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Hydrogeological conditions for the forming and quality of mineral waters in Serbia

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ABSTRACT

In the past researches conducted on the territory of Serbia, 5 regional geotectonic units have been distinguished with registered occurrences of 230 mineral springs. Recent analyses of the bottled mineral waters quality have not included systematic examinations of micro-components present in these waters. Based on the analyses of the bottled mineral waters (EuroGeoSurveys Geochemistry Expert Group), it has been observed that the water quality is greatly influenced by the chemical composition of igneous intrusions, regardless of the fact that the analyzed waters have been taken from different aquifers (Neogene sediments, limestone, flysch, schist).

Bottled waters in Serbia are usually HCO_3, with Na or Ca like dominant cation, and in large range regarding TDS. In some bottled waters high content of micro-components and trace elements was recorded.

The analyses of mineral waters prove the direct dependence between the hydrochemical composition of waters and complex geological properties in which the formation and movement of waters have been taking place, throughout the geological history.

1. Introduction

According to the density of occurrences and the diversity of physical and chemical features of the mineral waters, the territory of Serbia belongs to one of the most resourceful areas of the European continent, but only a smaller quantity of these mineral waters is used for bottling. Currently, there are 30 factories/bottling mineral water plants which have delivered around 560 000 m^3 of bottled water to the market in 2008. The consumption of mineral waters in Serbia amounts to around 75 L per capita. When compared to the total captured quantity of ground waters (around 600 million m^3/year), the exploitation of mineral waters for bottling purposes amounts to less than 0.1%.

The territory of Serbia is divided into 5 regional geotectonic units (Fig. 1): Pannonian Basin, Interior Dinarides, Vardar zone, Serbian–Macedonian massif and Carpatho-Balkans, which are significantly different according to the quantity and quality of ground water. In the Pannonian Basin, waters are predominantly accumulated within the Neogene sediments, in the Interior Dinarides and Carpatho-Balkanides areas water is accumulated within limestone, and in the central part (Vardar zone, Serbian–Macedonian massif) within different rocks of a metamorphic complex. The global geological conditions dictate the speed of water exchange, but they do not correspond completely to the quality of the ground water.

Based on the analyses of the bottled mineral waters (EuroGeoSurveys Geochemistry Expert Group), it has been observed that the water quality formation is greatly influenced by the chemical composition of igneous intrusions, regardless of the fact that the analyzed waters have been taken from different aquifers (Neogene sediments, limestone, flysch, schist).

According to the classification of Alekin (1970), which is based on the relationship between the prevailing ions, almost all waters are HCO_3 group (dominating anion), with different classes (dominating cation), I-types, respectively $HCO_3^- > Ca^{2+} + Mg^{2+}$.

2. Sampling and analytical methods

During 2008, 13 bottles of selected mineral waters of Serbia were sent to the laboratory of the Federal Institute for Geosciences and Natural Resources (BGR) in Berlin, Germany, where they were analyzed; 12 samples were taken from markets in PET bottles 0.5 L and one was taken from its spring (SRB011-1) before the beginning of the commercial sale.

71 parameter of all waters were analysed. The following techniques were used for sample analyses for this Project: quadrupole inductively coupled plasma-mass spectrometry (ICP-QMS, trace elements), inductively coupled plasma atomic emission spectroscopy (ICP-AES, major elements), ion chromatography (IC, anions), atomic fluorescence spectrometry (AFS, for Hg), titration (alkalinity), photometric methods (NH_4^+), potentiometric methods (pH) and conductometric methods (EC) (Birke et al., 2010a). Detailed analytical

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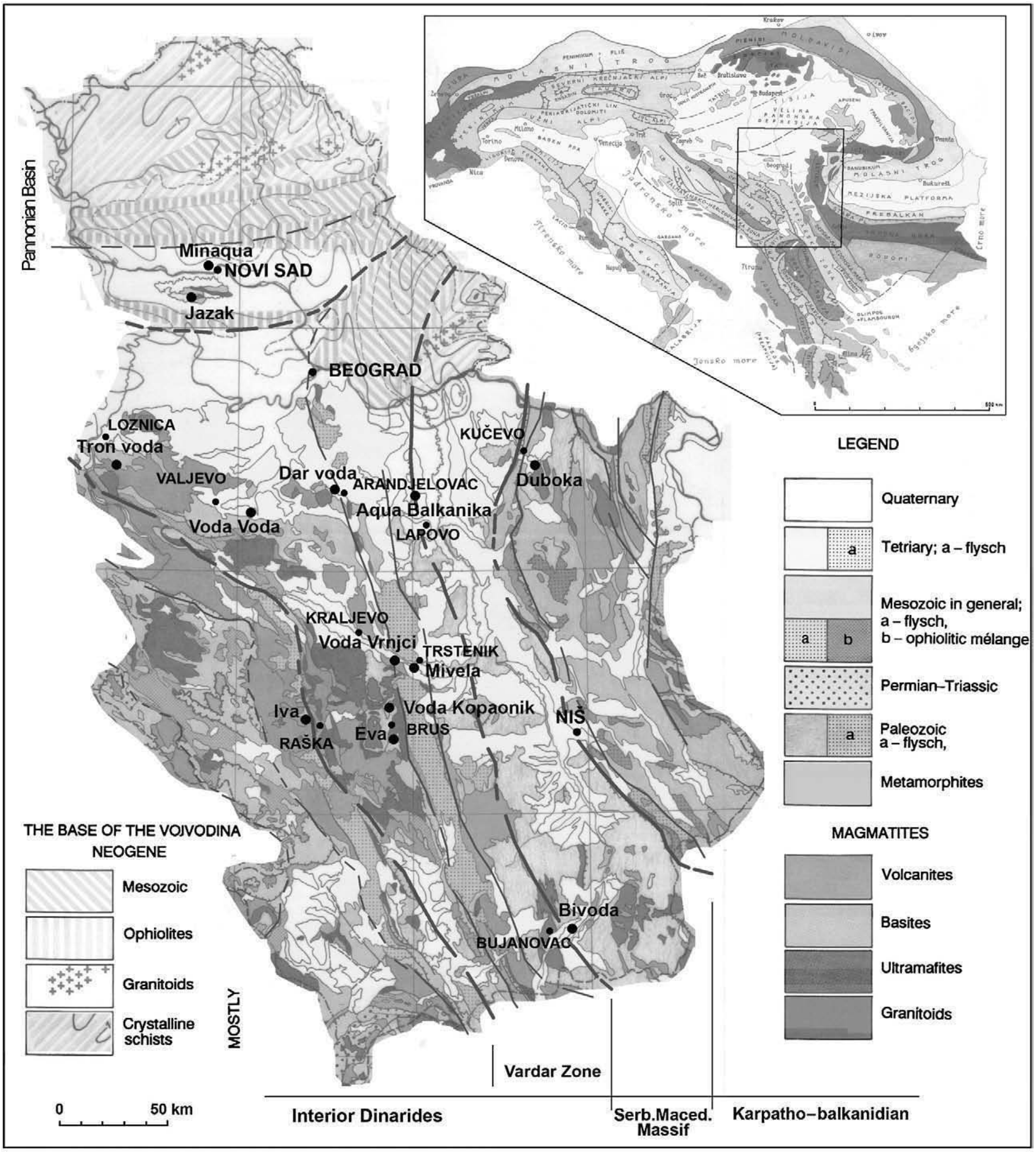

