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Composition and variation of major and trace elements in Croatian bottled waters

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ABSTRACT

Within the framework of the Pan-European project about the geochemistry of bottled mineral waters in Europe launched in 2007 by the European Geological Surveys (EGS) Geochemistry Expert Group fourteen brands of bottled natural waters from Croatia of both mineral and spring types were evaluated for getting more coherent spatial information about the natural variation of element concentration in bottled waters found at the European market. Results of chemical analysis show that not a single one out of fourteen analyzed bottled waters from Croatia exceeds the Croatian water standards sanctioning thereby their suitability for human consumption. Also, statistical tests performed for 41 analytes (including pH and EC) clearly show that the water chemistry is in a high degree of conformity with regional geology, depending on structural, stratigraphic and, above all, lithological diversity of aquifers. Thus Dinaric and Pannonian parts of Croatia differ largely with regard to their water types: Dinaric region is completely lacking mineral water types while, on the other side, in the Pannonian region even the spring waters show stronger mineralization in comparison with their Dinaric counterparts. Typically, all natural waters from Croatia bear the bicarbonate (HCO_3) signature. However, Ca–Mg cation pair combination is characteristic of spring waters while Na–K dominates in the mineral waters.

1. Introduction

Water is the basic necessity, an essential element for life and the world's most valuable asset in the prospects of future resources. Despite the fact that almost two thirds of our planet is covered with water only a tiny fraction of less than one percent is available for the needs of mankind as pure and healthy freshwater. Of this, almost all available resources are stored underground (about 99%) from where it must be tapped for drinking water supply as well as for agricultural, industrial and environmental purposes. Hosted in various types of aquifers under different stratigraphic, structural and lithological settings, the groundwater appears at the surface in the form of springs feeding streams and saturated wetlands. While still underground, it provides an estimated 25 to 40% of all drinking water on the planet (http://www.drinking-water.org/html/en/Sources/Where-is-the-Earths-Water.html), it can interact with various minerals in the aquifer, and become enriched in several elements some of which are good for the human health but some are less so and some can be even toxic if the critical concentrations are exceeded.

For a long time drinking water has been used mostly as the tap water accessible in every household in the modern world. In the last few decades, however, the consumption of bottled water increased rapidly (Samek, 2004) since a large number of inhabitants in Europe made a substantial shift in their opinion considering the bottled water to be of better quality than the tap water. Actually, a natural drinking water, either spring or mineral, moved quickly from commodity to fashion. Packed in plastic (polyethylene terephthalate, or PET), or glass bottles became fashionable also in less developed countries. This fashion launched a new and profitable business spreading fast through the consumer goods industry. For example, during the last few years the consumption of bottled water in Croatia increased rapidly as well as the number of mineral and spring water brands found in stores. Almost 329.9 million liters of bottled water (still and sparkling) was sold in Croatia during the year 2007 (http://www.poslovni.hr/79563.aspx).

There was a long-prevailed thought that only the natural water which is pure and without any ingredients such as salts is “healthy”. As a result of many cases of chemical contamination of drinking water in the last two decades (Chatterjee et al., 1995; Das et al., 1995; Barrett et al., 1998; Nkhuwa, 2003; Ćavar et al., 2005) more attention was paid not only to bacteriological but also to the chemical composition of drinking and mineral waters (Misund et al., 1999; Pip, 2000; Ikem et al., 2002; Versari et al., 2002; van der Aa, 2003; Güler, 2007; Baba et al., 2008). For instance, concentrations of arsenic and other 22 trace elements in 18 bottled waters in Croatia were examined by Fiket et al. (2007). Authors stated that the concentrations of all analyzed elements in bottled waters were below the maximum allowable levels according to Croatian, US EPA and WHO standards.

Most of the publications about the chemical composition of bottled mineral waters in Europe are limited to one particular region or

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country. Based on the analysis of 66 elements of 56 European bottled mineral waters Misund et al. (1999) described the clear regional dependency for some elements and large natural variation in concentration for many elements, mainly due to different geological settings. In order to get more spatial information about the natural variation of element concentration in bottled waters the EGS Geochemistry expert group started in 2007 the Pan-European project about the geochemistry of bottled mineral waters in Europe. Within the limits of this project the 886 bottled waters in 39 European countries were collected and analyzed so far. Subsequently, fourteen bottled natural waters (both spring and mineral) were selected for analysis in Croatia, of which five "samples" have been filled at springs situated in Dinaric part and nine originate from Pannonian part of the country (Fig. 1). Given the chemical composition of the collected bottled waters, the aim of this paper was to compare the two geologically and hydrogeologically different regions in Croatia based on statistical methods in order to suggest the rationale for the variability in water chemistry.

