ОРИГИНАЛЬНАЯ СТАТЬЯ

SELENIUM CONTENT IN GROUNDWATER OF THE CRIMEAN PENINSULA

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ABSTRACT. The main sources of essential trace element selenium (Se) to humans are plants, animals and water. Though Se concentration in water is low, the values are considered to be good markers of the environmental Se status. Se content in groundwater of 22 springs, wells and bottled water samples produced at the territory of the Crimea has been determined. Uneven distribution of Se at the territory of the Crimea was reflected in a broad concentrations range of the element from 0.082 to 7.85 μg/L with the highest values typical for Simferopol well and 2 samples of bottled water: 'Crimean paradise' and 'Kula' (1.25–1.38 μg/L). Two liters of water from Simferopol well provide up to 24% of the daily adequate Se consumption level. Chemical analysis of groundwater quality recorded high ecological risks connected with increased nitrates levels in more than 30% of samples investigated (up to 194 mg/L) and high mineralization (up to 1540 mg/L). Chemical analysis of fresh water demonstrated unsuitability for consumption of 'Saki' bottled water, characterized by significant MPC excess for nitrates (4.3 MPC), chlorides (1.4 MPC), fluorine (1.19 MPC) and mineralization (1.54 MPC). The work indicates the necessity of wide groundwater quality monitoring for the whole Crimean peninsula.

KEYWORDS: selenium, groundwater, Crimean peninsula, nitrates, mineralization.

INTRODUCTION

Trace element selenium (Se) is essential for human beings, providing powerful protection against cardiovascular, viral and oncological diseases (Golubkina, Papazyan, 2006; Kieliszek, 2016). Widespread distribution of Se-deficient soils in the world and uneven distribution of the element determines the importance of the Se status evaluation both of residents and environment. The most frequently used environmental objects for the Se status monitoring are soils, water, plants, animals, etc. (Ermakov, 1999). Despite the fact that water provides usually low Se consumption levels due to low Se concentration ranging from less than 0.0001 to more than 2 mg Se per L, it is highly valuable for geochemical characteristic of the territory (Ermakov, 1995). Participating in sedimentation, solution and macro- and trace elements transport in a system soil-plants – animals – human beings, groundwater is considered to be the most important component of terrestrial ecosystems. Chemical and mineral composition of groundwater is affected by biogeochemical peculiarities of the territory, redox potential, intensity of trace elements transport from the surface of the sea and oceans, long-term effect of volcanic activity and anthropogenic pollution (Baillie et al., 2018; Chen et al., 2019). According to USEPA data maximum contaminant level (MCL) of Se in drinking water is equal to 50 μg/L (Zhang et al., 2020a, b). Taking into account, that drinking water is a source of about 10% of the daily Se consumption dose, WHO recommends 20 μg/L Se concentration as the maximum allowable Se level in drinking water, while according to EU countries guidance (Guidelines…, 2022) the maximum concentration of Se in drinking water is equal to 10 μg/L. Prolonged contact of groundwater with soil provides higher Se levels compared to surface water.

The main chemical Se forms in water are sele-

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nates (Se^{+6}), predominating at high pH and oxygen excess, while in anaerobic conditions and low pH selenites (Se^{+4}) predominate (Kieliszek, Błazejak, 2016; Sharma et al., 2018) According to epidemiological investigations (Evstafieva et al., 2022) Simferopol residents record marginal Se deficiency with intensive dependence of the human Se status on imported cereals.

Fresh water deficit is a serious problem at the Crimean peninsular. This fact indicates the significance of Se levels evaluation in natural sources, such as springs and wells. In this respect industrial production of bottled water at the territory are of utmost importance. But up-to-date, Se levels in both bottled and ground-water of the Crimea have never been determined. The exception is the study of seasonal changes in groundwater quality at the territory of Karadag Nature Reserve (Golubkina et al., 2021). Selenium has never been evaluated in the Crimean bottled water, while the quality evaluation of the latter and of the Crimean groundwater is rather fragmental (Ivanutin et al., 2019, Kirienkova et al., 2019).

