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Metals into Thermo-mineral Waters in Sofia Valley

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ABSTRACT

The territory of Sofia Valley is about 1,200 sq.km. Tectonically, it represents a graben type separated by bordering faults from the surrounding mountain ridges. Major geothermal reservoirs are of Mesozoic age (sediments and volcanic rocks) as well as Neogene age (sand layers). The thermo-mineral waters in the frame of this region are essential factor for originated and development of the capital of Bulgaria - the city of Sofia. All over the valley, there are some groundwater sources with a total flow-rate of up to 110 L/s and a temperature from 21°C to 79.5°C (the borehole R-1, Kazichene). The thermo-mineral sources are mainly used in balneology, bottling, heating energy, spa tourism etc. Through a comparative analysis of data on the registered contents of metals in thermo-mineral sources in Sofia Valley are represented differences in chemical composition of waters in the geothermal fields (sites). The results of water samples from the sources obtained in the laboratory of the University of Antwerp (Belgium) as well unpublished data from the laboratory of the Scientific Institute (NIKFR) - Ovcha Kupel (Bulgaria) were used. Possible connections between the specific natural conditions, the temperature, pH and the concentration of metals in the waters of each source are considered. An assessment has been made of the suitability of the extracted waters in accordance with the current rules for the content of metals in the mineral waters used for bottling potable water.

1. INTRODUCTION

Sofia valley is rich in thermal waters, which was a major factor for the establishment and development of the capital of Bulgaria - Sofia city. The prevailing types of thermal waters are sourced from Mesozoic rocks at the base of Sofia graben. The water temperatures are in the range between 21°C-79.5°C and for most of the thermal mineral sources TDS is up to approximately 1 g/L. Utilization of the thermal water resources is mainly for bottling of natural mineral water. Some sources are used for balneology, sport, recreation and sanitation; however, their potential is not sufficiently utilized.

The present study is related to the presence of metals and some other chemical components in the thermal mineral waters from the localities in Sofia valley geothermal field. Results from the chemical analysis of these waters, conducted at the University of Antwerp (Belgium), of the Atomic Absorption Spectrometer (AAC) and Mass Spectrometer (MS) (Pentcheva et al., 1997) as well as unpublished data from the laboratory of the Scientific Institute (NIKFR) - Ovcha Kupel (Bulgaria) were used. The groundwater quality standard set out in Annex 1 to Regulation 1/10.10.2007 on the exploration, use and protection of groundwater, as well as the requirements for the protection of groundwater, have been applied to compare the analytical data with the threshold limit values as well as to water intended for drinking and domestic water supply (RegulationNo. 9 / 16.03.2001).

2.GEOLOGICAL AND HYDROGEOLOGICAL BACKGROUND

Sofia geothermal basin covers an area of about 1180 km^2. It is an elongated graben type structure, bounded by Balkan mountain to the northeast and Lyulin, Vitosha and Lozen mountains to the southwest (Antonov, Danchev 1980). The graben is of approximately 60 km long and 20-25 km wide (Fig. 1). The basement of it is composed of Mesosoic formations. In the south-western part, the basement formations comprise andesites, volcanic sedimentary rocks and sedimentary rocks of Upper Cretaceous age; the rest of the basement formations include carbonate and terrigenous rocks of Triassic, Jurassic and Upper Cretaceous age. The graben is filled with Neogene deposits mainly sands, clays, sandstones and lignite seams at places. The total thickness of the Neogenecomplex varies from 100 m to 1,200 m. The thickness of the Quaternary cover is between 50 m and 100 m. The graben structure is complicated by many fault displacements that form internal small horsts and depressions. These provide pathways for water circulation and hydraulic connections between different water bodies.

Geological, hydrogeological, hydrochemical and geophysical investigations have been carried out by many researchers in an attempt to figure out the processes of thermal water formation in the basin (Radoslavov 1918; Azmanov 1940; Kusitaseva, Melamed 1958; Shterev 1964; Petrov et al. 1970; Antonov, Danchev 1980; Petrov et al. 1996; Vladeva et al. 2000; Bojadgieva, Gasharov 2001; Hristov 2001; Penchev, Velichkov 2011; Hristov et al. 2016; Trayanova et al. 2018; etc). The thermal field forms a closed zone of enhanced thermal potential on the heat flow map of Bulgaria. The estimated average conductive heat flow is about 0.08 W/m^2 and the average geothermal gradient is 4.7°C/100 m (Bojadgieva, Gasharov 2001).

Some of the thermal sources (OvchaKupel, Pancharevo, Sofia Center, GornaBanya, Knyazhevo, Bankya) were initially natural springs only, around which abstraction wells were subsequently drilled in 1950-1960s. Following the construction of the wells, the yields decreased and some springs dried out completely. The other sources are revealed by wells only. All sources are attached to faults in the reservoir rocks at the base of Sofia graben. The only exception is Lozen which comprises water from the base, as well as from the overlying Pliocene aquifer complex of alternating clay, clayey sand and sand. It has been established that the thermal waters are influenced by seismic phenomena.

The thermo mineral fields (sites) that are taken under consideration in this paper are conditionally divided in two groups according to the lithological composition of their reservoirs: (1) thermomineral reservoir in a carbonate complex (OvchaKupel, Pancharevo1, Pancharevo 2, Ravno Pole and Kazichene) and (2) thermomineral reservoir in a volcanic sedimentary complex (Knyagevo, Bankya, GornaBanya, SofiaCenter)(Fig. 1, 2).