2. Materials and methods

2.1. Regional geological settings

The territory of Croatia belongs to the geotectonic systems of Dinarides, Alps and Pannonian Basin. It can be broadly divided into two geological and hydrogeological regions – Pannonian Basin and Dinaric – according to different stratigraphic, lithologic and structural settings along the line running from the southern parts of the Žumberak Mt. to the lower course of the Una River on the east (Croatian Geological Survey, 2009) (Fig. 1). Geologically, this borderline roughly corresponds to the boundary between the southern part of the Pannonian Basin and the northern Dinarides following their distinct geodynamic evolutions which resulted in specific regional geological settings. The Pannonian structures are represented mostly by the allochthonous Triassic and Paleozoic formations together with occurrences of Jurassic ophiolite mélange and deep marine deposits, and Cretaceous shallow marine carbonates,

Fig. 1. Generalized geological map of Croatia with spring/well locations.

Late Cretaceous–Eocene flysch and pelagites and Late Cretaceous–Eocene magmatic and metamorphic rocks (Tari and Pamić, 1998, and references therein). The Neogene extension of the Pannonian Basin System and concurring subsidence processes resulted in several thousand meters thick deposits of siliciclastic sedimentary rocks in the Sava and Drava depressions. Two types of aquifers developed in the region: granular reservoir rocks are predominant in the depressed areas; and karst aquifers developed in the carbonate rocks building a part of the Pannonian Mountains. The latter is more similar to Dinaric karst aquifers due to its prevailing fracture porosity.

Dinaric region occupies the southern parts of the country. Geologically, it comprises a large carbonate succession of the Croatian Karst (External or Outer) Dinarides of great thickness (in some places over 8000 meters) and ranges in age from the Middle Permian to the Eocene (Vlahović et al., 2005 and references therein). As fracture porosity dominates the entire Dinarides the physical hydrogeology of karst aquifers including the type of recharge, permeability and interconnections between fractures and conduits inevitably enhances the vulnerability of the groundwater supply system affecting the water chemistry variability in the karst springs (e.g. Biondić et al., 1998).

2.2. Sampling and analytical procedures

During 2008 fourteen 0.5 l bottles of available Croatian natural waters from randomly selected big stores in different Croatian cities (Zagreb, Varaždin, Osijek, Split and Gospić) were sampled for the purpose of this investigation (Table 1). Big stores were chosen considering their greater turnover with respect to the small ones as well as their proper depots where the stored bottles were not exposed to the direct sunlight. In the two-step simple random sampling five bottles of all available water brands were first collected in each store and then a single bottle from each brand was selected and sent to the laboratory. Among the fourteen samples the two were selected as duplicate samples. All analyses were performed in the Hydro- and Environmental Geochemistry Laboratory of Federal Institute for Geosciences and Natural Resources in Berlin. The analytical work was done within the framework of EGS Geochemistry Expert Group project "Geochemistry of bottled waters in Europe". The analytical methods and detection limits for all analytes are given in Table 2, while the detailed analytical procedures are described in Birke et al. (2010-this issue).

2.3. Statistical analysis

2.3.1. Description of dataset

A suite of 41 variables representing the 14 Croatian brands of bottled natural (both mineral and spring) waters including physical parameters, major ionic constituents and trace elements have been selected for statistical evaluation (Tables 3a and 3b). The sampled waters were roughly divided into specific groups according to geotectonic position of their apposite source locations (REGION), namely Pannonian and Dinaric, as well as according to their previously known mineralization (or absence thereof) which helped them become renowned in the country (MINERALIZATION), explicitly into mineral and spring (non-mineral) brands. Since all mineral waters, irrespective of lithological composition of their water aquifers (parent rocks) originate in the northern, Pannonian, part of the country these samples were excluded at the outset from the data collection with the purpose of the regional comparison. Thus, only the spring waters ($N=10$), five from both regions, have been used in the statistical analysis in the first division. However, a total dataset is utilized to evaluate the differences in chemical composition of mineral and spring waters (10 from Pannonian and 4 from Dinaric region).

Table 1
General data on Croatian bottled waters.

	Brand code	Brand name	Region	Spring name	Mineral/spring
1	CRO001-1	Jamnica	Pannonian	Ivino Vrelo	Mineral
2	CRO002-1	Jamnica	Pannonian	Janino Vrelo	Mineral
3	CRO003-1	Kristina	Dinaric	Unknown	Spring
4	CRO003-2	Kristina	Dinaric	Unknown	Spring
5	CRO004-1	Bistra	Pannonian	Topličica	Spring
6	CRO004-2	Bistra	Pannonian	Topličica	Spring
7	CRO005-1	Studena	Pannonian	Bukovac	Spring
8	CRO006-1	Jana	Pannonian	Sveta Jana	Spring
9	CRO007-1	Kapljice	Pannonian	Apatovac	Mineral
10	CRO008-1	Sveti Rok	Dinaric	Kozjak	Spring
11	CRO008-2	Sveti Rok	Dinaric	Kozjak	Spring
12	CRO009-1	Studenac	Pannonian	Grofova Vrela	Mineral
13	CRO010-1	Cetina	Dinaric	Veliko Vrilo	Spring
14	CRO011-1	Unique	Pannonian	Unique	Spring

Table 2
Analytical methods and detection limits.