The aim of the present study was evaluation of quality and Se accumulation by groundwater of the Crimean peninsula.

MATERIALS AND METHODS

Water Sampling. Groundwater samples from springs and wells were gathered in plastic containers (Laxen, 1981) in June, 2021–2022: 5 springs of the Karadag Nature Reserve (Gyaur-Chishme, Levinson-Lessing, Valley of Roses, Frog, Chobak-Chokrak) and spring of cape Martyan Nature Reserve; Ai-Petri and Simferopol springs and wells of Radostnoye, Topolevka, Kamenka, Simferopol, Kurortnoye, Karadag Biostation. Samples of bottled water (Kula, Bishuli, Crimean paradise, Crimean Saki, Krimskaya elite, Krimskaya table) were obtained from the shops of Nikita settlement. Samples were kept at 10 ºC in a refrigerator before the analysis. Groundwater sampling places and places of bottled water production are presented on Fig. 1.

Table 1 indicates geographical coordinates of bottled water production places, and of springs and wells studied in the present work.

Selenium. Selenium (Se) content was determined using fluorimetric analysis (Alfthan , 1984), after preliminary concentration of samples (350 mL of water per one determination). The method includes wet digestions of samples with a mixture of HNO_3:$HClO_4$, 5:7; reduction of Se^{+6} to selenic acid (Se^{+4}) using 6 N HCl and formation of a complex piazoselenol between Se^{+4} and 2.3-diaminonaphtalene. Selenium concentration was assessed using fluorescence value of piazoselenol in hexane at 519 nm (λ emission) and 376 nm (λ excitation). All determinations were achieved in triplicate.

Cl and F ions. Cl and F ion concentrations were determined using ion selective electrodes on ionomer Expert-001 (Econix corp., Moscow, Russia).