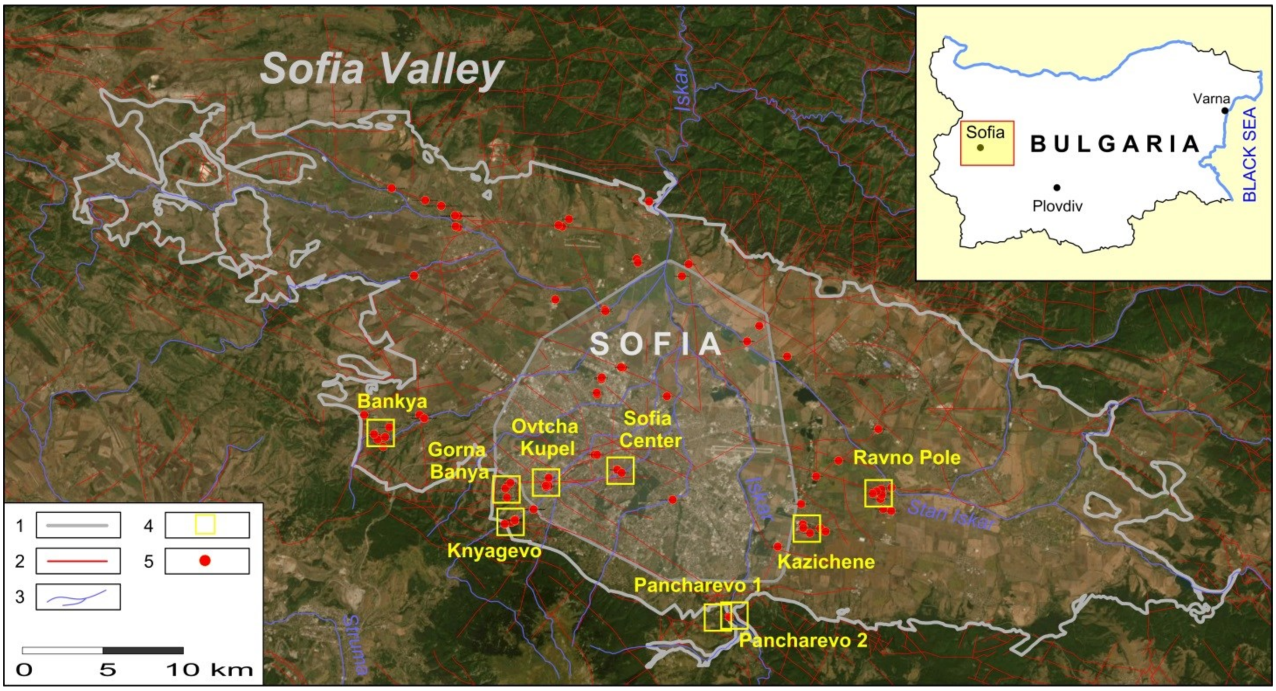

Figure 1: Sofia geothermal basin (field) with the nine site studied. 1 - boundary of the Sofia valley; 2 - faults; 3 - rivers; 4 - thermal mineral site(test point); 5 - thermal mineral source (captured natural spring, deep borehole).

3. HYDROCHEMICAL CHARACTERIZATION OF THERMO-MINERAL WATERS

The chemical composition of thermo-mineral waters depends on various factors, with essential importance are: (1) the chemical composition of the water entering the thermo-mineral reservoirs; (2) the mineral composition, the lithological characteristics and the secondary change of the water-bearing rocks; (3) geochemical barriers - pH, Eh, etc .; (4) temperature and pressure; (5) the duration of the "water-rock" interaction; (6) the hydrodynamic properties of the reservoir; (7) presence of ore into geological strata, etc.

During the systemization and analysis of the available information in the study, an attempt was made to link the composition of the thermo-mineral waters of Sofia Valley (mainly the content of metals in them) with some of the above mentioned factors.

3.1. Water temperature. Hydrogen indicator (pH)

The temperature of the water and the depth of formation path and movement are the main factors that obviously predetermine its macro-chemical composition. The maximum measured temperature for carbonate complex is 79.5°C and for volcanic-sedimentary complex it is 45.5°C. With increasing the water temperature pH values lightly decrease (Fig. 2).

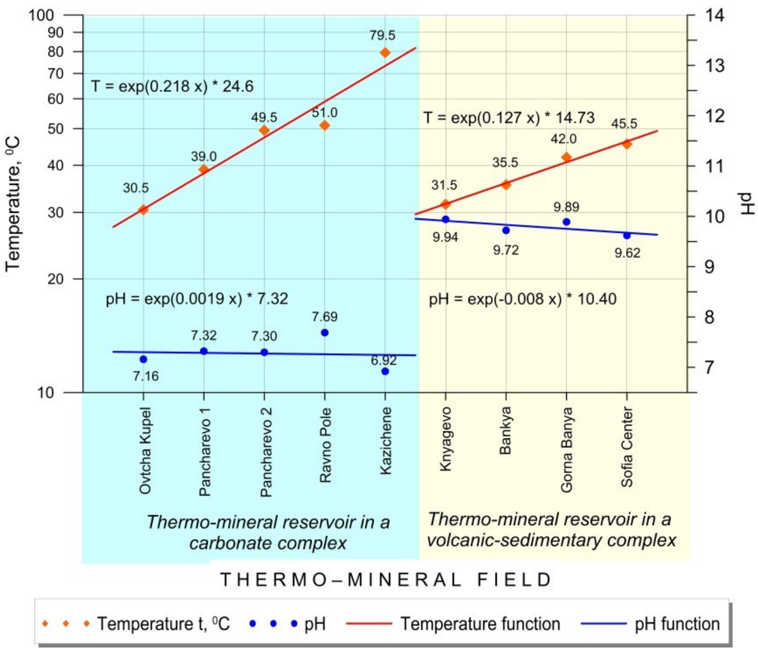

Figure 2: Water temperature and pH in thermo-mineral sites.

3.2. Macro components. Total dissolved solids (TDS). Fluoride.

The macro-component composition of the thermo-mineral waters in the studied area is illustrated by the graphical dependencies (Fig. 3,4).

The registered maximum values of the macro-components in the studied water sources in Sofia Valley do not exceed the normative threshold values for drinking water.

Generally, the thermal mineral waters of Sofia basin are fresh, with TDS less below 1.0 g /L, which means that they meet the requirements for drinking water supply according to this parameter. Only several of them (Novi Iskar "Kurilo" W-20, Birimirtsi W-1 etc.) are with higher TDS (above 1.0 g/L) and they are not suitable and used as drinking waters.