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Fig. 1. Geological map of Serbia (Dimitrijević, 1994).

procedures are described in Birke et al. (2010a). Analytical method and detection limit for all measured parameters are given in Table 1.

3. Regional geological settings

M. Dimitrijević (1994) defined geological structure of the territory of Serbia based on geotectonical units. General is divided into the following units: Pannonian Basin, Carpatho-Balkanides, Serbian Macedonian Massif, Vardar Zones and Interior Dinarides (Fig. 1). The following paragraphs give a basic overview of geological units.

The Pannonian Basin extends in the northern part of Serbia. It has a highly diverse base that consists of crystalline rocks, Mesozoic rocks, granitoids and ophiolites along the margins of the Vardar Zone unit. The Basin consists of Paleogene, Neogene and Quaternary sediments with a total maximum thickness of about 4000 m.

The Carpatho-Balkanides extend in the east part of Serbia. This unit is characterized by very complex geological properties, with the presence of all formations from the oldest ones (Precambrium) to the youngest (Quaternary). This unit is dominantly composed of Triassic, Jurassic, and Cretaceous limestones.

The Serbian Macedonian Massif is a crystalline core located between the Vardar Zone in the west, and the Carpatho-Balkanides in the east. Massif extends across Eastern F.Y.R.O.M. and Northern Greece into Turkey and further eastward. It consists of two complexes of crystalline schists: lower, highly metamorphosed and pre-

Table 1
Analytical method and detection limit.

Parameter	Unit	Analytical method	Detection limit	Parameter	Unit	Analytical method	Detection limit
pH	–	Potentiometric	–	Nd	μg/L	ICP-QMS	0.0002
EC	μS/cm	Conductometric	–	Ni	μg/L	ICP-QMS	0.01
Ag	μg/L	ICP-QMS	0.001	Pb	μg/L	ICP-QMS	0.002
Al	μg/L	ICP-QMS	0.3	Pr	μg/L	ICP-QMS	0.00005
As	μg/L	ICP-QMS	0.01	Rb	μg/L	ICP-QMS	0.001
B	μg/L	ICP-QMS	0.1	Sb	μg/L	ICP-QMS	0.002
Ba	mg/L	ICP-AES	0.001	Sc	μg/L	ICP-QMS	0.01
Be	μg/L	ICP-QMS	0.001	Se	μg/L	ICP-QMS	0.01
Bi	μg/L	ICP-QMS	0.0005	Sm	μg/L	ICP-QMS	0.0002
Ca	mg/L	ICP-AES	0.01	Sn	μg/L	ICP-QMS	0.001
Cd	μg/L	ICP-QMS	0.001	Sr	mg/L	ICP-AES	0.001
Ce	μg/L	ICP-QMS	0.0005	Ta	μg/L	ICP-QMS	0.001
Co	μg/L	ICP-QMS	0.002	Tb	μg/L	ICP-QMS	0.00005
Cr	μg/L	ICP-QMS	0.03	Te	μg/L	ICP-QMS	0.005
Cs	μg/L	ICP-QMS	0.001	Th	μg/L	ICP-QMS	0.0001
Cu	μg/L	ICP-QMS	0.01	Ti	μg/L	ICP-QMS	0.01
Dy	μg/L	ICP-QMS	0.0001	Tl	μg/L	ICP-QMS	0.0005
Er	μg/L	ICP-QMS	0.0001	Tm	μg/L	ICP-QMS	0.00005
Eu	μg/L	ICP-QMS	0.0002	U	μg/L	ICP-QMS	0.0005
Fe	μg/L	ICP-QMS	0.1	V	μg/L	ICP-QMS	0.01
Ga	μg/L	ICP-QMS	0.0005	W	μg/L	ICP-QMS	0.002
Gd	μg/L	ICP-QMS	0.0002	Y	μg/L	ICP-QMS	0.0005
Ge	μg/L	ICP-QMS	0.005	Yb	μg/L	ICP-QMS	0.0002
Hf	μg/L	ICP-QMS	0.0005	Zn	μg/L	ICP-QMS	0.05
Hg	ng/L	AFS	5.00	Zr	μg/L	ICP-QMS	0.001
Ho	μg/L	ICP-QMS	0.0001	Br^-	mg/L	IC	0.003
I	μg/L	ICP-QMS	0.2	$HCO3^-$	mg/L	titration	2
K	mg/L	ICP-AES	0.1	Cl^-	mg/L	IC	0.01
La	μg/L	ICP-QMS	0.0005	F^-	mg/L	IC	0.003
Li	μg/L	ICP-QMS	0.1	NH_4^+	mg/L	photometric	0.005
Lu	μg/L	ICP-QMS	0.00005	NO_2^-	mg/L	IC	0.005
Mg	mg/L	ICP-AES	0.01	NO_3^-	mg/L	IC	0.01
Mn	mg/L	ICP-AES	0.001	PO_4^{3-}	mg/L	ICP-AES	0.02
Mo	μg/L	ICP-QMS	0.001	SO_4^{2-}	mg/L	IC	0.01
Na	mg/L	ICP-AES	0.1	SiO_2	mg/L	ICP-AES	0.05
Nb	μg/L	ICP-QMS	0.001				

Cambrian in age, and the upper complex of green schists ranging in age from Proterozoic to Lower Paleozoic. These rocks were intruded by granitoids whose age ranges from Paleozoic to Tertiary age.