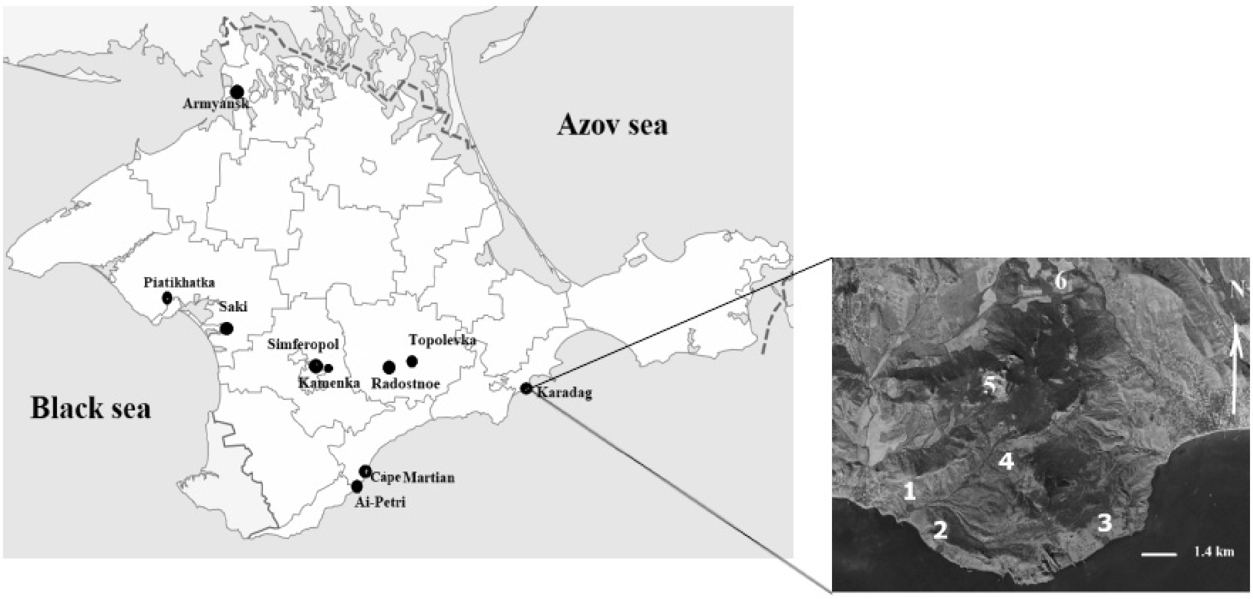

Fig. 1. *Places of water sampling. (1) Biostation well, (2) Levinson-Lessing spring, (3) spring in the Valley f roses, (4) Gyaur-Chishme spring, (5) Chobak-Chokrak spring, (6) spring 'Frog'*

Table 1. ***Geographical coordinates of ground-water sampling***

Title	Geographical coordinates	Region
Biostation well	N 44°92’72” E 35°20’47”	Karadag Nature Reserve
Levinson-Lessing	N 44°91’22” E 35°.22’16”	–
Valley of roses	N 44°93’17”, E 35°.24’75”	–
Gyaur-Chishme	N 44°55'52.1", E 35°13'12.3"	–
Chobak-Chokrak	N 44°56'08.4", E 35°12'41.5"	–
Frog	N 44 ° 96’02”, E 35° 20’05”	–
Radostnoye	N 44°59′43″, E 34°50′38″	Belogorsky region
Topolevka	N 45°00′40″, E 34°52′35″	–
Simferopol	N 44°56′53″, E 34°06′15″	Symferopol
Cape Martian	N 44°30′38″, 34°15′25″ E	Nikita Botanic Gardens
Kula	N 46°06′25″, E 33°41′35″	Armyansk region
Bishuli	N 45°19'18,70", E 34°15'47,50"	Piatikhatkinsk thermal water deposit
Crimean Saki	N 45°08′01″, E 33°34′38″	Saki health resort
Kamenka	N 45°40′00″, E 33°58′40″	Pervomaysk region

Mineralization. Total mineralization level was assessed using a portable conductometer TDS-3A (HM Digital, Inc., Seul, Korea).

Water hardness. Water hardness was determined via complexonometric titration using 0.05 M EDTA (GOST, 2012).

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. The results were expressed as means (three determinations for each water sample) and standard deviation (M±SD).

RESULTS AND DISCUSSION

Se accumulation. As can be seen from Figure 1, most of water samples were gathered at the territory of the Crimean Mountains and foothills of the mountain range which was in accordance with the well known natural water resources distribution. Indeed, according to literature data (Kaukova et al., 2014; Tarasenko, 2003) the Crimean water resources are located predominantly in the Crimean mountains and reach about 0.83 km^3/year, while only 0.04 km^3/year correspond to the flat part of the peninsula.

Determination of Se content in water samples revealed high heterogeneity of Se distribution (Fig. 2).