Parameter	Unit	Analytical method	Detection limit
pH	–	Potentiometric	–
EC	µS/cm	Conductometric	–
Ca	mg/l	ICP-OES	0.01
K	mg/l	ICP-OES	0.1
Mg	mg/l	ICP-OES	0.01
Na	mg/l	ICP-OES	0.1
Ba	mg/l	ICP-OES	0.001
Mn	mg/l	ICP-OES	0.001
SiO_2	mg/l	ICP-OES	0.05
Sr	mg/l	ICP-OES	0.001
Br	mg/l	IC	0.003
Cl	mg/l	IC	0.01
F	mg/l	IC	0.003
HCO_3	mg/l	titration	2.0
NH_4	mg/l	photometric	0.005
NO_2	mg/l	IC	0.005
NO_3	mg/l	IC	0.01
PO_4	mg/l	ICP-OES	0.02
SO_4	mg/l	IC	0.01
Al	µg/l	ICP-QMS	0.3
As	µg/l	ICP-QMS	0.01
B	µg/l	ICP-QMS	0.1
Cd	µg/l	ICP-QMS	0.001
Co	µg/l	ICP-QMS	0.002
Cr	µg/l	ICP-QMS	0.03
Cs	µg/l	ICP-QMS	0.001
Cu	µg/l	ICP-QMS	0.01
Fe	µg/l	ICP-QMS	0.1
I	µg/l	ICP-QMS	0.2
Li	µg/l	ICP-QMS	0.1
Mo	µg/l	ICP-QMS	0.001
Ni	µg/l	ICP-QMS	0.01
Pb	µg/l	ICP-QMS	0.002
Rb	µg/l	ICP-QMS	0.001
Sb	µg/l	ICP-QMS	0.002
Sc	µg/l	ICP-QMS	0.01
Se	µg/l	ICP-QMS	0.01
U	µg/l	ICP-QMS	0.0005
V	µg/l	ICP-QMS	0.01
Zn	µg/l	ICP-QMS	0.05
Zr	µg/l	ICP-QMS	0.001

2.3.2. Nonparametric statistics

Due to the small number of analyzed samples ($N=14$) comparison between the two different groups of univariate data (contained in the bottled water database) was performed in this work applying the nonparametric alternative to the *t*-test for two independent samples (groups). This approach is much more efficient relative to standard parametric statistics, or ANOVA, which are usually not so reliable if the sizes of the analyzed groups of data tend to be relatively small ($N<50$). Moreover, as the reduction of the data severely affects assumptions of normality nonparametric statistics is still more

Table 3a
Analytical results of physical parameters and major ionic constituents in 14 Croatian bottled waters.

Brand code	Physicochemical properties																		
	pH	EC	Ca	K	Mg	Na	Ba	Mn	SiO_2	Sr	Br	Cl	F	HCO_3	NH_4	NO_2	NO_3	PO_4	SO_4
CRO001-1	7.50	1088	73.3	3.3	28.9	136.0	0.030	0.132	12.7	0.169	0.124	53.30	0.274	638.00	0.491	n.d.	0.63	0.12	15.700
CRO002-1	6.10	3680	105.0	23.7	39.6	846.0	0.033	0.231	12.6	0.497	0.269	239.00	0.623	2154.00	1.030	n.d.	0.63	0.25	109.000
CRO003-1	5.30	341	55.2	0.3	10.5	2.6	0.004	n.d.	2.5	0.220	0.002	2.57	0.048	216.00	n.d.	n.d.	2.08	0.16	7.420
CRO003-2	7.70	345	56.4	0.3	11.1	2.0	0.005	n.d.	2.6	0.229	0.001	2.72	0.049	213.00	n.d.	0.091	2.09	0.02	7.560
CRO004-1	7.50	451	57.6	0.7	24.5	2.8	0.049	n.d.	7.9	0.156	0.004	3.12	0.099	283.00	n.d.	0.043	1.27	0.06	12.700
CRO004-2	5.35	446	55.8	0.6	24.3	2.9	0.049	n.d.	7.8	0.159	0.004	3.12	0.101	284.00	n.d.	n.d.	1.26	0.15	12.700
CRO005-1	7.90	656	92.0	1.3	30.4	13.0	0.038	n.d.	28.0	0.228	0.015	2.23	0.180	437.00	0.569	0.059	0.32	0.06	15.100
CRO006-1	7.80	516	61.8	0.4	34.0	1.7	0.010	n.d.	4.6	0.120	0.005	1.25	0.052	347.00	n.d.	0.042	1.04	0.06	5.790
CRO007-1	6.00	3140	62.5	5.9	26.1	672.0	0.050	0.115	35.7	0.198	1.500	376.00	0.106	1500.04	0.560	n.d.	1.81	0.81	8.220
CRO008-1	5.20	367	53.8	0.2	13.2	4.7	0.014	n.d.	3.3	0.033	0.007	6.65	0.025	233.00	n.d.	n.d.	0.89	0.15	2.820
CRO008-2	7.80	404	60.7	0.3	14.8	4.6	0.017	n.d.	3.5	0.037	0.008	7.60	0.023	251.00	n.d.	0.084	1.17	0.04	3.195
CRO009-1	5.50	960	77.4	11.1	25.1	99.6	0.043	0.002	27.9	0.292	0.171	47.30	1.410	544.00	0.718	0.013	0.12	0.22	32.000
CRO010-1	7.90	340	54.9	0.3	11.0	1.8	0.006	n.d.	2.5	0.236	0.002	2.51	0.044	210.00	n.d.	0.110	2.19	0.04	6.940
CRO011-1	7.60	563	90.2	0.8	19.4	4.6	0.047	n.d.	16.2	0.276	0.001	2.41	0.102	361.00	0.014	0.056	3.22	0.08	12.400

