Multidiszciplináris tudományok, 12. kötet. (2022) 3 sz. pp. 299-306 **https://doi.org/10.35925/j.multi.2022.3.28**

CHEMICAL COMPOSITION ANALYSIS OF THERMAL WATER OF HAJDÚDOROG

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Abstract
In our work, a chemical analysis of the thermal water of Hajdúdorog was performed to identify the therapeutic possibilities of the water. Two sampling campaigns were performed in August 2021 and March 2022. The chemical composition and characteristic of thermal water were determined in situ on-site and in labor investigations. According to the chemical analysis, we found the water type of thermal water is very rare, called NaCl type like the seawater. Its rareness is known by Lajos Marton (Marton, 2009; Marton, 2013), only 3,5% of the thermal waters of the Hungarian Great Plain can be grouped into the sodium chloride water type. But the high bromine (0.9 mg/l) and its supposed iodine content of the thermal water can make it unique in therapeutic application. Some trace metals (Cu, Fe, Mn) also increase the healing effect of water.

Keywords: *thermal water, water chemistry, medicinal water*

Absztrakt
Kutatómunkánk során a hajdúdorogi termálvíz kémiai elemzését végeztük el annak érdekében, hogy megítéljük a víz gyógyászati célokra történő felhasználásnak alkalmasságát. Két mintavételi kampányban gyűjtöttük a mintákat, 2021 augusztusában és 2022 márciusában. A laboratóriumi kémiai összetétel elemzést in situ vizsgálatokkal is kiegészítettük. Az elemzési eredmények alapján megállapítottuk, hogy egy ritka NaCl típusú vízről van szó a Hajdúdorogi termálvíz esetében. Ritka, ugyanis Marton Lajos alapján (Marton, 2009; Marton, 2013) tudjuk, az alföldi 35°C-nál melegebb hévizek 3,5%-a tartozik a tisztán nátrium-kloridos víztípusba. A víz gyógyászati célú felhasználását a víz bróm és jód tartalma indokolja, az olyan nyomelemek mellett, mint a réz, vas és a mangán.

Kulcsszavak: *termálvíz, vízkémia, gyógyvíz*

1. Introduction

Because of the high dielectric constant of water, it can dissolve the polar ions and molecules easily (Padisák, 2005). In the surface and subsurface waters the main cations and their order in their general concentration are $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$, while the main anions are $CO_3^{2-}/HCO_3^{-} > SO_4^{2-} > Cl^{-}$. These ions give the main part of the total dissolved solids (TDS) [mg/l] content of the waters (Wetzel, 2001). There could be dissolved other ions in the water, like $Fe^{2+,}$ $Mn^{2+,}$ $Cu^{2+,}$ $Zn^{2+,}$ or NO_2^{-}, NO_3^{-}, and PO_4^{3-}. Generally, their concentration is very low, but in special cases, they can be found in high concentrations like in acid mine water, in intensive agriculture production affected groundwater, or in organic contamination affected water (Kresic, 2006) (Wetzel, 2001) (Zákányiné Mészáros & Zákányi, 2011) (Kovács, et al., 2016) (Szűcs & Ilyés, 2019).

The main cations and anions according to their persistence could be categorized into dynamic and conservative groups. The concentration of conservative ions is just slightly or not affected by biological activity while the concentration of dynamic ions is significantly affected by metabolism. Conservative macro ions of water are Mg, Na, K, and Cl, dynamic macro ions are Ca, HCO3, and SO4 (Wetzel, 2001).

Generally, as was seen in the previous section, most surface and subsurface water are categorized in the Ca-HCO_3 type. But according to the geological situation of surface or subsurface water very special water types could be resulted. The thermal water of Hajdúdorog is one of the special water types.

2. Materials and methods

The thermal well of Hajdúdorog (well cadaster number: K-73) was drilled in 1976. The diluvium sediment is clay and loam but the majority is gravelly sand. Its formation boundary is 140 m below the surface. The following Levantian stage can be found between 140 m and 550 m and its material is clay. The Upper Pannonian stage can be found between 550 m and 1100 m. The bottom of the formation is the best for thermal water production. The screening of the well can be found from 907 m to 913m, from 932 m to 945 m, and from 969 m to 978 m. The stationary water level in the well is 24 m below the surface. The discharge of the well is 600 l/ min and its outflow temperature is 64°C.