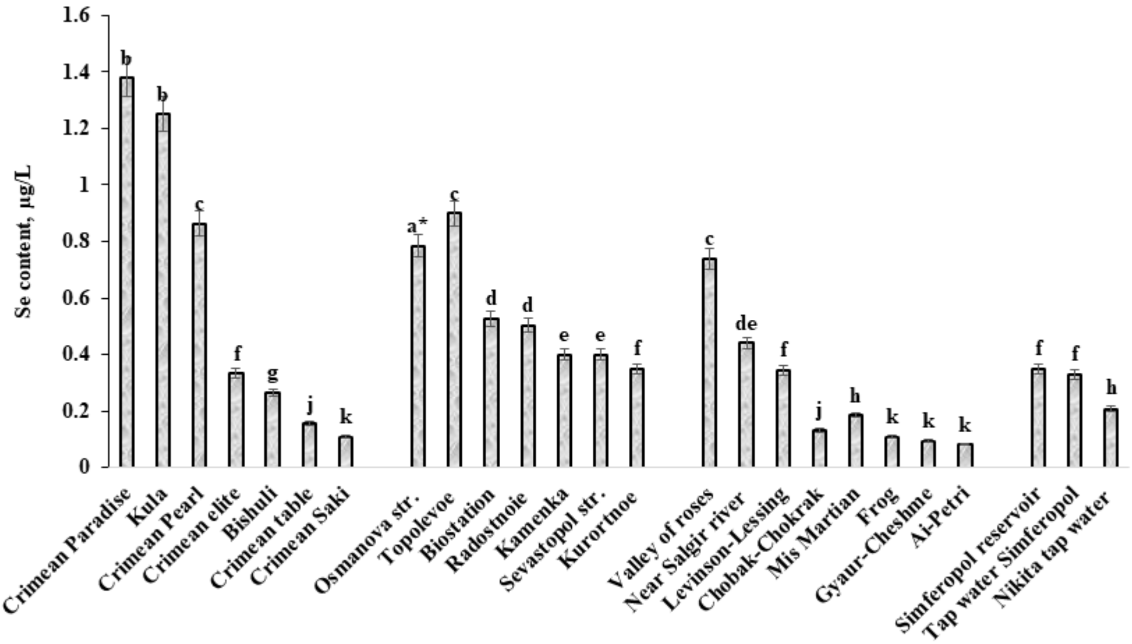

Fig. 2. *Selenium content in water of the Crimean Peninsula:*
** – the value is decreased 10 times (Osmanova street and Sevastopol street are situated in Simferopol); values with the same letters do not differ statistically according to Duncan test at p<0.05*

Thus, Se content in bottled water samples varied from 0.109 µg/L to 1.380 µg/L with the highest values typical for bottled water 'Crimean paradise' (1.38 µg/L), 'Crimean pearl' (0.863 µg/L) and 'Kula' (1.25 µg/L) and the lowest for bottled water 'Saki' (0.109 µg/L). Even a larger interval of Se concentration range (0.35–7.85 µg/L) was assessed for wells water.

Thus, water from Osmanova street well in Simferopol was characterized by the highest Se concentration – 7.85 µg/L. Relatively high level of Se was registered in Topolevka settlement (0.9 µg/L). Significant variations in Se levels were also recorded for water samples of springs at the territory of Karadag Nature Reserve (0.093–0.74 µg/L) (Golubkina et al., 2021), Ai-Petri 'spring of youth' (0.082 µg/L), spring of cape Martian Nature Reserve (0.186 µg/L) and spring in the vicinity of Salgir river in Simferopol (0.44 µg/L).

Our previous investigation of Karadag groundwater seasonal mineral dynamics proved Se content increase during autumn and winter, and a phenomenon of Se concentration decline with altitude and the distance from the sea shore (Golubkina et al., 2021). Indeed, the lowest Se levels were typical for Ai-Petri 'Spring of youth' and Gyaur-Chishme, Chobak-Chkrak and Frog springs, while the highest Se levels were registered in water of springs, situated in the near vicinity of the sea (Valley of roses and Levinson-Lessing springs of the Karadag Nature Reserve). Unusually high level of Se in well water at Osmanova street attracts special attention. Thus, according to the Se analysis, water from this well should be considered as a medicinal one. Indeed, 2 L of this water may provide up to 22.4% of the adequate Se consumption level – 70 µg/day (Kipp et al., 2015). Utilization of bottled water 'Kula' and 'Crimean paradise' may provide only 2.8–3.8% of the adequate Se consumption level.

Among factors affecting Se content in groundwater one should mention the sulfuric acid production in Armyansk- the town famous by its bottled water 'Kula'. Chemical similarity of Se and S provides increased risks of Se emission during the sulfuric acid technological process leading to the increase of Se concentrations in the environment (Ullah et al., 2022; Golubkina, Mironov, 2018).