The Vardar Zone is composed of several blocks of diverse composition, geological history and provenience, and it includes characteristic oceanic elements. Western part of Vardar Zone is composed of several blocks of a diverse composition, rich in ultramafites; then, of Santonian Ophiolitic Melange with metamorphism ranging up to the Cretaceous. This part also includes granitoids and volcanic rocks. The central part of Vardar Zone is covered by belt of Lower Cretaceous para-flysch resting on Jurassic Ophiolitic Melange, while metamorphism varies on age. Easter part of Vardar Zone is comprised of crystalline schists of unknown age, the Santonian flysch and volcanics.

The Interior Dinarides extend in the Western parts of Serbia, and continues to the west. Geologically, area is very heterogeneous both in lithological composition and in the age of the rocks. The most common are sediment rocks from Paleozoic and Mesozoic ages (Triassic limestone and dolomites), while Tertiary deposits appear sporadically. Volcanic and basic rocks occur only occasionally, as well as metamorphic rock.

4. Results and discussion

4.1. Regulations and standards

There are two regulations in Serbia concerning the quality of water for human use. These are: Regulation on the Hygienic Acceptability of Potable Water (Official Gazette of FRY, number 42/98 and 44/99), and Regulation on Quality and Other Requirements for Natural Mineral Water, Spring Water and Bottled Drinking Water (Official Gazette of Serbia and Montenegro, number 53/05).

Comparison of Regulations and Standards in Serbia with EU Directive and World Health Organization (WHO, 2006) is shown in the Table 2.

The Regulation on the Hygienic Acceptability of Potable Water defines the Maximum acceptable concentrations (MAC) of chemical substances in water for public water supply, and beside that it particularly gives MAC for certain minerals in bottled water (Al, Ba, Ca, Cl, CN, Cu, F, Fe, Hg, Ng, Mn, Na, Ni, NO_2, NO_3, SO_4, Zn, and electro conductivity less than 500 μS/cm). Except for As, B and U, all of the MAC in this regulation are lower than the one given by the World Health Organization (WHO).

Regulation on Quality and Other Requirements for Natural Mineral Water, Spring Water and Bottled Drinking Water defines the MAC of certain chemical parameters that can be a risk to human health, indicators of water quality and nomenclature of mineral waters. If the concentration of a certain parameter in the mineral water is higher than the one given in Table 2, (value n*), then this must be highlighted in the water name (on bottle label). Example: "bicarbonate water" if $HCO_3>600$ mg/l, or "Mg water" if Mg>50*, etc...

MAC for F (1.5 mg/l), Cl (250 mg/l), CN (70 μg/l) and SO_4 (250 mg/l) must not be exceeded, while for water rich in CO_2, pH value can be less than 6.8. This regulation applies to all ground water, regardless of the overall mineralization. The term "spring water" was used meaning "captured water on the location". The regulation is harmonized with WHO standards, except in case of B content, for which two times higher maximum concentration is allowed.

Significantly higher concentrations (two times and more) than the ones allowed by Serbian regulations and the WHO, are recorded for B (Bivoda and Voda Kopaonik), Mg (Mivela water), Na (Bivoda, Voda

Table 2
Comparison of regulations and standards in Serbia with the EU Directive and WHO.

PARAMETER	UNIT	EU Directive 1998/83/EC DRINKING WATER	EU Directive 2003/40/EC MINERAL WATER	EU Directive 2009/54/EC NATURAL MINERAL WATER	WHO	Measurement Concentration in Analytic Samples		Regulation on the Hygienic Acceptability of Potable Water (Official Gazette of FRY, number 42/98 and 44/99)		Regulation on Quality and Other Requirements for Natural Mineral Water, Spring Water and Bottled Drinking Water (Official Gazette of Serbia and Montenegro, number 53/05)
						MIN	MAX	MAC of chemical substances in water for public water supply	MAC for certain minerals in bottled water	
pH		≥6.5–≤9.5	n.d.	–		5.6	7.5	6.8–8.5	6.8–8.5	
EC at 20 °C	μS/cm	2500 g.v.	n.d.	–		340	4560	<1000	<500	2500
Ag	μg/l	n.d.	n.d.	–		<0.001	0.00357		10	
Al	μg/l	200 g. v.	n.d.	–	200	<0.001	8.38	200	50	200
As	μg/l	10	10	–	10	0.085	6.26	10	50	10
B	μg/l	1000	–	–	500	22.3	5660	300	1000	1000
Ba	mg/l	n.d.	1	–	0.7	<0.01	0.637	0.7	0.1	
Be	μg/l	n.d.	n.d.	–		<0.001	0.512		0.2	
Br	μg/l	n.d.	n.d.	–		/	/			
Ca	mg/l	n.d.	n.d.	>150		22.2	241	200	100	150*
Cd	μg/l	5	3	–		<0.001	0.00589	3	5	3
Cl	mg/l	250 g.v.	n.d.	>200	300	1.35	287	200	25	200*–250
CN^-	μg/l	50	70	–		/	/	50	–	50–70
Cr	μg/l	50	50	–	50	0.09	2.4	50	50	50
Cs	μg/l	n.d.	n.d.	–		0.0425	84.7			
Cu	μg/l	2000	1000	––	2000	0.113	2.48	2000	100	2000
F	mg/l	1.5	5 (1.5: label)	>1	1.5	<0.002	2.39	1.2	1	1*–1.5
Fe	μg/l	200 g.v.	n.d.	–	300	0.13	101	300	50	200
Fe^{2+}	mg/l	n.d.	n.d.	>1		/	/			1*
Ge	μg/l	n.d.	n.d.	–		0.00532	17.8			
HCO_3^-	mg/l	n.d.	n.d.	>600		200	3290			600*
Hg	μg/l	1	1	–	6	<5	<5	1	1	1
I	μg/l	n.d.	n.d.	–		1.68	686			
K	mg/l	n.d.	n.d.	–		0.8	52	12	10	
Li	μg/l	n.d.	n.d.	–		0.762	985			
Mg	mg/l	n.d.	n.d.	>50	50	12.08	324	50	30	50*
Mn	μg/l	50 g.v.	500	–	400	<1	465	50	20	50
Mo	μg/l	n.d.	n.d.	–	70	0.131	0.537	70		
Na	mg/l	200 g.v.	n.d.	>200	200	1.8	1216	150	20	200*
NH_4^+	mg/l	0.5 g.v.	n.d.	–		<0.005	4.4			0.5
Ni	μg/l	20 g.v .	20	–	70	0.0246	9.12	20	10	20
NO_2^-	mg/l	0.5 g.v.	0,1	–	3	<0.005	0.144	0.03	–	0.1
NO_3^-	mg/l	50 g.v.	50	–	50	<0.01	9.25	50	5	50
Pb	μg/l	10	10	–	10	0.00297	0.0855	10		10
Rb	μg/l	n.d.	n.d.	–		0.388	205			
Si	mg/l	n.d.	n.d.	–		(SiO_2) 4.8	(SiO_2) 88.8			
Sb	μg/l	5	5	–	20	0.161	2.93	3	10	5
Sc	μg/l	n.d.	n.d.	–		0.0194	0.348			
Se	μg /l	10	10	–	10	<0.01	0.149	10	10	10
SO_4	mg/l	250 g.v.	n.d.	>200	250	0.02	173		25	200*–250
Sr	mg/l	n.d.	n.d.	–		0.05	1.49			
Tl	μg/l	n.d.	n.d.	–		0.00441	1.11			
U	μg/l	n.d.	n.d.	–	15	0.00166	1.83		50	
V	μg/l	n.d.	n.d.	–		0.037	4.45		1	
W	μg/l	n.d.	n.d.	–		0.0182	11			
Zn	μg/l	n.d.	n.d.	–	3000	0.0609	3.27	3000	100	