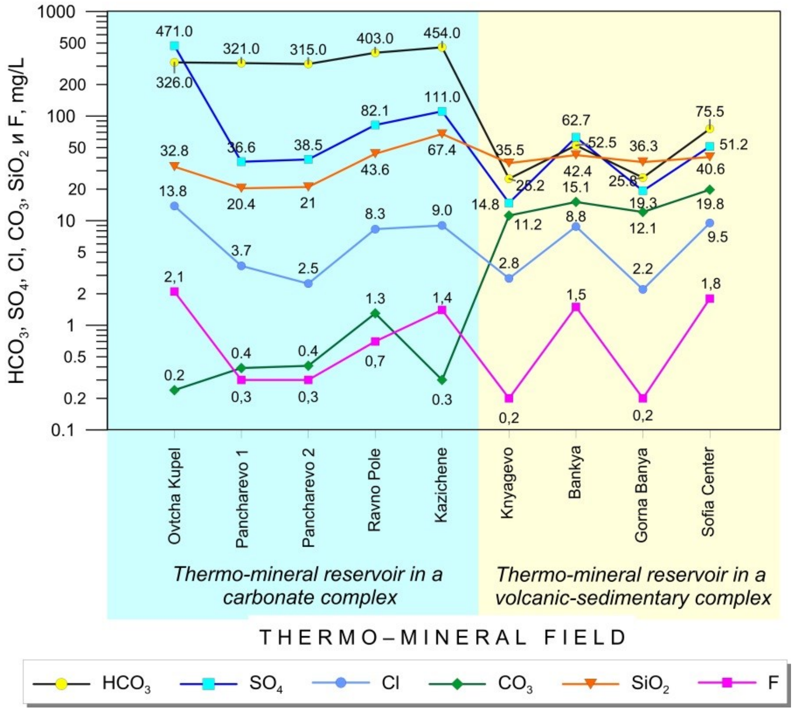

Figure 3: Concentration of HCO₃, SO₄, CO₃, SiO₂and Fin the waters of the studied water sources.

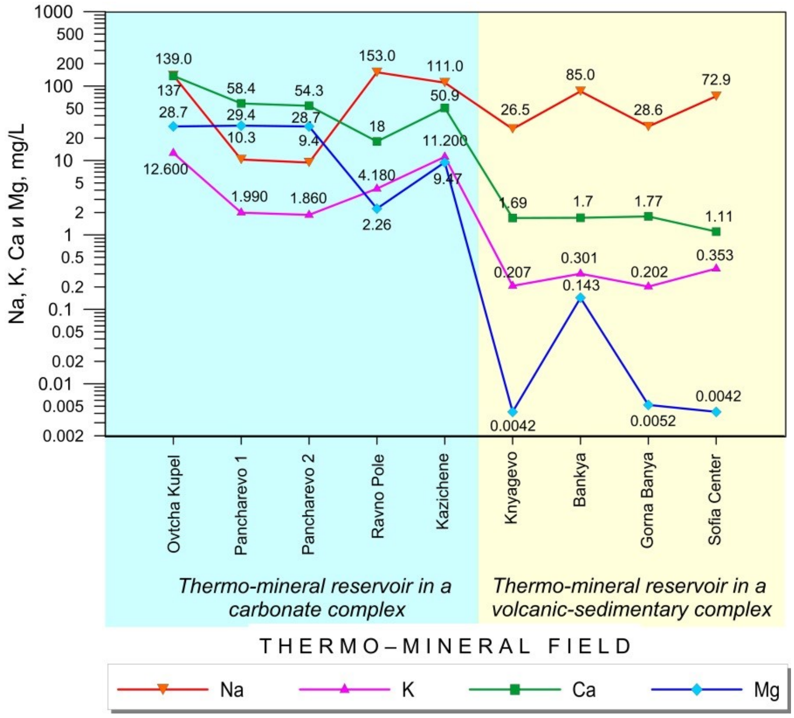

Figure 4: Concentration of Na, K, Caand Mgin the waters of the studied water sources.

The contain of F determines which water sources can be bottled as natural mineral water. Fig. 5 shows that most of thermal water sources have F concentration threshold limit values. Exclusions are made only for OvchaKupel and Sofia Center where the values are higher than 1.5 mg/L (Fig. 5). These water sources are suitable for caries prevention but they are not recommended for children under the age of seven (there should be a mandatory note on each bottle label if they will be used for bottling) and for excessive use by elder people.

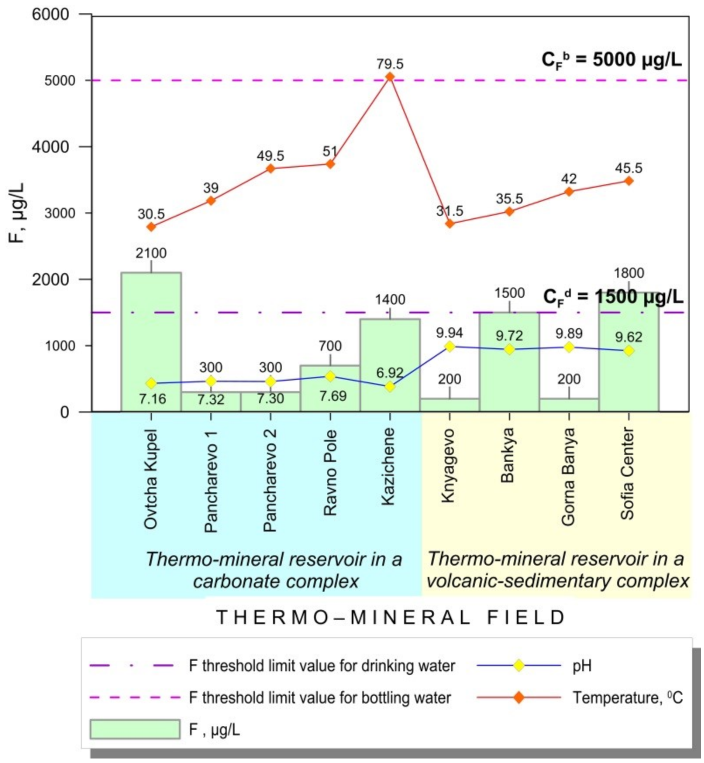

Figure 5: Concentration of Fin the waters of the studied water sources.