Note: n.d = not detectable.

advantageous in testing the differences between locations (means) and scales (variances) of the two small data collectives (Rock, 1988).

Following the standard procedure in the statistical software package of STATISTICA, Release 7.1 (StatSoft, Inc., 2006), two powerful nonparametric tests were applied to the two-group comparisons, namely, Mann–Whitney *U* test (M–W) for comparing unrelated locations, and Kolmogorov–Smirnov two-sample test (K–S) for comparing overall distribution (both location and spread). For the two tests the same significance level $p<0.05$ (>95% chance for rejection the null hypothesis of the “equality” of the data) is accepted although both are not equally powerful. Appropriately, only in cases where both tests show critical values lower than established significance level the null hypothesis that the two groups of univariate data (hydrochemical composition) derive from the same population is rejected meaning that means across the groups in whatever division are significantly different in magnitude. However, taking into account that K–S test is sensitive not only to differences in locations but also in the data spread it is also worth considering the results meeting only the respective criterion. It becomes obvious that a selection of hydrochemical variables in both divisions will emerge having the characteristic discriminatory potential in spite of the small number of objects and unequal size of groups. Summary statistics for the entire dataset entered into analysis (minima, maxima and medians) is displayed in the breakdown table of descriptive statistics together

Table 3b
Trace element concentrations in 14 Croatian bottled waters.

Brand code	Trace elements									
	Al	As	B	Cd	Co	Cr	Cs	Cu	Fe	I	Li
CRO001-1	2.890	0.1920	298.00	0.00146	0.70000	0.0463	0.62900	0.0580	0.388	66.70	96.500
CRO002-1	2.960	0.4970	2850.00	0.00903	1.14000	0.2460	7.55000	0.2500	3.710	105.00	880.000
CRO003-1	4.100	0.0943	25.30	0.00353	0.03810	0.5960	0.00639	0.2620	1.350	2.76	0.432
CRO003-2	2.220	0.0953	13.30	0.00519	0.04100	0.6870	0.00340	0.4200	0.640	2.41	0.287
CRO004-1	1.020	1.5000	12.70	0.00166	0.00895	0.5680	0.12100	0.1360	0.261	3.20	3.170
CRO004-2	1.510	1.4200	11.60	0.00187	0.00849	0.5350	0.11800	0.2700	0.815	1.97	3.150
CRO005-1	1.010	0.2430	15.10	0.00188	0.02690	0.1650	0.01520	0.0359	0.662	12.70	11.300
CRO006-1	0.942	0.2260	9.27	0.00146	0.01040	0.3330	0.04560	0.0955	0.306	6.49	3.130
CRO007-1	1.630	0.9520	652.00	0.00662	0.10000	0.4390	0.07360	3.6700	2.550	423.00	509.000
CRO008-1	16.600	0.0472	9.02	0.00982	0.02460	0.3470	0.00599	0.4790	15.800	21.90	0.253
CRO008-2	11.900	0.0477	6.65	0.00879	0.02320	0.2590	0.00361	0.4210	5.150	8.75	0.165
CRO009-1	1.780	0.9360	256.00	0.00210	0.01890	0.0823	2.47000	0.0867	0.503	55.40	123.000
CRO010-1	3.060	0.1080	7.63	0.00315	0.01800	0.2390	0.00369	0.2680	0.295	5.96	0.307
CRO011-1	1.260	0.2340	10.50	0.00189	0.05780	0.4690	0.00241	5.3100	0.632	5.09	2.290