Note: n.d. – not detectable: g.v. – groundwater: n* – donja granica nomenclature.
MAC – Maximum acceptable concentrations.

Kopaonik and Minaqua waters) and F (Voda Kopaonik). All of these parameters have geological origin, and they represent the natural composition of these waters, also recorded in other waters within surrounding area.

4.2. General hydrogeochemistry

The total of 71 parameters were examined for each sample, and some of the results are given in Table 3.

The pH value of the analyzed water ranged from 5.6 to 7.8. According to the Regulation on the Hygienic Acceptability of Potable Water (Official Gazette of FRY, number 42/98 and 44/99), the pH should be in a range from 6.8 to 8.5. Nitrogen compounds in water are present as ammonia at high pH values, while at low pH values they are in form of ammonium ions (Cicchella et al., 2010), like in water Minaqua.

In analyzed water with a low pH value, there is a natural CO_2 (Dar voda, Minaqua, Voda Vrnjci, Mivela, Bivoda).

The EC value is in a range from 340 to 4560 μS/cm. According to Regulation on Quality and Other Requirements for Natural Mineral Water, Spring Water and Bottled Drinking Water (Official Gazette of Serbia and Montenegro, 2005), recommended value of EC should be up to 2500 μS/cm.

In Mivela and Bivoda, high EC values depend on the high value of Dry Residue, respectively from the value of TDS (Total Dissolved Solids).

Piper diagram (Fig. 2) includes, beside macrocomponents of analyzed water, macrocomponents from other bottled water in

Table 3
Results of the analysed samples.

Sample	pH	EC	Ca	Mg	Na	Cl	SO_4^2	HCO_3	K	B	Cs	Cr	Ge
Voda Kopaonik	7.5	1700	28.3	12.8	409	18.9	0.32	1183	7.4	1400	20.9	0.304	17.8
Aqua Balkanika	7.6	672	78.5	28.3	33.9	5.23	18	440	2.1	92.9	0.043	1.27	0.007
Eva	7.8	340	47.8	15.2	3.1	1.88	15.8	200	1	22.3	0.596	0.967	0.014
Dar voda	5.6	990	90.6	22.6	92.4	28.4	80.5	521	17.2	249	84.7	0.125	1.36
Minaqua	5.75	1974	22.2	19.9	412	287	0.35	768	3.6	1250	0.78	0.0905	0.22
Jazak	7.5	690	77	45.6	6.9	5.53	29.5	427	3.5	27.2	1.52	2.4	0.018
Duboka	6.9	1365	241	19.7	55	15.4	9.61	956	5.1	158	3.33	0.284	0.38
Voda Voda	7.5	623	78.3	14.8	41.5	7.5	13	392	3.1	408	38.4	0.97	1.99
Voda Vrnjci	6.4	1696	76.3	55.4	241	15.5	29.1	1177	35.1	631	52.7	0.101	15.3
Mivela	6.3	2510	26.3	324	120	12.8	0.02	2047	8.4	783	25.9	0.152	2.65
Iva	7.3	423	58.7	20.7	3.4	1.97	7.26	275	0.8	39.8	0.325	1.47	0.057
Bivoda	6.5	4560	85.4	20.6	1216	54.1	173	3290	52	5660	0.385	0.296	16.2
Tron voda	7.45	630	83	38.7	1.8	1.35	22.2	401	0.6	22.1	0.219	0.302	0.005
Sample	F	Fe	I	Li	Mn	Ni	Rb	Sb	Tl	V	W	NH_4	SiO_2
Voda Kopaonik	2.39	3.03	11.6	283	0.003	0.679	18	0.359	0.00524	0.868	0.0711	−0.005	23.8
Aqua Balkanika	0.005	0.277	13.6	31.2	−0.001	0.359	1.43	0.397	0.00441	0.0371	0.0182	0.006	4.8
Eva	0.084	0.34	2.97	2.02	−0.001	4.85	1.23	2.93	0.00892	0.115	0.0279	−0.005	9.5
Dar voda	1.39	101	58.1	331	0.465	3.68	148	0.313	0.0125	0.396	0.319	0.205	23.6
Minaqua	0.459	3.29	686	72.8	0.025	0.0469	3.68	0.394	0.0127	0.213	0.457	4.4	26.7
Jazak	0.135	0.237	3.52	3.96	−0.001	0.537	1.34	0.402	0.0166	0.293	0.0642	−0.005	12.1
Duboka	0.477	1.27	10.2	43.5	−0.001	0.839	17.1	0.585	0.052	1.18	0.0488	−0.005	22.7
Voda Voda	0.747	0.193	4.85	200	−0.001	2.48	17.3	1.61	1.11	0.207	11	−0.005	17.0
Voda Vrnjci	1.7	0.324	7.04	464	0.003	9.12	205	0.41	0.0114	0.085	0.231	0.012	80.4
Mivela	0.155	6.85	12.8	300	0.039	7.87	40.7	0.161	0.0056	0.0961	0.233	0.114	64.4
Iva	0.106	0.912	2.7	1.9	0.001	1.61	0.875	0.311	0.0104	0.622	0.0677	−0.005	15.8
Bivoda	−0.002	3.88	19.1	985	0.036	1.29	163	0.813	0.0074	4.45	0.102	1.16	88.8
Tron voda	0.089	0.132	1.68	0.762	0.001	0.0551	0.388	0.607	0.0544	0.275	0.0327	−0.005	6.7