3.3. Metals

The metalsbelong to a large group, accounting for over 80% of all chemical elements found so far. The metals are divided into several subgroups: alkaline (Li, Na, K, Rb, Cs, Fr); alkaline earths (Be, Mg, Ca, Sr, Ba, Ra); transitions (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Cd, Ag, Hf, Ta, W, Re, Os, Ir, etc.); (B, Si, Ge, As, Sb, Te and Po), lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Ho, Tm, Yb and Lu) and actinides (Ac, Th, U, Np, Pu, Am, etc.).

The results of the analysis of water samples from Sofia Valley conducted at the University of Antwerp, Belgium (Pentcheva et al., 1997) and unpublicized data NIKFR, Sofia show that in the thermo-mineral waters of Sofia geothermal basin there are more than 30 metals, of approximately 1/3 of the existing ones in nature. The results are shown and discussed for the metals with a significant presence in the water sources of the studied field and/or they are defined as very toxic and very dangerous, even in very insignificant concentrations. The latter are used as markers for assessing the quality and ecological status of groundwater. They are divided into two main types:

Priority ingredients – Ni, Cd, Hg andPb

Specific pollutants – Al, As, Cr, Cu, Fe, Mn, Zn, U, Ra

Alkaline metals

The follow alkaline metals are analyzed: Na, K, Li, Rb and Cs. Sodium (Na) and Potassium (K) were reviewed in the Macro Components section. The maximum concentrations for the remaining three metals Li, Rb and Cs are not exceeded in any of the water sources.

Lithium is the lightest metal (relative weight 0.53, approximately twice lighter than water). It is very important for thermo-mineral waters, because together with the noble gas helium are the two best indicators in the search for geothermal water. They are not unsafe to human health but are also suitable for the treatment of certain diseases and therefore no maximum threshold limits for the lithium content of drinking water are required. The lithium concentration for analysed waters are shown on Fig. 6.

Alkaline earth metals

Four elements (Mg, Ca, Sr, Ba) are analyzed from alkaline earth metals and two of them (Mg, Ca) discussed in the Macro Components section. The established concentrations for Sr and Ba in all water sources are below the standard maximum threshold values.

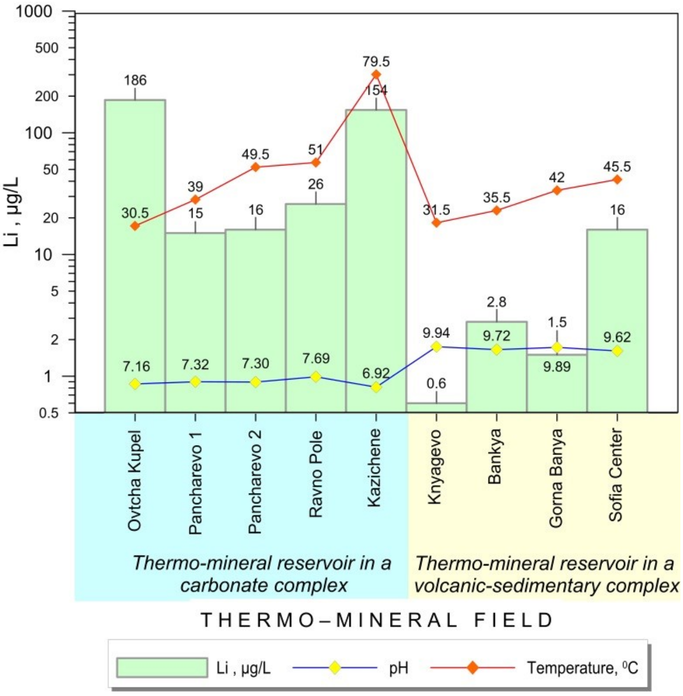

Figure 6: Concentration of Li in the waters of the studied water sources.

Transition metals

Up to20 transition metals have been studied (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Cd, Ag, Au, Hg,Hf, Ta and W). Most of them (Ti, V, Co, Y, Zr, Nb, Mo, Ag, Au, Hf, Ta and W) have very low contents in nature that they are not subject to the applicable drinking water. The other (Fe, Cd and Hg) are in concentrations below or around the detectable minimum of the measuring equipment. With regard to the other metals studied in this group, thermo-mineral waters are suitable for drinking.

The Ni, Cr, Mn, Cu and Zn concentrations, which are of particular importance in the environmental aspect and are assigned to the Ni and the specific contaminants (Cr, Mn, Cu and Zn)are shown at Fig. 7-11. The highest values are found in Kazichene site but all data are from 2-3 to more than 100 times below threshold limit values. All thermal mineral waters in Sofia Walleye are not contaminated by analysed components. For example for very low concentration is Cr (Fig. 8) which is found only in Pancharevo 1 and its value is 0.27 µg/L or about 150 times lower than threshold limit.

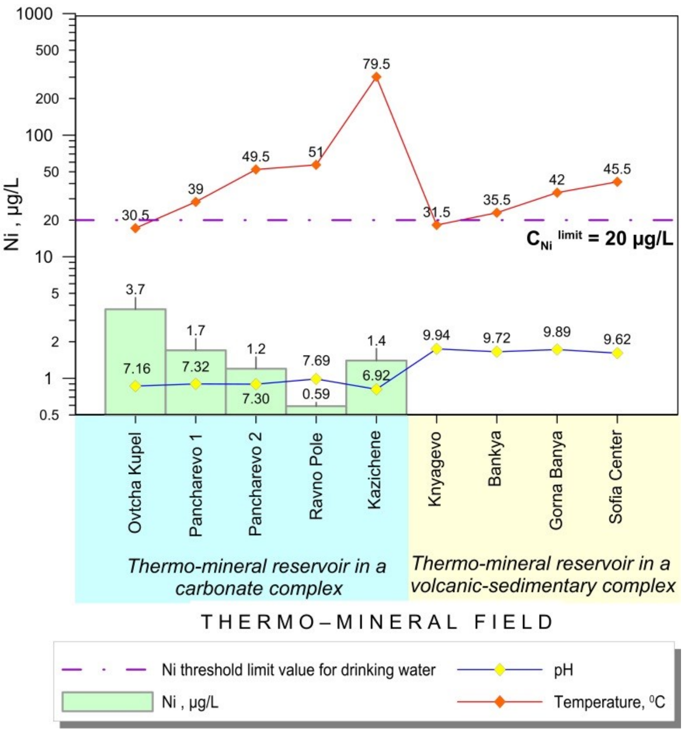

Figure 7: Concentration of Ni in the waters of the studied water sources.