Brand code	Trace elements									
	Mo	Ni	Pb	Rb	Sb	Sc	Se	U	V	Zn	Zr
CRO001-1	0.2700	2.2000	0.01040	7.050	0.514	0.0682	0.0145	0.0852	0.0599	0.424	0.03370
CRO002-1	0.3340	5.2800	0.08390	72.000	0.761	0.1470	0.2990	0.1490	0.1460	1.690	0.91800
CRO003-1	1.1200	0.7500	0.06420	0.360	0.228	0.0262	0.1320	0.6600	0.6470	0.831	0.01540
CRO003-2	0.9890	0.1260	0.65000	0.332	0.231	0.0218	0.0876	0.5340	0.5380	0.792	0.01120
CRO004-1	1.0100	0.2410	0.00478	0.904	0.225	0.0369	0.3470	0.8250	0.2680	0.460	0.00151
CRO004-2	1.0000	0.2900	0.00804	0.897	0.239	0.0325	0.3520	0.8290	0.3470	0.567	0.00618
CRO005-1	0.3390	0.1130	0.00805	2.080	0.143	0.0583	n.d.	1.3800	0.0441	1.010	0.00478
CRO006-1	0.3670	0.0594	0.01610	0.566	0.507	0.0387	0.0918	0.9620	1.0100	0.190	0.00553
CRO007-1	0.5900	0.9680	0.06740	3.450	0.702	0.1740	0.1290	0.6690	0.5760	1.960	0.97100
CRO008-1	0.0558	2.6900	0.03660	0.275	0.267	0.0385	0.0369	0.2690	0.2170	1.310	0.03310
CRO008-2	0.0468	0.1130	0.02150	0.266	0.550	0.0299	0.0397	0.3180	0.2130	0.673	0.00652
CRO009-1	0.3470	0.1100	0.00448	31.200	0.870	0.1100	0.0287	0.7070	0.0706	1.150	0.00751
CRO010-1	1.0100	0.0929	0.00690	0.314	0.218	0.0212	0.1040	0.6940	0.6260	1.240	0.03780
CRO011-1	0.1360	0.1230	0.03480	0.238	0.166	0.0718	0.2490	1.1200	0.2670	4.130	0.00762

Note: n.d. = not detectable.

with the results of the tests while the characteristic differences between the groups can be seen by examples in box and whisker plots by the group later in the text.

3. Results and discussion

3.1. Regulations and standards

In the last few years several new regulations were introduced into Croatian law concerning the maximum allowable concentration levels for different kinds of bottled spring and mineral waters, e.g. for natural mineral water and natural spring water (Croatian Official Gazette, 2009a), for water from karst areas (Croatian Official Gazette, 2008), and for table water (Croatian Official Gazette, 2009b). The highest measured concentration for any particular element in Croatian bottled waters is reported in Table 4 and compared with the limits established by the Croatian government together with water standards prepared by the World Health Organization (WHO, 2006), and with the United States of America Environmental Protection Agency drinking water standards (US EPA, 2003). The compared data reveal that the concentrations of almost all analyzed elements in bottled natural waters are below the prescribed maximum limits by Croatian, WHO and US EPA standards. As the Croatian regulations and standards do not prescribe the upper limit for some elements and other determinands in mineral waters as opposed to their spring counterpart even the considerably higher content of B, Na, Cl, NH_4, PO_4 and Br found in CRO007-1 and CRO002-1 is not considered a potential health hazard. Concentrations of boron and sodium found in CRO002-1 and CRO007-1 would exceed the allowable level for natural spring water by almost three times (2850 µg/l) and by more than four times (846 mg/l), respectively. The same can be said of Cl (376 mg/l; CRO007-1), NH_4 (1.03 mg/l; CRO002-1) and PO_4 (0.81 mg/l; CRO007-1) among the major ionic constituents which also exceed the levels defined by standards for natural spring waters but no limits are set for mineral waters. However, caution is needed in the case of rather high concentrations of Br (1.5 mg/l) measured in CRO007-1 which could be potentially hazardous (having a sedative effect) even in mineral water if excessively consumed (Misund et al., 1999).

Table 4
Comparison of maximum measured values in natural bottled waters from Croatia with maximum admissible level allowed by Croatian regulations and with WHO and US EPA drinking water standards given in µg/l.