In situ on-site and laboratory measurements were also performed. During the in situ measurements, the general environmental condition indicators were determined (pH, ORP, EC) with a Hanna HI 9829 multimeter.

During the laboratory analysis, the main cations and anions were determined. The carbonate and bicarbonate determination were performed according to the Hungarian Standard of MSZ 448/11-86. The chlorine analysis happened according to the Hungarian Standard of MSZ 448/15-82. For sulfate analysis, a HACH DR2000 spectrophotometer was used. The methodology of sulfate analysis is based on the $BaSO_4$ precipitation formation in presence of barium ions from $BaCl_2$. The opacity of the sample is proportional to the sulfate presence in water that can be properly measured with the equipment.

The trace and macro element analyses were performed with an Agilent 4210 microwave plasma atomic emission spectrophotometer (MP-AES). The specialty of the equipment, the ionization of elements happens in plasma like in the case of an ICP (inductively coupled plasma)-AES but the plasma in the MP-AES is nitrogen plasma with a temperature of 5000°K. At this low temperature, the analytical performance of the equipment is lower than an ICP-AES, so the detection limit changes between ppm and ppb and depends on the measured element and on the matrix. The equipment also ensures multielement measurements like an ICP-AES.

To evaluate the chemical analysis result Piper plots and Stiff plots were created.

Accelerator mass spectrometry (AMS) was performed to determine the ^{14}C age of thermal water in the laboratory of Isotoptech Zrt. This analytical technique accelerates ions to extraordinarily high kinetic energies before mass analysis. The special strength of AMS among the mass spectrometric methods is its power to separate a rare isotope from an abundant neighboring mass (for example ^{14}C from ^{12}C). (McNaught & Wilkinson, 1997)

Table 1. *The analyses results*

		Hajdúdorog Aug 2021	Hajdúdorog Mar 2022	Hajdúnánás (Gyógycentrum, 2017)
B	mg/l	24.1	34.0	-
Ba	mg/l	28.0	20.9	-
Ca	mg/l	130.0	158.1	102.0
K	mg/l	41.0	38.4	42.0
Li	mg/l	1.4	1.2	-
Mg	mg/l	33.0	35.1	26.6
Na	mg/l	3080.0	3689.3	2750.0
Si	mg/l	8.8	16.0	-
Sr	mg/l	25.0	38.5	-
Cl^-	mg/l	4826.0	5772.0	4180.0
HCO_3^-	mg/l	657.0	642.0	939.0

3. Results and discussion

The on site measurements gave quick results about the water condition. The reaction of the thermal water is neutral (pH 7.2). The value of oxidation-reduction potential was -34.3 mV. This value indicates reductive environment compared to the typical ORP value of surface waters. In case a deep subsurface water the reductive condition is not surprising because the water spent thousands of years closed to air. The EC (specific conductance) value of water is 18.06 mS/cm. This value suggests the water has a high dissolved solid content.

According to the results of the chemical analysis, it is visible the water samples have extremely high Na^+ and Cl^- content (***Table 1***). These experiences suggest the type of water, but the special plots can introduce properly the types of water. To compare the water samples composition to general surface water, the concentration of B, Ba, and Sr is also extremely high which is also typical in the case of deep groundwater resources.

The Piper plot is a proper tool to compare different water types, more water samples can be interpreted at the same time. The Stiff-plot is also a plot type to introduce the types of water samples but one plot only contains one water type. The order of cation-anion pairs is defined so the shape of the plot serves the water type information.

As can be seen in ***Figure 1*** and ***Figure 2*** the type of the thermal water of Hajdúdorog and Hajdúnánás is NaCl. This water type generally characterizes seawater.

Special chemical components of the thermal water of Hajdúnánás are the Br^- and the I^- ions (Gyógycentrum, 2017). The analytical work of Nagy (Nagy, et al., 1960) and Cziráky (Cziráky, 1971) the Br^- and the I^- ions concentration in the thermal water of Hajdúnánás are 11.2 and 2.9 mg/l, respectively. In our laboratory, there is no equipment to determine these components but according to the literature review, a couple of pieces of evidence were found the thermal water aquifer is the same in the case of the two thermal baths.