Serbia. Chemical data were taken from bottle labels. All waters are bicrbonate (HCO_3), except for water Minaqua which is HCO_3, Cl. Content of cation is in a large range, in some waters Na + K ions prevail, in some Ca ions, and Mg is the cation that prevails only in one sample (Mivela).

The cation composition is related to the TDS (Fig. 2). Na + K is predominant in mineral waters (>1 g/l), while cation Ca in non-mineral waters (<1 g/l).

The Piper diagram of bottled waters (Fig. 2) shows that it is almost impossible to find any similarity between waters from the same geotectonic unit. This is due to the complex geological properties, especially tectonic, structural, stratigraphic and, above all, lithological diversity of aquifers where movement of waters has been taking place throughout geological history.

Minaqua water, which is HCO_3, Cl–Na, was sampled in Pannonian Basin, and has a composition that is similar to some Croatian waters from Pannonian Basin, e.g. Kapljice water in terms of anions, or Studena water in terms of chloride and increased concentration of iodine (Peh et al., 2010). Jazak water was taken from Pannonian Basin, but the spring area belongs to Mt. Fruška gora, so the water shows characteristics of that area.

In Mivela water (Vardar Zone) Mg ion prevails. Magnesium water is very rare which makes this water very special. Besides in Serbia, Mg water is also bottled in Slovenia (Donat), while in Germany (Birke et al., 2010b), Italy (Dinelli et al., 2010) and Croatia (Peh et al., 2010) similar water does not exist.

On the Piper diagram of tap waters (Fig. 3), waters are clearly separated according to geotectonic units. In Serbia, tap waters are predominantly derived from alluvium. Tap water is also bicarbonate, while being Ca or Ca, Mg in view of cations, except for waters from the Pannonian Basin where Na is predominant cation.

The Genetic diagram (D'Amore et al., 1983), based on macro-components, has been proven to be very reliable for better understanding of aquifers lithologic (Fig. 4), especially for occurrences formed in more complex conditions (Milivojević and Perić, 1990). To understand better this diagram, a comparison has been made with Serbian thermal waters (Milivojević and Perić, 1990).

Forming of water in the carbonate rocks is shown by parameters ABCDEF for Tron, Jazak, Iva and Eva water (Fig. 4). Parameters for Bivoda and Voda Kopaonik are the same and they indicate an origin from granitoid rocks, while parameters for Duboka water indicate possible origin from these rocks. Parameters for Voda Voda indicate that the water is formed in carbonate rocks beneath the Neogene sediments. Serpentine origin is indicated for Mivela and Voda Vrnjci. Other waters are formed in complex geological conditions.

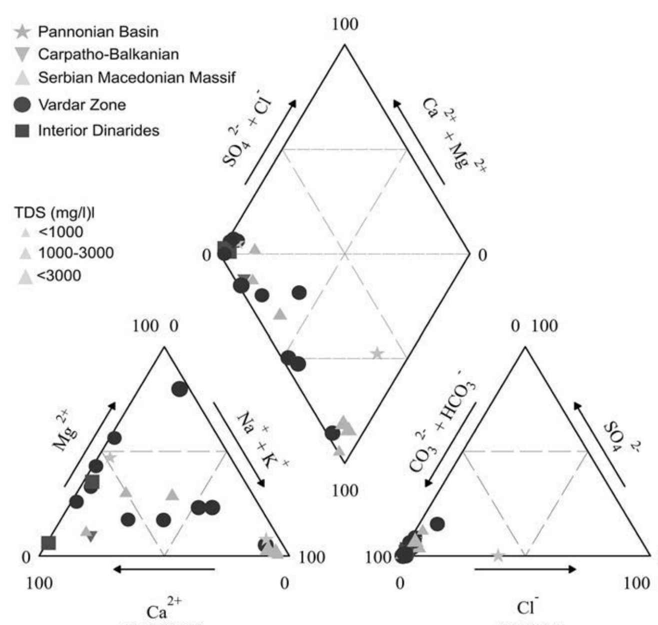


Fig. 2. Piper diagram of bottle water according to geotectonic units.

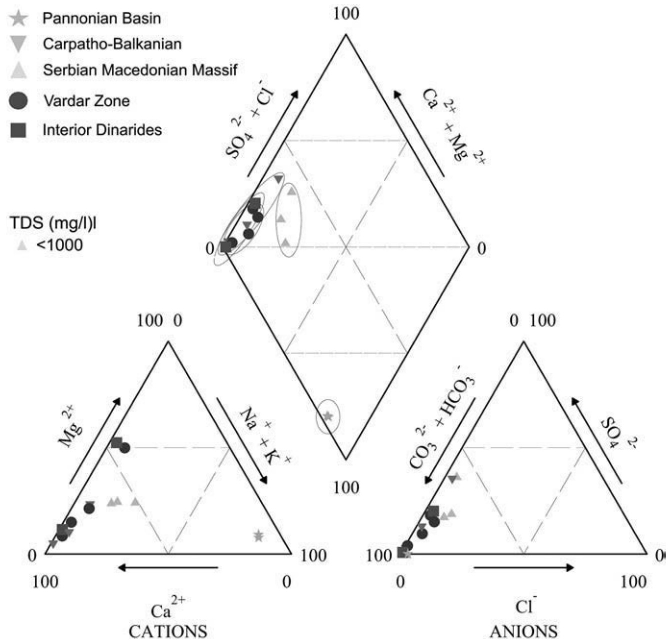


Fig. 3. Piper diagram of tap water according to geotectonic units.