Element	Bottled water[a]	Natural mineral water[b]	Natural spring water[b]	Water from karst area[c]	Table water[d]	WHO	US EPA
Al	16.60		200.00	200.00	200.00	200.00	50–200.00
Ag	0.0919			10.00			10.00
As	1.50	10.00	10.00	10.00	10.00	10.00	10.00
B	2850.00		1000.00		1000.00	500.00	
Ba	50.00	1000.00		700.00		700.00	
Cd	0.00982	3.00	5.00	5.00	5.00	3.00	
Co	1.14						
Cr	0.687	50.00	50.00	50.00	50.00	50.00	
Cs	7.55						
Cu	5.31	1000.00	2000.00	2000.00	2000.00	2000.00	1000.00
Fe	15.80		200.00	200.00	200.00	300.00	300.00
Hg	n.d.	1.00	1.00	1.00	1.00	6.00	
I	423.00						
Li	880.00						
Mo	1.12					70.00	
Ni	5.28	20.00	20.00	20.00	20.00	70.00	
Pb	0.65	10.00	10.00	10.00	10.00	10.00	
Rb	72.00						
Sb	0.87	5.00	5.00	5.00	5.00	20.00	
Sc	0.174						
Se	0.352	10.00	10.00	10.00	10.00	10.00	50.00
Sn	0.0543						
U	1.38					15.00	20.00
V	1.01			5.00			
Zn	4.13			3000.00		3000.00	5000.00
Zr	0.971						
Ca	105,000.00						
K	23,700.00						
Mg	39,600.00					50,000.00	
Na	846,000.00		200,000.00		200,000.00	200,000.00	
Mn	231.00	500.00	50.00	50.00	50.00	400.00	50.00
SiO_2	35,700.00						
Sr	497.00						
Br	1500.00		10.00		10.00		
Cl	376,000.00		250,000.00		250,000.00	300,000.00	250,000.00
F	1410.00	5000.00	1500.00	1500.00	1500.00	1500.00	2000.00
HCO_3	2,154,000.00						
NH_4	1030.00		500.00	500.00	500.00		
NO_2	1030.00	100.00	500.00	500.00	500.00	3000.00	
NO_3	3220.00	50,000.00	50,000.00	50,000.00	50,000.00	50,000.00	
PO_4	810.00			300.00			
SO_4	109,000.00		250,000.00		250,000.00	250,000.00	500,000.00

n.d. = not detectable.

[a] Maximum values measured in Croatian bottled waters.

[b] Maximum allowed values in natural mineral waters and in natural sping waters by Croatian regulations (Croatian Official Gazette 57/2009).

[c] Maximum allowed values in water from karstic areas by Croatian regulations (Croatian Official Gazette, 56/2008).

[d] Maximum allowed values in table waters by Croatian regulations (Croatian Official Gazette, 92/2009).