The first evidence is the same water type as the two thermal water.

The second piece of evidence is related to the stable isotope characteristic of the waters. According to the stable isotope investigations, the thermal water of Hajdúnánás and Hajdúdorog are members of fossil salt waters (***Figure 3***) (Marton, 2012). Moreover, the thermal water resource of Hajdúnánás shows oxygen enrichment, and its water originated in warmer geological ages. This water could be diluted seawater (Marton, 1982).

The third piece of evidence is the depth of water resources. The Well Fürdő of Hajdúnánás screen the Upper Pannonian sand in a depth of 1002-1013 m (Cziráky, 1960), while the well of Hajdúdorog screen the Upper Pannonian sand aquifer in the depth of 1030-1037 m. The distance between the two well is 6-7 km. With high probability, they screen the same aquifer.

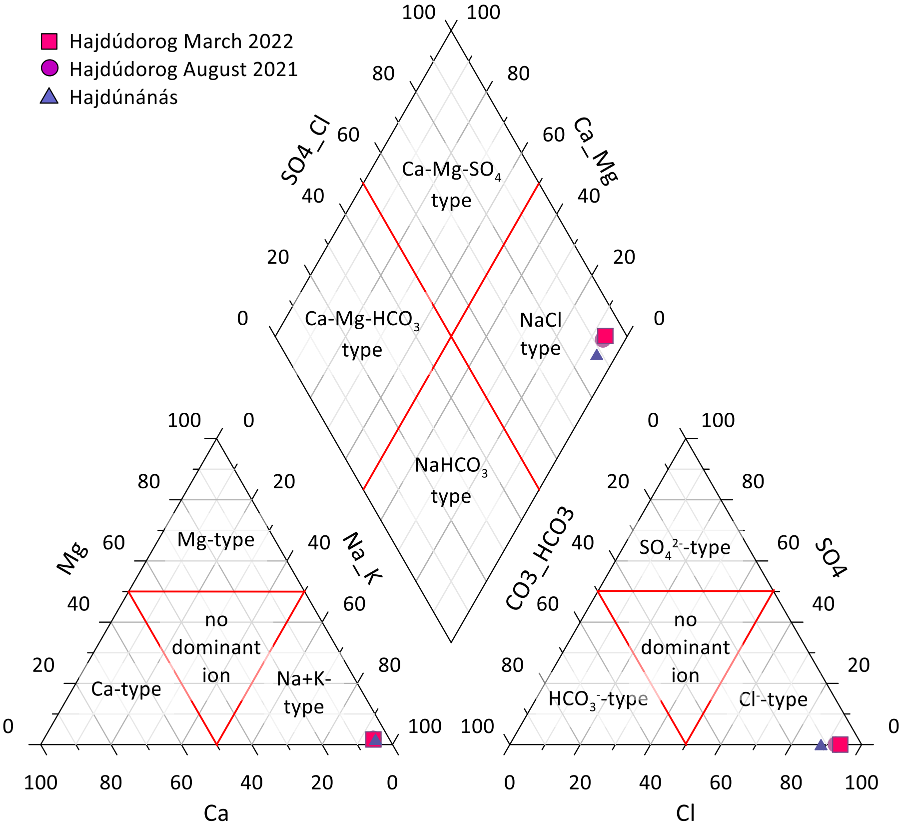

Figure 1. *The water types of thermal bath of Hajdúdorog and Hajdúnánás in a Pipet-plot (own data and (Gyógycentrum, 2017))*

