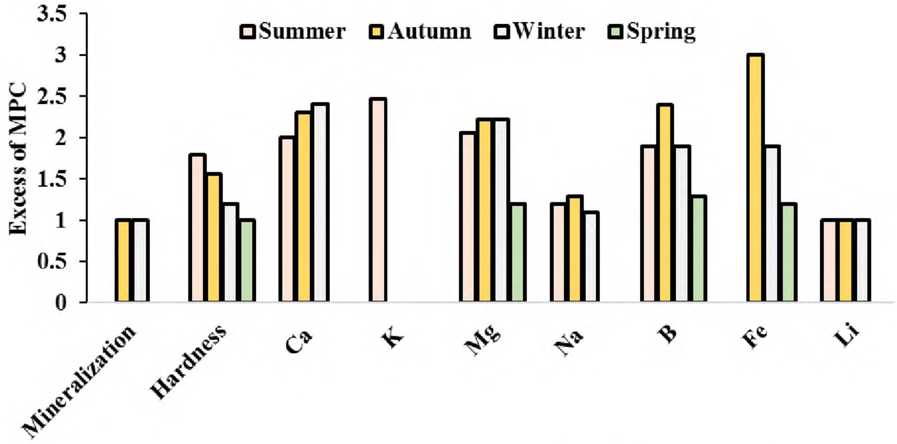


Fig. 6 Seasonal excess of MPC in well water for different elements

Much more serious is the case with Biostation well water, used by the residents of settlement. Fig. 6 suggests a significant uptake all year round, by patterns such as water hardness, Mg and B content. In summer, autumn and winter, Ca, Na, Fe and Li uptake increases. Mineralization reaches MPC in autumn and winter, while in summer K level exceeds MPC by 2.5 times. All the aforementioned facts indicate the necessity of water filters utilization, which decreases at least partially the levels of Ca, Mg and Fe.

Volcanic activity usually causes Al contamination of the environment [1]. As far as Al is concerned, its concentration in groundwater of the paleovolcano territory was rather high. Relatively high level of Al in groundwater may relate to the chance both of Al solubilization by soil alumosilicates, sedimentary rocks, and of concentration. Indeed, the detected levels were much higher than those described in India (from 1.8 to 3 mg L^{-1}) [4]. Fig. 7 indicates that the lowest groundwater Al concentrations occur in autumn which may be due to Al compounds precipitation. A general pattern of Al accumulation is a constant increase of this element level depending on the season, according to the sequence autumn<winter<spring.

Despite the territory investigated belongs to the Nature Reserve lacking a significant anthropogenic uptake of heavy metals, whereas Mn, Co, Mo and Cu are present in trace amounts, there exist certain ecological risks of groundwater consumption, exclusively referring to the water from Biostation well.

Conclusion

The results of the present investigation give the first picture of groundwater mineral composition and its seasonal dynamics at the territory of paleovolcano, demonstrating increased levels of B, Li and Se in the environment, positive correlations between mineralization levels and Ca, Mn and Sr and Na, Se, B, Cl, Li and negative correlations with flow rate of springs and distance from the sea shore. Typical high concentrations of P, K, Si, Na in spring, B, Zn, Fe, Se, F in autumn; Ca, Se, F, Cl, I in winter, and Sr in spring and autumn reflect the intensity of soil-water interaction, temperature and rainfall effect, mineral transfer from the sea surface and plants wastes leaching. Health-threatened values of mineralization, water hardness, Ca, K, Mg, Na, B, Fe and Li demonstrated in anthropogenic loading zone (Biostation well), cause ecological risks, especially significant in summer, autumn and winter period.

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Голубкина Н.А, Лапченко В.А., Лапченко Е.В., Зуев А.В., Карузо Дж. Сезонная динамика минерального состава грунтовых вод на территории палеовулкана // Bull. Of the State Nikita Botan. Gard. – 2022. – № 142. – P. 129-140

Проведена оценка сезонной динамики концентраций 25 элементов в подземных водах Карадага. Были зарегистрированы повышенные уровни B, Li и Se, а также отрицательные корреляции между минерализацией воды и скоростью потока источников, и расстоянием от берега моря (r = -0,840 и r = -0,945), а также высокие сезонные колебания уровней P и K (78-130% и 80-118% соответственно). Положительные корреляции были обнаружены между Ca, Mg, Sr (r = 0,82-0,96); Li, B, Na (r = 0,72-0,90); Li, Na, минерализация (r = 0,80-0,90) и Se, Na (r = 0,551). Самые высокие концентрации P, K, Si, Na были зарегистрированы весной, B, Zn, Fe, Se, F осенью; Ca, Se, F, Cl, I зимой и Sr весной и осенью. Ca, K, Mg, Na, B, Fe, Li, минерализация и жесткость воды родниковой воды биостанции продемонстрировали высокие сезонные колебания и превышение предельно допустимых концентраций.

Ключевые слова: *подземные воды; минеральный состав; сезонные колебания; палеовулкан*