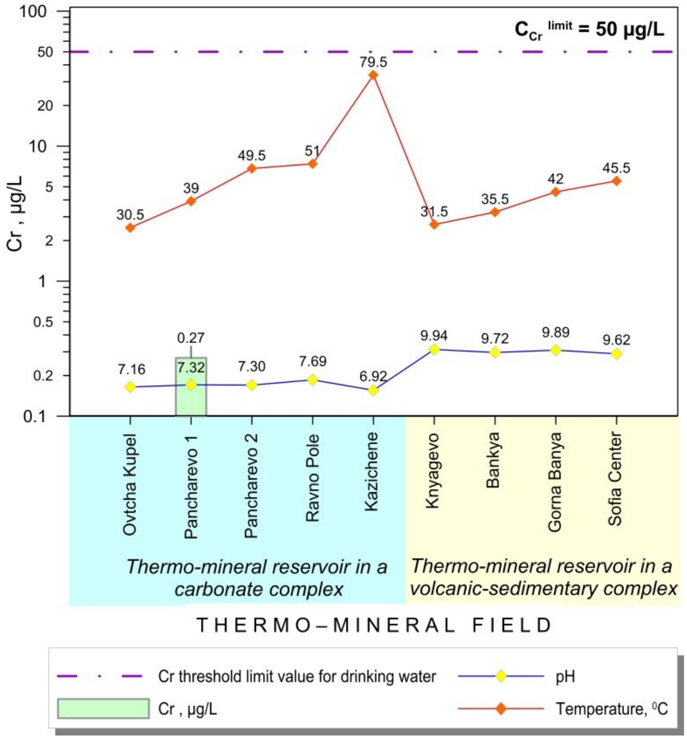

Figure 8: Concentration of Cr in the waters of the studied water sources.

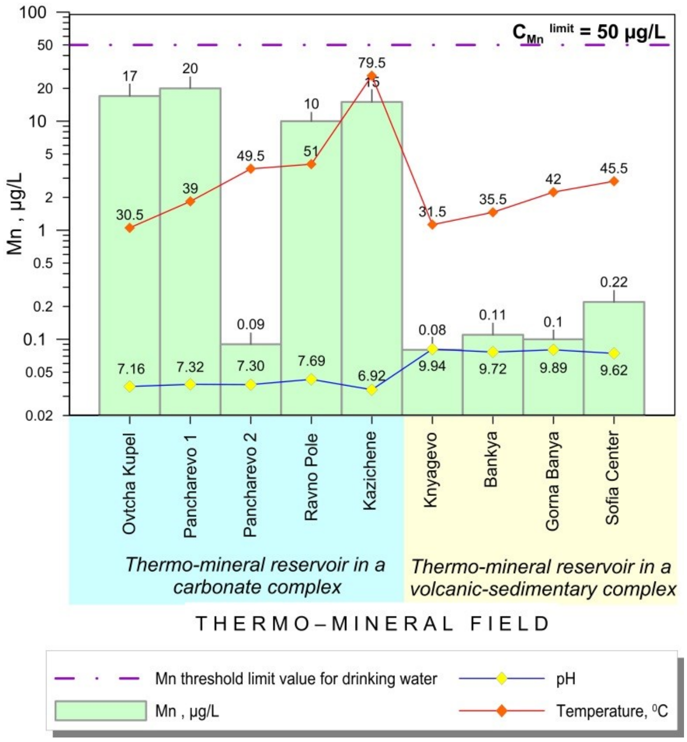

Figure 9: Concentration of Mnin the waters of the studied water sources.

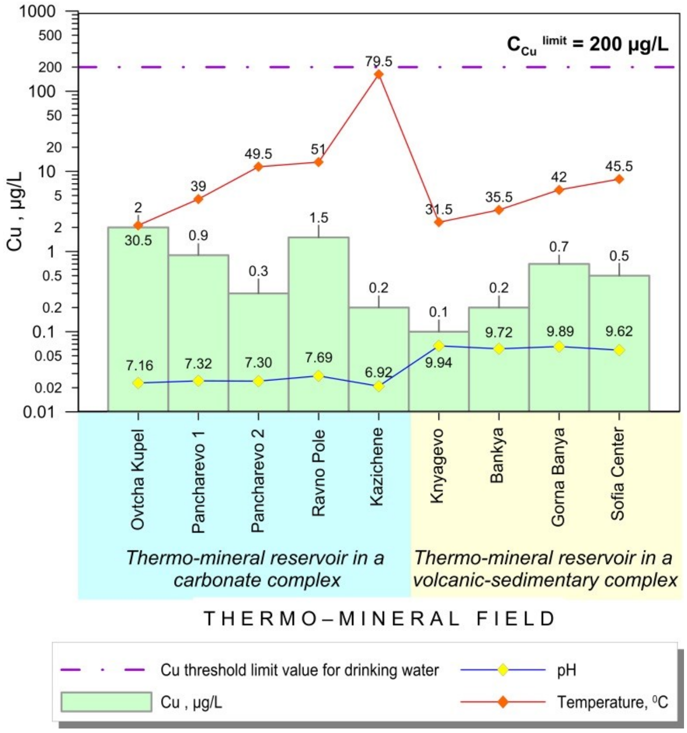

Figure 10: Concentration of Cu in the waters of the studied water sources.