4.3. Hydrogeochemistry of analyzed waters

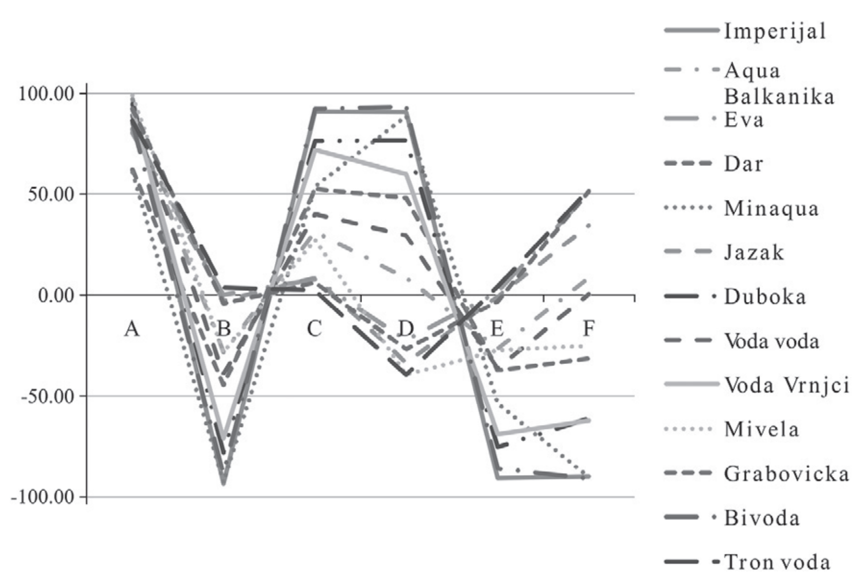
Based on the available data about the geological and hydrogeological properties of areas where waters are captured, water forming conditions and specific chemical composition are partly explained (Table 4).

From the Pannonian Basin Minaqua and Jazak waters were analyzed.

Minaqua has been captured from the Neogene sediments of the Pannonian Basin. Since the water is formed in anaerobic conditions, higher concentrations of I (0.686 mg/l) and NH_4 (4.4 mg/l) which are of a natural organogenic origin have been observed in the mineral water. Higher concentrations of NH_4^+ indicate that the water has been formed in areas where oil and gas is found. Ammonium has a toxic effect on human health only if the intake becomes higher than the capacity to detoxify, which is about 33.7 mg of ammonium ion per kg of body weight per day (Cicchella et al., 2010). Chlorides (Cl) indicate that the water is formed in a shallow environment of the Pannonian Basin. From a medical point of view, iodine improves memory, mood, normal functioning of the thyroid gland, quality of hair, skin, teeth and nails, which gives this water a special value.

Jazak water from Fruška Gora, has been captured from Triassic sediments, which have their source in carbonated facies rocks. (limestone, dolomite) (Vukićević and Demić, 2005). This is confirmed by the relation of rCa/rMg of 1.68. The water is HCO_3–Ca, Mg, whereby it can be stressed that good water quality is impacted by a considerable amount of Ca (77.0 mg/l) and Mg (45.6 mg/l), as well as a low amount of Na (6.9 mg/l) and Cl (5.53 mg/l). The amount of micro-components is far lower than the maximum recommended quantity for bottled waters. Compared to other analyzed waters, Jacek water has a slightly higher content of Cr (2.4 μg/L), which originates from gabbros that occur east from Jazak village. The concentration of Cr in Jazak gabbros reaches 498 ppm (Srećkovic-Batočanin et al., 2010). Water Jazak emerges through a fracture-karst aquifer of considerable yield, and according to these features the location is not typical for the Pannonian Basin.

The majority of the analyzed samples of mineral water from the territory of Central Serbia contain higher concentrations of Cs, Li, Rb and Sb, which indicate that the water source is from granite intrusions (Beaucaire and Michard, 1982). These elements most often appear in CO_2 water with a predominant HCO_3 and Na content (Protić, 1988).



$$A=\left[\frac{100}{\sum(-)}\left(HCO_3-SO_4\right)\right]$$

$$B=100\left[\left(\frac{SO_4}{\sum(-)}\right)-\left(\frac{Na}{\sum(+)}\right)\right]$$

$$C=100\left[\left(\frac{Na}{\sum(+)}\right)-\left(\frac{Cl}{\sum(-)}\right)\right]$$

$$D=100\left(\frac{Na-Mg}{\sum +}\right)$$

$$E=100\left[\left(\frac{Ca+Mg}{\sum(+)}\right)-\left(\frac{HCO_3}{\sum(-)}\right)\right]$$

$$F=100\left(\frac{Ca-Na-K}{\sum +}\right)$$

Fig. 4. Genetic diagram based on cations and anions expressed in %eq. (according to D'Amore et al., 1983).

Table 4
Review of the chemical composition of the analyzed mineral waters (classification waters according to Alekin (1970)).