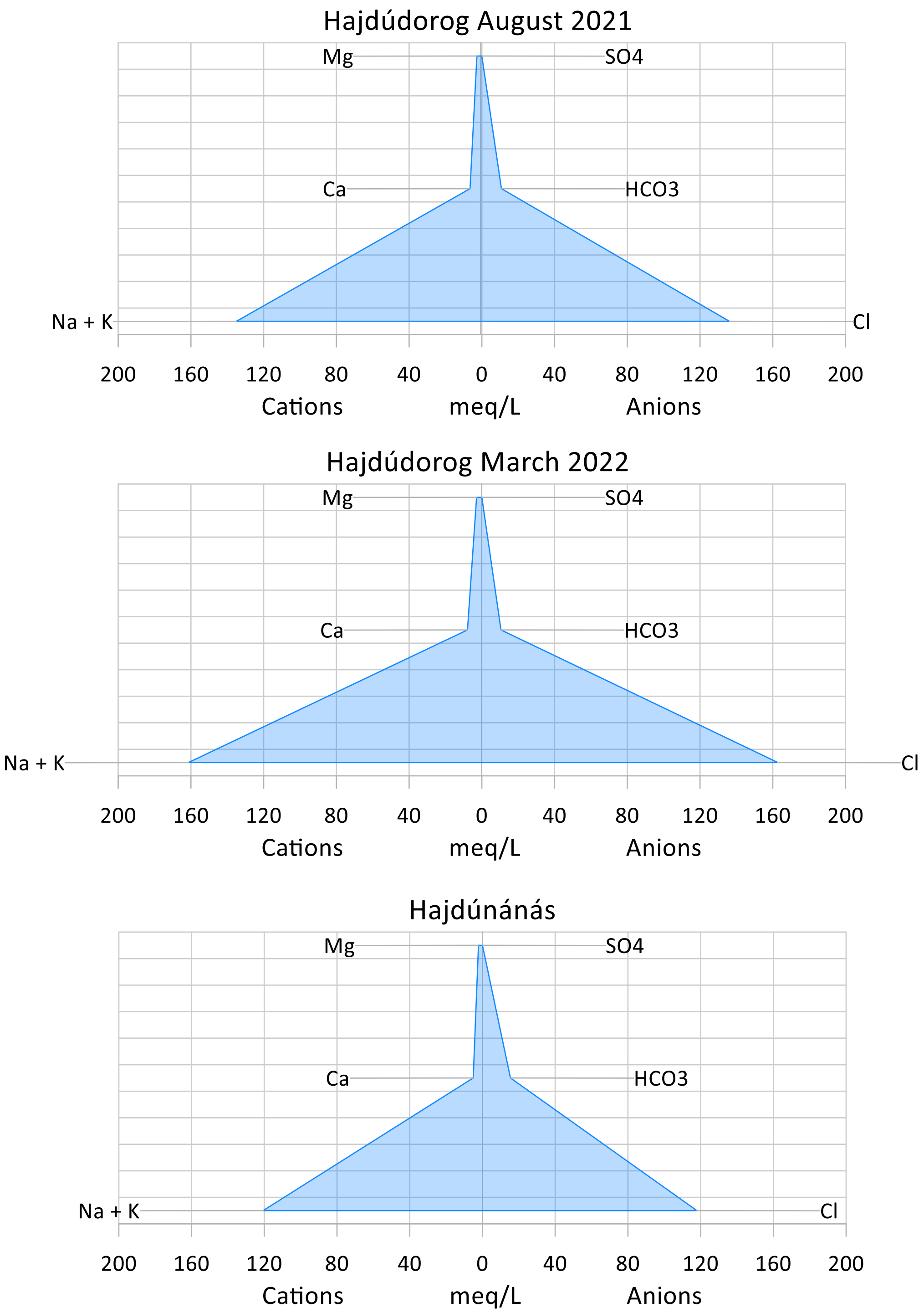

Figure 2. *The water types of thermal bath of Hajdúdorog and Hajdúnánás in Stiff-plots (own data and (Gyógycentrum, 2017))*

3.1. Evaluation of thermal water of Hajdúdorog from the therapeutic aspect

The waters that contain radium, radon, and thorium have a significant healing effect but the minor iron, iodine and sulfur content of waters also possess physiological effects (Nagy, et al., 1960) (Bodnár, 1941). Other trace elements that have significant vital acts are also important in the healing waters like copper, cobalt, manganese, molybdenum, and zinc (Bodnár, 1941). In the thermal water were found some of these trace elements (***Table 2***.).