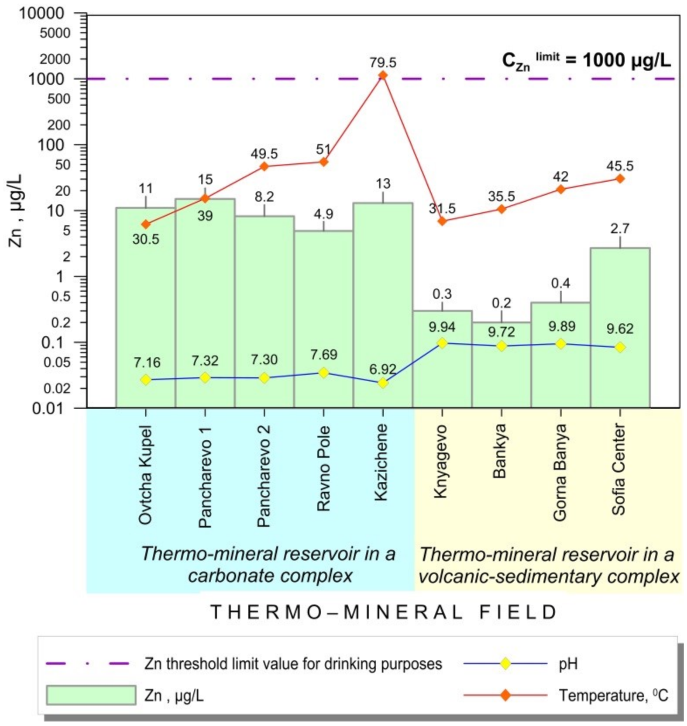

Figure 11: Concentration of Zn in the waters of the studied water sources.

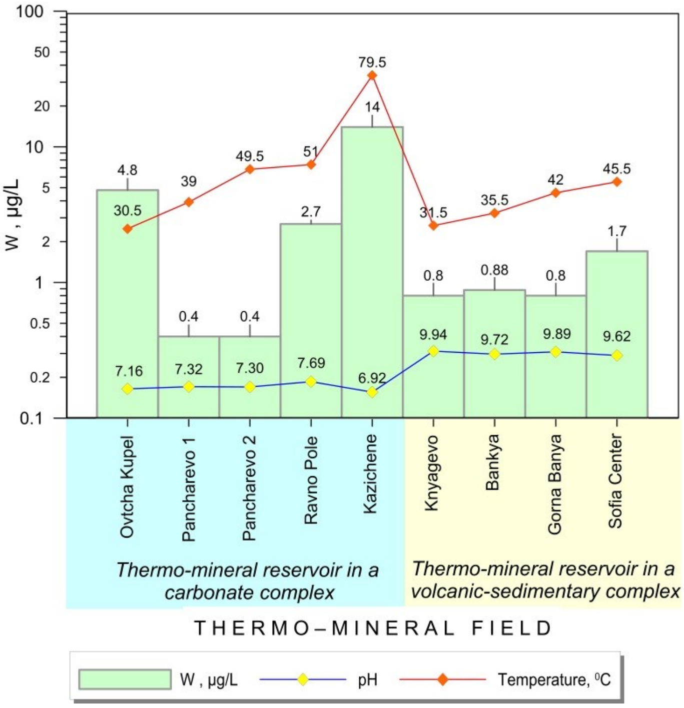

Figure 12: Concentration of W in the waters of the studied water sources.

Post-transition metals

The study included 7 post-transition metals (Al, Ga, In, Sn, Tl, Pb and Bi) out of a total of 11 elements constituting this subgroup. Most of them (Ga, In, Sn, Tl and Bi) have low contents and are not regulated in the documents defining the quality requirements for drinking water.The established concentrations of the other two studied elements in the group do not exceed the drinking water standards. The analyzed metalloids are arsenic, antimony and germanium, and silicon in the form of SiO_2. Of particular interest is the presence of the specific pollutant As and the toxic element Sb, which are also included in the list of norms for assessing the suitability of drinking water. Not relevant to the composition and quality of natural waters is Ge, as it has low content and is an inert element. The concentration of SiO_2 in the studied waters is high, which is directly related to their genesis.

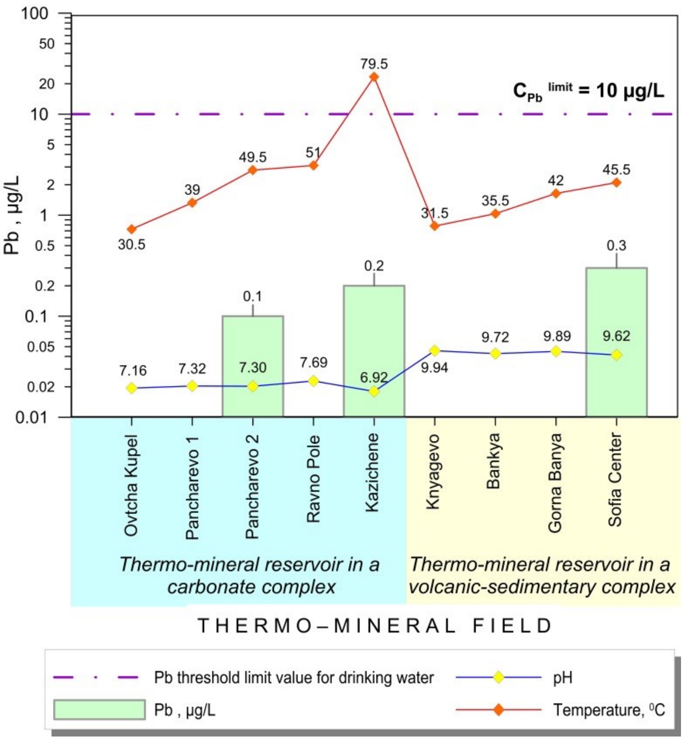

Figure 13: Concentration of Pbin the waters of the studied water sources.