It should be also emphasized, that pipe water of Sinferopol and Nikita settlement in the close vicinity of cape Martyan Nature Reserve contains relatively high levels of Se ranging between 0.207–0.35 µg/L. Lack of a valuable anthropogenic loading both in the vicinity of Nikitsky Botanic Gardens (Nikita settlement) and Simferopol reservoir indicates specific geochemical peculiarities of these territories. According to Ermakov (1999), Se concentration higher that 0.3 µg/L in surface water is considered to be sufficient for domestic animals protection against white muscle disease, caused by Se deficiency, which is in good agreement with epidemiological data (Evstafieva et al., 2021).

Taking into account seasonal fluctuations of Se content in groundwater, revealed for Karadag springs (Golubkina et al., 2021), one may suppose that Se content in wells and springs of the Crimea may be higher in autumn and winter than registered in the present work in June. Nevertheless, this hypothesis needs additional investigations. Besides, it should be indicated that heterogeneity of Se accumulation in groundwater seems to be typical for mountainous areas, which is in agreement with the investigation of groundwater mineral composition of numerous springs in Valeric settlement of the Chechen Republic (Amagova et al., 2020).

Chemical analysis data. Up-to-date, evaluation of fresh water quality in the Crimea has been limited by the determination of hardness, mineralization level, pH and chloride ion concentration (Ivanutin et al., 2019, Kerienkova et al., 2019). The results of the present research recorded the existence of elevated mineralization in most groundwater samples, reaching in separate cases the levels of MPC and higher (Bottled water 'Crimean Saki', Kurortnoe settlement well). Optimal levels of mineralization (about 200 mg/L) were demonstrated only for bottled water 'Krimskaya stolovaya', in Karadag spring Gyaur-Chishme, Ai-Petri 'Spring of youth' and in tap water of Nikita settlement and in Simferopol reservoir.

Episodic cases of ammonium MPC excess seem to be connected with anthropogenic activity. One should also indicate low quality of bottled water 'Saki' with values of mineralization, hardness, chloride and fluoride ion levels exceeding MPC. The phenomenon is in good accordance with literature indication of high mineralization levels in the Crimean fresh water (https://www.saki.ru/news/6015.html).

According to Table 2 data elevated concentrations of F seem to be typical for Piatikhatkinsk thermal water deposit and Saki health resort with the maximum concentration level recorded in 'Crimean Saki' bottled water exceeding MPC value by 18.7%.

On the other hand, the present investigation records a serious problem of the Crimean fresh water - high nitrates levels- the phenomenon, connected exclusively with anthropogenic loading.

The number of water sources with nitrate levels higher than MPC reached 30%. Up-to-date no data have been published on the nitrate content in the Crimean fresh water. MPC excess was in the range from 1.02 (cape Martian spring) to 4.3 times (bottled water 'Crimean Saki') (Fig. 3).