Sample	Well location	Brand name	Group	Class	Specific components	TDS1 (mg/l)	TDS1 (mg/l)	TDS (mg/l)
SRB001-1	Grasevacka river -Brus	Voda Kopaonik	HCO_3	Na	Cs, Ge	1106.30	9.23	1115.54
SRB002-1	Smederevska Palanka	Aqua Balkanika	HCO_3	Ca		393.71	1.08	394.79
SRB003-1	Brzece-Brus	Eva	HCO_3	Ca	Sb	199.98	2.62	202.60
SRB004-1	Darosava -Arandjelovac	Dar voda	HCO_3	Na	Fe, Mn, F	629.96	7.52	637.48
SRB005-1	Novi Sad	Minaqua	HCO_3-Cl	Na	I, NH_4	1171.77	9.93	1181.70
SRB006-1	Jazak-Fruska Gora	Jazak	HCO_3	Ca, Mg		400.89	9.70	410.60
SRB007-1	Neresnica-Kucevo	Duboka	HCO_3	Ca		860.13	4.77	864.91
SRB008-1	Gornja Toplica-Mionica	Voda Voda	HCO_3	Ca	Tl, W, Sb	381.40	3.55	384.96
SRB009-1	Vrnjci	Voda Vrnjci	HCO_3	Na, Mg	Cs, Ge, Si, Rb	1169.54	5.26	1174.80
SRB010-1	Veluce-Trstenik	Mivela	HCO_3	Mg		1618.06	2.21	1620.28
SRB011-1	Grabovacka spa	Iva	HCO_3	Ca, Mg		255.61	4.94	260.55
SRB012-1	Rakovac-Bujanovac	Bivoda	HCO_3	Na	B, Ge, Rb, Li, K, Si, V, NO_2	3388.18	12.65	3400.83
SRB013-1	Tronosa -Loznica	Tron voda	HCO_3	Ca, Mg		358.87	5.80	364.67

Note: groups and classes according to Alekin.
TDS1 = Σmacrocomponents.
TDS2 = Σmicroelements + trace elements.
TDS = TDS1 + TDS2.

Specific chemical composition of Dar Voda and Bivoda is the result of the forming and outflow of mineral waters. The primary spring is fed by infiltration of rain waters through the fault system in uncovered parts of the terrain built up of altered rocks and granite. Enrichment by mineral substances and generation of primary chemical composition occur in deeper aquifer (Vujanović et al., 1971). Water circulates through the fault system whereby it is enriched with gas, CO_2 and then it arrives to the aquifer in the Neogene sediments (sands), where it is captured.

Dar Voda is captured from Neogene sand-clay deposits, beneath which granite-monzonite is expected. The pH value of 5.6 indicates low acid environment, while its elevated to water hardness (14.0–17.3°dH) classifies it among the fairly hard waters according to Klut-Olszewski (Olszewski, 1945). Higher concentrations of Fe (0.101 mg/l) and Mn (0.465 mg/l) in Dar Voda can be related to the weathering of granite rocks, or the presence of basic rocks which are not found on the surface, or in the borehole. Fluorine (1.39 mg/l) in water is related to granitoid minerals — apatite, biotite, fluorite (Dangić and Protić, 1995; Chae et al., 2007). Based on the determination of the balneology value of Dar Voda, the water is classified as an Na–HCO_3–Li–F–$SiCO_2$-cool mineral water and it is recommended for the preventive healing of gastritis, stomach diseases, gall and liver diseases, diabetes and osteoporosis.

According to ionic composition *Bivoda* is HCO_3–Na, K with high value of TDS (3400.83 mg/l). Such a hydrochemical type of ground-ground water is related to acidic igneous rocks. The water is characterized by considerable amounts of free CO_2 which emerges from deep fault structures and gives the water an acidic flavor (Zlokolica-Mandić, 2000). The presence of free CO_2 is also related to the pH value which is somewhere at the cross point between low acid waters and neutral waters with a pH value of 6.5.

In Bivoda increased concentration of NO_2, B, Si, Ge, Rb, Li, Sr, V is observed.

Content of NO_2 is 0.144 mg/l. According to EU Directive 98/83/EC, the European Commission established that in potable water $[NO_3^-]/50+[NO_2^-]/3\leq 1$. The result of this equation in Bivoda is 0.0572, which indicates that there are no negative effects on human health.

Increased concentrations of boron can indicate anthropogenic contamination due to the number of uses of boron compounds in industry and household (glass production, detergents, bleaches, wood preservatives, fertilizers, herbicides, astringents, antiseptics, neutron absorbers in nuclear reactors) (Birke et al., 2010b). Value of B in Bivoda is 5.66 mg/l. Boron is detected in all of the mineral waters in the Bujanovac Basin (also in bottled mineral water Heba, and in the Bujanovac spa).

According to one theory, the high percentage of boron indicates that the mineralization is derived from a magnesite complex of Neogene sediments, since high concentrations of boron and boron mineral searlesite occur (Dangić and Rakočević, 1993). According to another theory, boron in the ground water derives from mineral tourmaline, which is found in pegmatite present in the area of Bujanovac (Dragišić, 1997).

Higher content of silicon has been noted in Bivoda. Silicon gives stability to bones, elasticity to connective tissue, tautness to the skin, and it also has good influence on hair, fingernails and toenails (D'Haese et al., 2004).

Increased content of Li, Rb i Cs is associated with CO_2–Na waters (Krajnov and Švec, 1987). In Bivoda, these elements are associated with younger Tertiary magmatic bodies intruded into Bujanovac granitoid, which are also the heat source in this waters (Petrović, 2010).

According to the Serbian Regulation (Official Gazette of FRY, number 42/98 and 44/99) maximum allowed concentration for vanadium in bottled water is 1 μg/l, while in other Directives and Regulations there is no maximum limited value for vanadium. Content of V in Bivoda is 4.45 μg/. There is no data regarding V toxicity and available evidence does not indicate that V in drinking water is a problem (Cicchella et al., 2010).

The natural carbon-acidic *Aqua Balkanika* water is also related to igneous rocks, but it is captured from Neogene sediments. The presence of free CO_2 in the water is related to regional metamorphic processes (cooling and solidification) of igneous intrusions in deeper parts of the earth's crust. During magma crystallization, easily released components, such as CO_2, are partly built into the rock minerals, and a considerable part of it is released during contact with groundwater. CO_2 moves along joints and faults toward the surface (Komatina and Popović, 1994) Underlying these Neogene sediments there is crystalline schist with a considerable presence of calcschist and marble. In the south of the location, these rocks appear on the surface in the recharge area. The water is HCO_3–Ca.