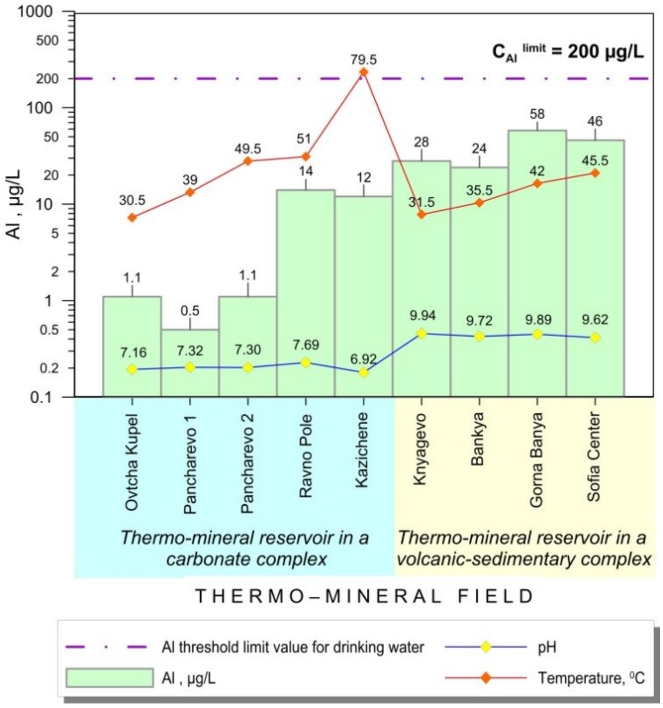

Figure 14: Concentration of Al in the waters of the studied water sources.

Metalloids

The analyzed metalloids are arsenic (As), antimony (Sb) and germanium (Ge), and silica (Si) in the form of SiO_2. Of particular interest is the presence of the specific pollutant As (Fig. 15) and the toxic element Sb (Fig. 16), which are also included in the list of norms for assessing the suitability of drinking water. An exception is the Kazichene site, where the concentration of Sb slightly exceeds the threshold limit values. Not relevant to the composition and quality of natural waters is Ge, as it has low content and is an inert element.

Three of geothermal sites in carbonate complex (Ovcha Kupel ,Ravno Pole and Kazichene) have got from 17 to 28 times higher As concentration than threshold limit values and they are not suitable as drinking waters. All geothermal sources among volcanic-sedimentary complex have As concentration below threshold limit.

All sources are with Sb concentration (Fig. 16) below or near to threshold limit values.

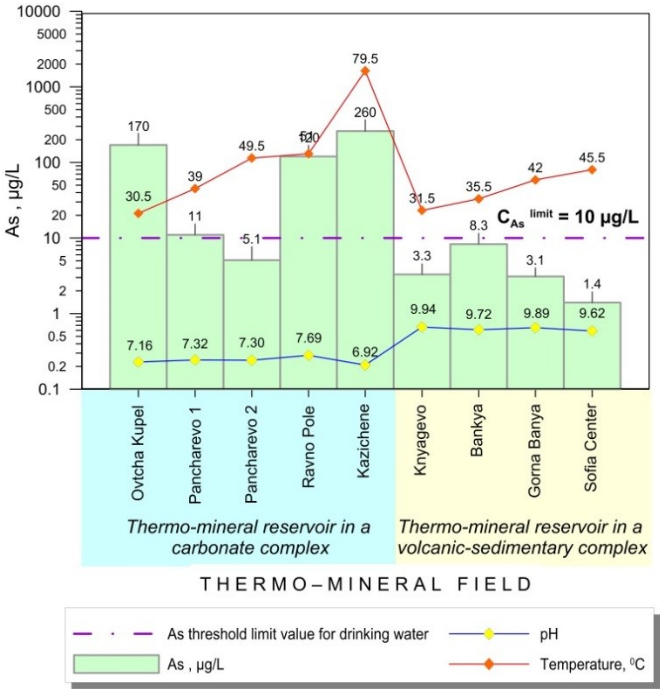

Figure 15: Concentration of Asin the waters of the studied water sources.

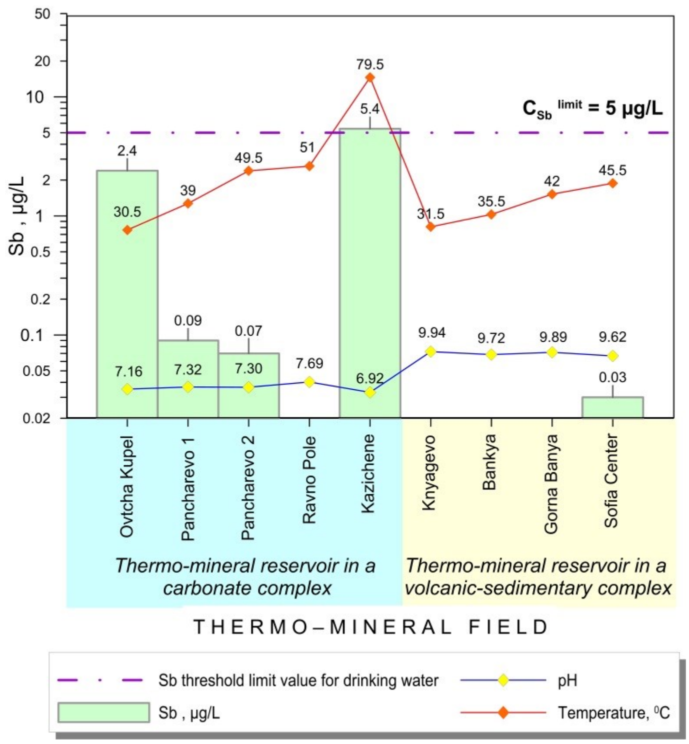

Figure 16: Concentration of Sbin the waters of the studied water sources.

Lanthanides

Lanthanides elements (La, Ce, Nd, Sm, Eu, Tb, Ho, Yb and Lu) in this group were studied. The results of the analyzes show that their concentrations are usually below the detectable minimum of the apparatus. Only in single cases are recorded negligible concentrations of La and Ce, too close to the accuracy of the laboratory technique and the methods used.