Table 2. ***Quality parameter of the Crimean fresh water***

Samples	pH	Cl^{-1}, mg/L	F^{-1}, mg/L	Ammonium, mg/L	Nitrates, mg/L	Hardness	Mineralization, mg/L
Bottled water							
Crimean Paradise	7.65^{a}	57^{c}	0.35^{c}	0.68^{c}	54^{c}	3.0^{bc}	474^{c}
Kula	5.41^{b}	40^{d}	0.37^{c}	1.09^{b}	54^{c}	2.5^{d}	480^{c}
Crimean Pearl	6.18^{b}	12^{f}	0.13^{d}	0.27^{e}	12^{f}	2.85^{cd}	308^{d}
Crimean elite	7.83^{a}	31^{e}	0.10d	0.24^{e}	17^{e}	0.6^{f}	365^{d}
Bishuli	6.24^{b}	125^{b}	1.20^{b}	2.30^{a}	92^{b}	3.4^{b}	1200^{b}
Crimean table*	8.00^{a}	30^{e}	0.33^{c}	0.42^{d}	30^{d}	1.0^{e}	232^{e}
Crimean Saki	6.45^{b}	495^{a}	1.78^{a}	2.10^{a}	194^{a}	7.5^{a}	1540^{a}
Range	5.41–8.00	30–495	0.10–1.78	0.24–2.30	12–194	0.6–7.5	232–1540
Wells							
Osmanova str*	7.70^{a}	113^{bc}	1.0^{a}	0.97^{b}	33^{c}	3.8^{cd}	445^{c}
Topolevoe	7.77^{a}	16^{f}	0.20^{d}	0.17^{e}	13^{d}	3.2^{d}	305^{d}
Biostation	7.08^{a}	408^{a}	0.24^{d}	0.47^{d}	55^{ab}	10.0^{a}	735^{b}
Radostnoie	8.06^{a}	28^{e}	0.25^{d}	0.13^{f}	11^{d}	2.1^{e}	271^{d}
Kamenka	7.60^{a}	97^{c}	0.50^{b}	3.00^{a}	54^{b}	5.4^{b}	752^{b}
Sevastopol str*	7.50^{a}	48^{d}	0.40^{c}	0.97^{b}	33^{c}	4.1^{c}	490^{c}
Kurortnoe	7.23^{a}	120^{b}	0.24^{d}	0.57^{c}	66^{a}	12.0^{a}	922^{a}
Range	7.08–8.06	16–408	0.2–1.00	0.13–3.00	11–66	2.1–12.0	271–922
Springs							
Valley of roses	7.68^{b}	21.2^{e}	0.20^{d}	0.19^{d}	15^{e}	3.4^{b}	325^{d}
Near Salgir river	7.30^{b}	68.0^{a}	0.60^{a}	4.00^{a}	34^{b}	4.3^{a}	480^{ab}
Levinsona-Lessing	7.87^{ab}	25.0^{de}	0.24^{d}	0.28^{c}	25^{c}	2.9^{bc}	531^{a}
Chobak-Chokrak	8.25^{a}	56.0^{b}	0.48^{b}	0.07^{f}	19^{d}	2.5^{c}	416^{bc}
Cape Martian	7.47^{b}	30.4^{cd}	0.51^{ab}	0.50^{b}	46^{a}	2.5^{c}	384^{cd}
Frog	7.57^{b}	11.2^{f}	0.16^{e}	0.09^{e}	15^{e}	1.9^{d}	312^{d}
Gyaur-Cheshme	7.63^{b}	35.0^{c}	0.35^{c}	0.10^{e}	8^{f}	2.0^{d}	209^{e}
Ai-Petri	7.66^{b}	26.3^{cd}	0.34^{c}	0.23^{d}	37^{b}	2.5^{c}	251^{e}
Range	7.47–8.25	11.2–68.0	0.16–0.60	0.10–4.00	8–46	1.9–4.3	209–480
Reference samples (Simferopol)							
Reservoir	7.8^{a}	62.0^{a}	0.23^{c}	4.90^{a}	14^{b}	2.4^{b}	225^{b}
Tap water	7.5^{a}	5.5^{c}	0.40^{a}	1.23^{b}	36^{a}	4.3^{a}	501^{a}
Nikita tap water	7.22^{a}	30.0^{b}	0.30^{b}	0.27^{c}	33^{a}	2.5^{b}	254^{b}
MPC	>6.5 <8.5	350	1.5	2.0	45	7	1000

N o t e : * – Simferopol; for each group of samples values in columns with similar letters do not differ statistically according to Duncan test at $p<0.05$.