Vrnjačka Banja is the most popular spa centre in Serbia. There are several springs of medicinal water in it. The "Snežnik" spring, which is used for balneotherapy, is also used for water bottling under the name *Voda Vrnjci*. Next to the spring there is a borehole made in serpentine rocks. The oldest rocks in the wider area are Paleozoic schist and amphibolites, with layers of marble through which considerable quantities of mineral waters circulate. The water circulates through serpentines and gabbros, which are quite tectonically disturbed, implying very good filtration characteristics and also increased concentrations of Mg ions (55.4 mg/l) (Nikolić, 2009). The presence of geochemical assemblage Cs, Rb, Si, Ge, indicates that granitoids influence water forming. There is a granitoid occurring on the surface 10 km to the South-East of Vrnjačka Banja (Željin, Crni Vrh). Higher content of Ni (9.12 μg/l) indicates the presence of ultrabasic rocks (gabbros and diabase). Voda Vrnjci is characterized by an increased TDS up to 1174.80 mg/l and CO_2 (700–1044 mg/l). According to the Alekin classification (Alekin, 1970) the water is HCO_3–Na, Mg.

Mineral water *Mivela* is bottled in the Trstenik area (Veluće village). The hardness of the water is around 80°dH, which classifies it among very hard waters according to the Klut–Olszewski classification (Olszewski, 1945). The water is characterized by an extremely high concentration of Mg (324.0 mg/l), which originates from serpentine. Water is mineral (TDS = 1620.28 mg/l).

Due to its high concentration of Mg, it is very helpful for the prevention of hypertension, regulation of blood sugar levels, heart arrhythmia, endocrinologic diseases and nervous system diseases.

Eva water is bottled at the foothill of the Kopaonik mountain (Brzeće-Brus). The water is captured from limestone breccia in the lower part of Santonian (K_2^3) flysch deposits. On the terrain surface there are volcano-sedimentary rocks. The water is characterized by its low TDS of 202.6 mg/l, which classifies it as a non mineral water. Higher content of Sb (2.93 μg/l) in this water originates from the hydrothermal alteration of serpentine. According to the Alekin classification, the water is HCO_3–Ca, which indicates a limestone origin.

Voda Kopaonik is located in the vicinity of Eva water, yet it has essentially different qualities. Voda Kopaonik is HCO_3–Na. Increased concentrations of Cs, Li, Sr, and Ge indicate its igneous origin. The presence of fluorine F (2.39 mg/l) in the groundwaters most probably originates from granitoid minerals such as fluorite, cryolite, apatite. The origin of boron (1.4 mg/l) is not definitely defined. However, the presence of Ni, which is also found in Voda Kopaonik, is related to the presence of ultrabasic rocks (gabbro and diabase).

Water Iva is captured from Grabovačka banja (Engl. Grabovac Spa), where water issues under pressure from Middle Triassic limestone. The recharge is done through the infiltration of in the open part of the karst aquifer located North-East of the spa. The geological structure of the terrain is made of phyllite, schist and metasandstone, within layers of Paleozoic age, overlain by Triassic rocks (marble, limestone). Thick-bedded and massive dolomites and limestone are situated above them. The terrain is considerably tectonically fractured which makes inflow of the waters from serpentine possible (Letić and Djokić, 2008). Based on the cationic and anionic composition, the mineral water is HCO_3–Ca, Mg. The relation of rCa/rMg (2.83) as well as total water hardness of 12.2 to 13.9° dH, indicate that primary circulation and accumulation occur in carbonate rocks (limestone, dolomite). The water is non mineral (TDS = 260.55 mg/l). All hydrochemical parameters are within the limits for drinking water which make it suitable for bottling.

Voda Voda is bottled in the Gornja Toplica area (Mionica) from natural spring. The water is HCO_3–Ca, originating from limestone found in the bottom of Neogene sediments. Higher concentration of Tl, W and Sb are related to diabase and spilite. The contents of other micro-components, as well as radioactive components are within the limits for drinking water, so it can be consumed without any restrictions. The TDS of the water is 384.96 mg/l, which classifies it as a non mineral water.

The natural spring water from the Devet Jugovica spring is bottled under the name *Tron* water. The extremely low content of Na (1.8 mg/l) is related to TDS (364.67 mg/l). The relation of rCa/rMg is 2.144, indicates that dolomite and dolomitic limestone are the primary environment for water circulation. The trace elements are far below the limits for drinking water. According to the Alekin classification, the water is HCO_3–Ca, Mg.

Natural mineral water *Duboka* of Kučevo belongs to the Carpatho-Balkanian hydrogeothermal province. It is characterized by increased concentrations of HCO_3 (956.0 mg/l) and Ca (241.0 mg/l) as the result of the weathering of limestone and calcium feldspars in magmatic rocks (granite monzonite). The water temperature is 20 °C, so it is classified as a thermo-mineral water. The content of CO_2 (450.0 mg/l) makes it a low acid water (Sobar-Puškaš, 2002). Observations, over one hydrologic year, have confirmed that the water quality was constant with no considerable oscillations during seasonal changes. Based on the geological structure, it is obvious that the granodiorites, which are located near the mineral water occurring below the limestone, have an influence on the water quality.

5. Conclusion

The analyzed mineral waters of Serbia significantly vary regarding the TDS from 202.6 to 3400.83 mg/l. All waters are HCO_3, except Minaqua which also contains Cl among the leading anions. In the cation composition, there are two major groups: with a dominant content of Na + K, and with a dominant content of Ca (i.e. Ca + Mg). In this grouping, Mivela is an exception, because it is dominantly Mg.

Generally, Na water contains a large number of micro-components, which is of course a consequence of its high mineralization, but also of genetic relation to the presence of acidic igneous intrusions in the source zone of these waters. However, these rocks are not always outcropping on the surface, in the nearest zone of infiltration, and are not registered in the exploitation wells. A good example is Duboka water, which emerges from limestone (leading cation Ca), but is genetically linked to waters in contact with granitoid intrusions. The unusually high TDS (864.91 mg/l) and presence of free CO_2 speak in favour of such an interpretation, because these are not characteristics of waters originating from limestone. Minaqua water has a similar genetic diagram, but the presence of Na could be primarily linked to the high content of Cl and undeniable presence of NaCl minerals in the sediments and water of the Pannonian Basin marginal area.

The analyses of mineral waters prove the direct dependence between the hydrochemical composition of waters and complex geological properties in which the formation and movement of waters have been taking place, throughout the geological history. The velocity of turnover, and the related age of water were not analyzed on this occasion.

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