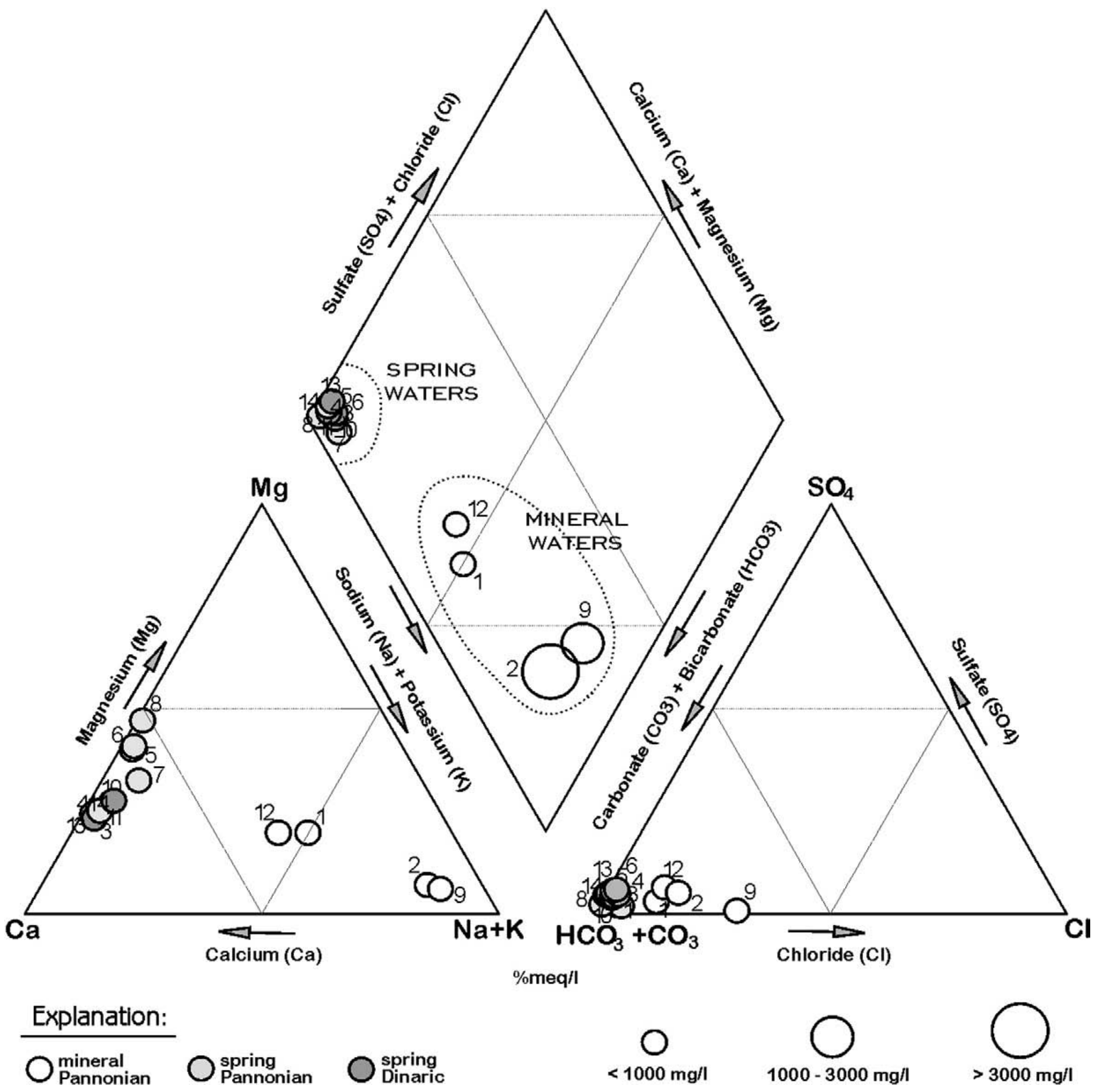

Fig. 2. Piper diagram, showing the major ion chemistry of Croatian bottled waters. Sample numbers are from Tables 1 and 5.

3.2. General hydrochemistry

Differences in chemical composition of Croatian water brands are best displayed on the Piper diagram (Rao, 1998) (Fig. 2) which clearly separates mineral and spring waters, particularly on a trilinear diagram illustrating the main cation concentrations. Conversely, differences displayed by main anion concentrations are much less obvious: all water brands are typically of bicarbonate (HCO_3) type with slightly elevated salinity in the mineral group, particularly in the case of CRO007-1 which contains up to 30% meq/l of Cl. Sulfates are present in almost negligible quantities. Mineral waters, on their part, form two distinct clusters one of which is of strongly Na–K-bicarbonate type (CRO007-1 and CRO002-1) containing over 80% meq/l of Na + K. The other is of a mixed Ca–Na–K-bicarbonate type (CRO001-1 and CRO009-1) with over 40% meq/l of Na + K. These two clusters differ also according to the total concentration of dissolved solids (TDS) (Table 5) which is more than three times greater in the Na–K cluster. Also, the content of trace elements is much greater in mineral waters, which is particularly evident in the case of the most mineralized of all Croatian mineral brands – Jamnica (CRO002-1) – containing almost 4 mg/l of the trace dissolved compounds (Table 5). As a rule, the mineral water brands are at least ten times richer in trace elements with respect to spring water. On the other side, some spring water brands are considerably increased in all major constituents – CRO005-1 and CRO011-1 – which is a trend usually observed in mineral waters (Table 3a). Regularly, all spring waters are of Ca-bicarbonate type, plotted in the region of “temporary

Table 5
Total content of dissolved solids in analyzed waters (in mg/l).

No.	Sample	TDS-1	TDS-2	TDS-3	TDS-4
1	CRO001-1	948.500	14.6730	0.4768	963.6498
2	CRO002-1	3516.300	16.1660	3.9332	3536.3992
3	CRO003-1	294.590	5.0205	0.0398	299.6503
4	CRO003-2	293.080	5.0885	0.0244	298.1929
5	CRO004-1	384.420	9.5845	0.0270	394.0315
6	CRO004-2	383.420	9.5295	0.0260	392.9755
7	CRO005-1	591.030	29.4695	0.0464	620.5459
8	CRO006-1	451.940	5.9325	0.0247	457.8972
9	CRO007-1	2650.760	40.8520	1.6037	2693.2157
10	CRO008-1	314.370	4.4255	0.0697	318.8652
11	CRO008-2	342.195	4.8825	0.0357	347.1132
12	CRO009-1	836.500	30.8890	0.4749	867.8639
13	CRO010-1	287.450	5.1315	0.0223	292.6038
14	CRO011-1	490.810	19.9965	0.0324	510.8389

Note: TDS-1) Standard variables of the Piper diagram; TDS-2) The reminder of major ionic constituents from Table 3a; TDS-3) Sum total of the trace element concentration from Table 3b; and TDS-4) TDS-1 + TDS-2 + TDS-3.

Table 6
Nonparametric statistical tests and breakdown table of descriptive statistics for REGION and MINERALIZATION groups.