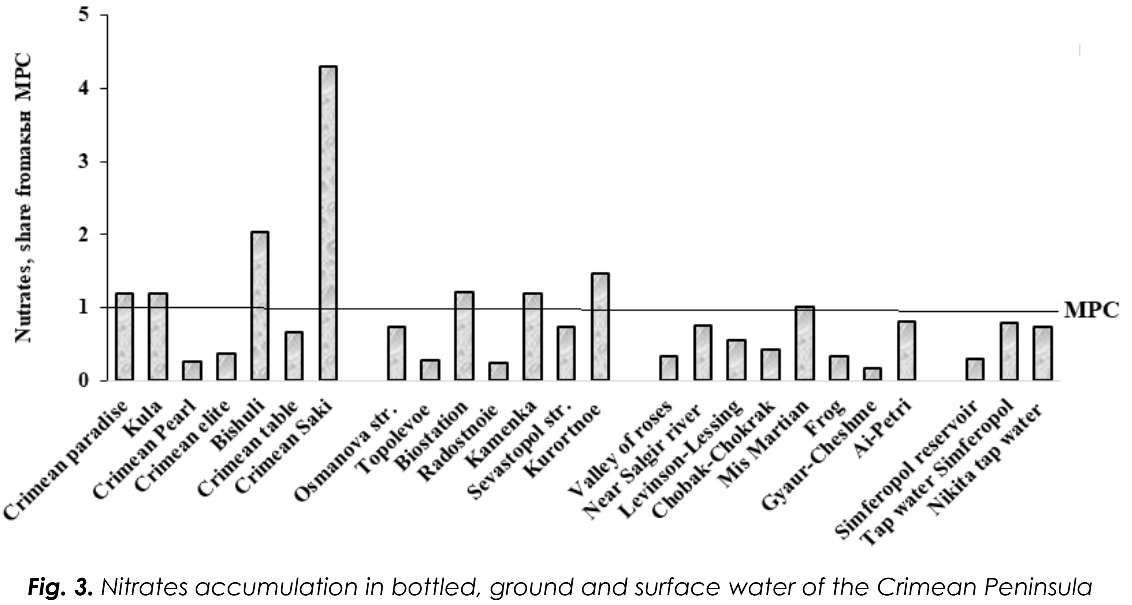

Fig. 3. *Nitrates accumulation in bottled, ground and surface water of the Crimean Peninsula*

Figures 2,3 data indicate the existence of significant risks of oncological diseases development in Krasnogvardeisk region, where the balneological health resort is situated and bottled water 'Crimean Saki' and 'Bishuli' are produced. Both bottled water samples are characterized by significant nitrate levels and low content of Se.

According to Internet data, oncological diseases morbidity in the Crimea is higher, than in other regions of Russian Federation. High nitrate consumption levels are connected with risks of cancer occurrence and development due to biochemical reaction in human organism: nitrates – nitrites – nitrosamines, the latter known as powerful carcinogens (Darvishmotevalli et al., 2019). Nitrate excess in drinking water is a potential health problem primarily for infants. Methaemoglobinemia has been considered as the end-point of concern for humans from long-term exposure to nitrate in drinking water. Though high consumption levels of fruit and vegetables and high Se levels in separate water samples may decrease the risks of high nitrates consumption with water (Deryagina et al., 2019), in conditions of the Crimean peninsula with relatively moderate Se levels in ground and surface water, such a protection seems to be insufficient. In this respect bottled water 'Crimean Saki' production should be forbidden due to high levels of nitrates, F, Cl, hardness and mineralization and low pH. Determination of low pH level of the 'Kula' bottled water was in agreement with Ivanutin et al. (2019) investigation, who recorded also relatively low levels of chloride ions in Simferopol tap water and bottled water 'Kula' and 'Crimean pearl'. Certain differences in total mineralization between the present work and the results published earlier (Ivanutin et al., 2019) may be connected with seasonal variability of quality parameters, recorded earlier for Karadag springs (Golubkina et al., 2022). The present investigation revealed for the first time ecological risks of elevated nitrate levels in the Crimean groundwater both from wells and bottled water and even in one spring of cape Martian Nature Reserve, situated in the near vicinity below Nikita settlement. Comparison of ecological coefficients of variation for different parameters tested indicates the highest values of Cl, F, NO_3 ions and mineralization level in bottled water, ammonium accumulation in springs and Se in wells (Fig. 4).