Table 2. *Trace metals with vital act in water of Hajdúdorog*

Cu mg/l	**Fe** mg/l	**Mn** mg/l	**Zn** mg/l
0.3	2.3	0.2	udl*

*under detection limit (<0.01)

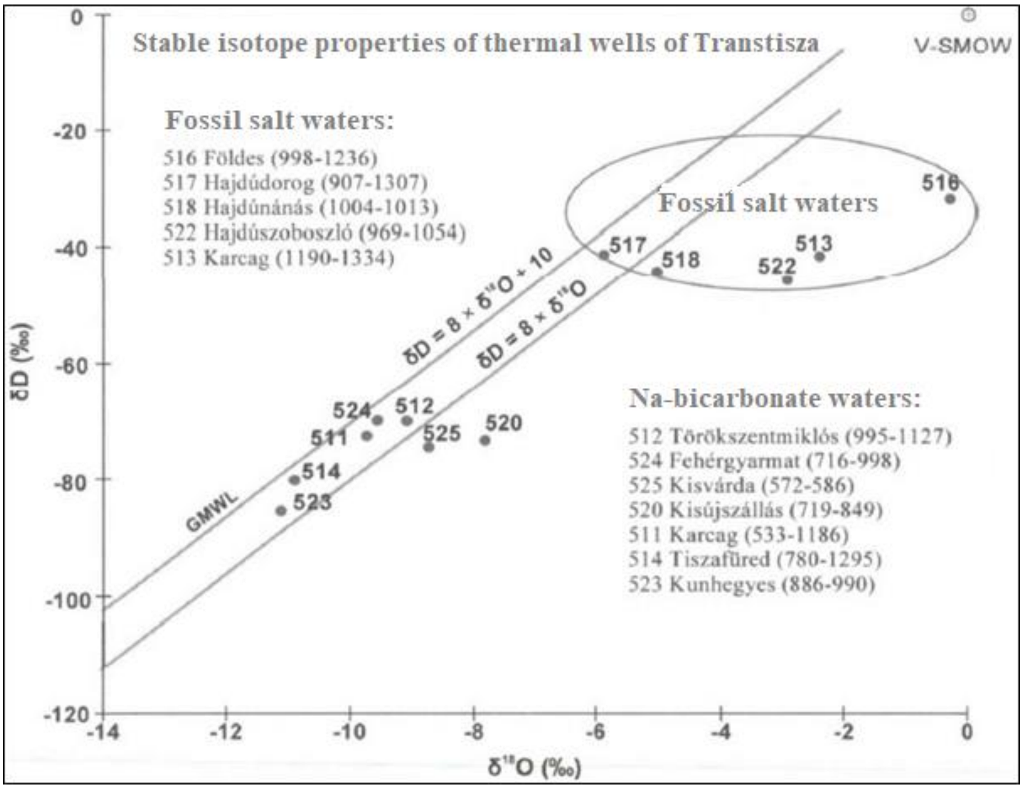

Figure 3. *Stable isotope characteristic of some thermal water from the Tiszántúl* (Marton, 2012)

3.2. Aging of thermal water

The result are corrected to -25‰ $\delta^{13}C$ value, where the $^{13}C/^{12}C$ isotope fraction was taken into account in per thousand unit (‰). $\delta^{13}C$ value is -25‰ in case of the most organic material.

^{14}C age was calculated with Ingerson-Pierson model. The error of age estimation just contains the measurement's analytical error and does not contain the error of age model that could be significantly higher than the given analytical error (***Table 3***).

Table 3. *Water age results*

	Conventional ^{14}C age (year BP)(±1σ)	$\delta^{13}C$ (VPDB) (‰) (±0.2‰)	^{14}C water age (Ingerson-Pierson model)
Hajdúdorog, Thermal water	>40000 year	-2.43	>24500

The mixing of water in the aquifers makes harder to identify the proper age of the investigated water resource. In case of the thermal water of Hajdúdorog the dilution is probable. The effective age of the water should be older than the calculated value if the water is really diluted seawater.

4. Summary

Aim of our work was to identify the special components of thermal water of Hajdúdorog that can help to force the utilization of water in therapy. Our analytical work highlighted the thermal water of Hajdúdorog has a special NaCl water type. The water resource of the thermal bath is a fossil salt water, what could be diluted sea water. According to our investigation and the information of previous articles the thermal water about its bromine and iodine content and trace element content (Cu, Fe, Mn) is properly applicable for therapy. This water is not unique as it was shown in the paper because this water is a member of fossil salt waters against Földes, Hajdúszoboszló, Karcag, Hajdúnánás (Marton, 2012) but the community of Hajdúdorog can feel lucky itself because of possession of a rare natural resource like this healing water.

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