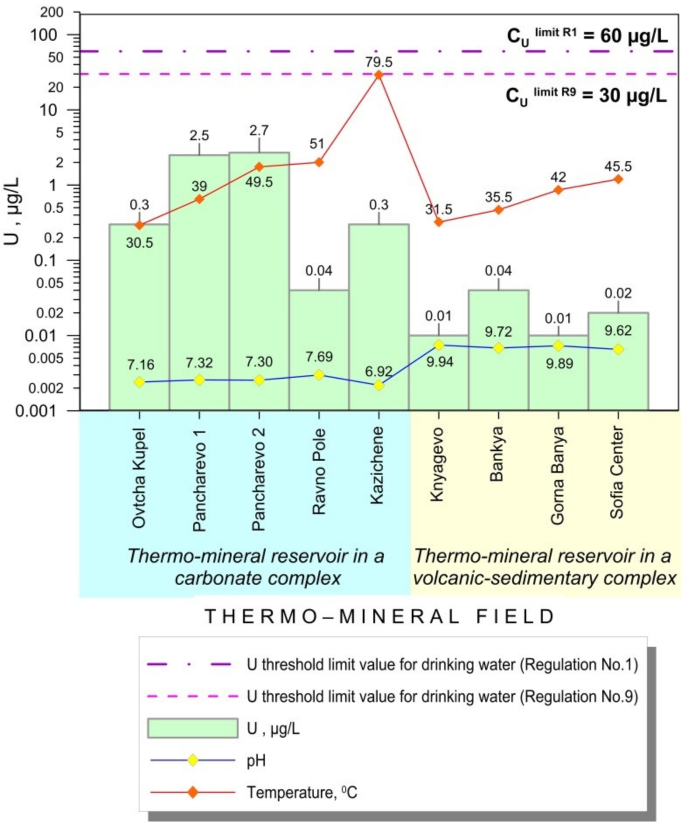

Figure 17: Concentration of U in the waters of the studied water sources.

Actinides

Only the content of uranium and thorium is studied from actinides. The results obtained about the contents for both of U (Fig. 17) and Th in all samples were below the detectable minimum. The concentration of Th into all samples are below the accuracy of the laboratory technique and the methods used.

4. CONCLUSIONS

The complex analysis of the metal concentration in geothermal sources of the Sofia valley gives the following main conclusions and recommendations:

- The clustering and the quantitative ratio of different metals is predetermined by the rock composition and the thermodynamic conditions in the main reservoir and the water conducting zones, the water-rock interaction and the drainage conditions at each water source;
- All components studied for thermal mineral water sources are below threshold limit values accordingto Bulgarian and the European Union requirements for drinking mineral waters. Some exceptions are found out concerning As concentration in Ovcha Kupel, Ravno Pole and Kazichene which are not suitable for drinking as well bottling potable water;
- The mineral waters from most sources in Sofia Valley could be applied for balneological properties and are recommended for treatment of cardiovascular, rheumatic, traumatic, nerve, gynecological, gastrointestinal, hepatic-biliary, renal, urological, skin and other diseases and for caries prophylaxis.

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REFERENCES

Antonov, H., and Danchev, D.: Groundwater in People’s Republic of Bulgaria. Tehnika, (1980),359 p. (in Bulgarian)

Azmanov, A.: Die BulgarischenMineralquellen. Sofia, DarzhavnaPechatnitsa, (1940),260 p. (in Bulgarian with a German abstract).

Hristov, V.: Application of Chemical Geothermometers and Helium Method for Iinvestigation of Geothermal Fields in Sothern Bulgaria. PhD Thesis, Sofia, Geological Institute, Bulg. Acad. Sci., (2001), 187 p. (in Bulgarian).

Pentcheva, E. N., L. van Dack, Veldeman, E.,Hristov,V.,and Gijbels,R.: HydrogeochemicalCharacteristics of Geothermal Systems in South Bulgaria. UniversiteitAntwerpen, (1997), 121 p.

Petrov, P., Martinov, S.,Limonadov, K., and Straka,Y.: Hydrogeological Studies of Mineral Waters in Bulgaria. Sofia, Technika, (1970), 195 p. (in Bulgarian).

Shterev, K.: Mineral Waters in Bulgaria. Sofia, Nauka I Izkustvo, (1964), 172 p. (in Bulgarian).

Vladeva, L., Krasteva, D.,Yordanov, Y.,and Kostadinov,D.: A Guide for Bulgarian Mineral Waters.Sofia, IPK Nauka i Tehnika, (2000), 225 p. (in Bulgarian).

Bojadgieva, K., and Gasharov, S.: Catalogue of geothermal data of Bulgaria,GorexPress, Sofia, (2001),163p.

Hristov, V., Benderev, A., and Bojadgieva, K.: Assessment of hydrogeological conditions and geothermal application in Sofia Municipality (Bulgaria). Proc. 2nd IAH Central European Groundwater Conference "Groundwater risk assesment in urban arreas", Bucurest, 14-16 Oct. 2015, ed. Adr.Iurciewicz, I. Popa,(2016),36-44.

Kusitaseva, V., and Melamed, Y.: Composition of Bulgarian mineral waters. J. Medicine and Sports, (1958),280 p. (inBulgarian)

Penchev, P., and Velichkov, V.: Fields of mineral water in the region of Sofia. Sofia Municipality BAPV, (2011),43 p.(in Bulgarian)

Petrov, P., Yotov, I., Gasharov, S., Hristov, V., and Benderev, A.:Hydrogeothermal conditions of Sofia Basin. Report by the Geological Institute at the Bulgarian Academy of Science to the Ministry of Environment and Water - comissionNo. 69, 06.04.1998, - Reassessment of the of the geothermal energy resources. (1996)

Radoslavov, B.: Mines, quaries and mineral waters in Sofia district. Sofia,(1918),169 p. (in Bulgarian)

Trayanova, M., Hristov, V., Atanassova, R., Haslinger, E., Plank, O., Wyhlidal, S., and Benderev, A.: Potential ofcorrosion and/or deposition of solid phases in the thermal waters in the region of Sofia Valley, Bulgaria,depending on their chemical composition. Bulgarian Chemical Communications, vol. 50, Special Issue G,(2018),28-33