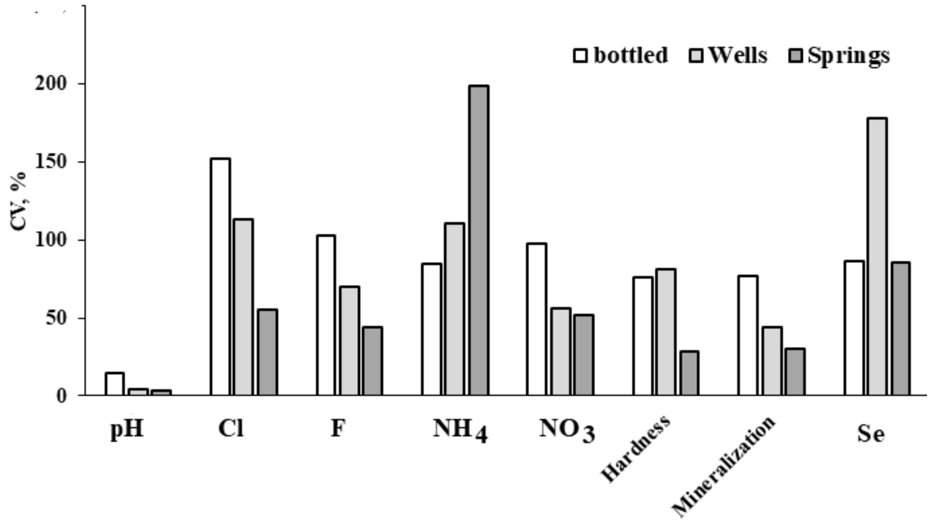

Fig. 4. *Variation coefficients of different parameters of bottled, wells and springs water*

CONCLUSION

Evaluation of Se levels in ground water of the Crimea records uneven Se distribution with the highest values typical for bottled water 'Kula' and 'Crimean paradise', Osmanova street well (Simferopol) and Karadag springs, situated in the near vicinity of the sea shore. Chemical parameters of bottled water, springs, wells and surface water of the Crimean Peninsula emphasizes for the first time high risks of 'Bishuli' and 'Saki' bottled water consumption due to significant MPC nitrates and mineralization excess.

The results indicate the necessity of wide drinking water monitoring in the Crimea, including Se content for evaluation of ecological risks and sources, capable to provide high quality drinking water.

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CONFLICT OF INTEREST

The authors declare no conflict of interests.

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СОДЕРЖАНИЕ СЕЛЕНА В ГРУНТОВЫХ ВОДАХ КРЫМА

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РЕЗЮМЕ. Основными источниками эссенциального для человека микроэлемента селена (Se) являются растения, животные и вода. Несмотря на то, что концентрации селена в воде низкие, этот показатель считается хорошим маркером селенового статуса исследуемой территории. Впервые установлено содержание селена в грунтовых водах 22 родников, скважин и бутилированной воде, производимой на территории Крыма. Неравномерность распределения селена на Крымском полуострове отражалась в широком интервале наблюдаемых концентраций от 0,082 до 7,85 мкг/л при наибольших уровнях селена, установленных для образца воды из скважины Симферополя и двух образцов бутилированной воды «Крымский рай» и «Кула» (1,25–1,38 мкг/л). Два литра воды из скважины Симферополя обеспечивают до 24% суточной потребности человека в селене. Химический анализ грунтовых вод выявил высокие экологические риски, связанные с повышенным содержанием нитратов более чем в 30% образцов (до 194 мг/л) и высокой минерализацией (до1540 мг/л). Химический анализ питьевой воды установил непригодность бутилированной воды «Саки» для использования в связи с превышением ПДК по нитратам (4.3 ПДК), хлоридам (1.4 ПДК), фторидам (1.19 ПДК) и уровню минерализации (1.54 ПДК). Результаты исследования свидетельствуют о необходимости проведения широкомасштабного мониторинга качества воды Крымского полуострова.

КЛЮЧЕВЫЕ СЛОВА: селен, грунтовые воды, Крымский полуостров, нитраты, минерализация.

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