Var	p1	p2	REGION						Var.	p1	p2	MINERALIZATION					
			Dinaric ($N=5$)			Pannonian ($N=5$)						Spring ($N=10$)			Mineral ($N=4$)		
			Med	Min	Max	Med	Min	Max				Med	Min	Max	Med	Min	Max
pH	0.841	$p>.10$	7.7	5.2	7.9	7.6	5.35	7.9	pH	0.304	$p>.10$	7.65	5.2	7.9	6.05	5.5	7.5
*EC	0.008	$p<.025$	345.0	340.0	404.0	516.0	446.0	656.0	*EC	0.002	$p<.01$	425.0	340.0	656.0	2114.0	960.0	3680.0
Ca	0.056	$p>.10$	55.2	53.8	60.7	61.8	55.8	92.0	Ca	0.054	$p<.10$	57.0	53.8	92.0	75.35	62.5	105.0
*K	0.008	$p<.025$	0.3	0.2	0.3	0.7	0.4	1.3	*K	0.002	$p<.01$	0.35	0.2	1.3	8.5	3.3	23.7
*Mg	0.008	$p<.025$	11.1	10.5	14.8	24.5	19.4	34.0	Mg	0.054	$p<.10$	17.1	10.5	34.0	27.5	25.1	39.6
Na	0.690	$p>.10$	2.6	1.8	4.7	2.9	1.7	13.0	*Na	0.002	$p<.01$	2.85	1.7	13.0	404.0	99.6	846.0
Ba	0.032	$p<.10$	0.006	0.004	0.017	0.047	0.01	0.049	Ba	0.240	$p>.10$	0.0155	0.004	0.049	0.038	0.03	0.05
Mn	-	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	*Mn	0.002	$p<.01$	n.d.	n.d.	n.d.	0.124	0.002	0.231
*SiO_2	0.008	$p<.025$	2.6	2.5	3.5	7.9	4.6	28.0	SiO_2	0.036	$p<.10$	4.05	2.5	28.0	20.3	12.6	35.7
Sr	0.841	$p>.10$	0.22	0.033	0.236	0.159	0.12	0.276	Sr	0.188	$p>.10$	0.1895	0.033	0.276	0.245	0.169	0.497
Br	0.690	$p>.10$	0.002	0.001	0.008	0.004	0.001	0.015	*Br	0.002	$p<.01$	0.004	0.001	0.015	0.22	0.124	1.5
Cl	0.222	$p>.10$	2.72	2.51	7.6	2.41	1.25	3.12	*Cl	0.002	$p<.01$	2.645	1.25	7.6	146.15	47.3	376.0
*F	0.008	$p<.025$	0.044	0.023	0.049	0.101	0.052	0.18	*F	0.004	$p<.025$	0.0505	0.023	0.18	0.449	0.106	1.41
*HCO_3	0.008	$p<.025$	216.0	210.0	251.0	347.0	283.0	437.0	*HCO_3	0.002	$p<.01$	267.0	210.0	437.0	1069.02	544.0	2154.0
NH_4	0.310	$p>.10$	n.d.	n.d.	n.d.	n.d.	n.d.	0.569	*NH_4	0.008	$p<.025$	n.d.	n.d.	0.569	0.639	0.491	1.03
NO_2	0.548	$p>.10$	0.084	n.d.	0.11	0.043	n.d.	0.059	NO_2	0.076	$p>.10$	0.0495	n.d.	0.11	n.d.	n.d.	0.013
NO_3	0.690	$p>.10$	2.08	0.89	2.19	1.26	0.32	3.22	NO_3	0.106	$p>.10$	1.265	0.32	3.22	0.63	0.12	1.81
PO_4	0.548	$p>.10$	0.04	0.02	0.16	0.06	0.06	0.15	PO_4	0.014	$p<.10$	0.06	0.02	0.16	0.235	0.12	0.81
SO_4	0.056	$p<.10$	6.94	2.82	7.56	12.7	5.79	15.1	SO_4	0.024	$p<.10$	7.49	2.82	15.1	23.85	8.22	109.0
*Al	0.008	$p<.025$	4.1	2.22	16.6	1.02	0.942	1.51	Al	0.839	$p>.10$	1.865	0.942	16.6	2.335	1.63	2.96
*As	0.008	$p<.025$	0.0943	0.0472	0.108	0.243	0.226	1.5	As	0.240	$p>.10$	0.167	0.0472	1.5	0.717	0.192	0.952
B	0.548	$p>.10$	9.02	6.65	25.3	11.6	9.27	15.1	*B	0.002	$p<.01$	11.05	6.65	25.3	475.0	256.0	2850.0
*Cd	0.008	$p<.025$	0.0052	0.0032	0.0098	0.0019	0.0015	0.0019	Cd	0.733	$p>.10$	0.0025	0.0015	0.0098	0.004	0.0015	0.009
Co	0.421	$p>.10$	0.0246	0.018	0.041	0.0104	0.0085	0.0578	Co	0.054	$p<.10$	0.0239	0.0085	0.0578	0.4	0.0189	1.14
Cr	0.841	$p>.10$	0.347	0.239	0.687	0.469	0.165	0.568	Cr	0.076	$p>.10$	0.408	0.165	0.687	0.164	0.0463	0.439
Cs	0.151	$p<.10$	0.0037	0.0034	0.0064	0.0456	0.0024	0.121	Cs	0.008	$p<.10$	0.0062	0.0024	0.121	1.55	0.0736	7.55
Cu	0.310	$p>.10$	0.42	0.262	0.479	0.136	0.0359	5.31	Cu	0.454	$p>.10$	0.269	0.0359	5.31	0.168	0.058	3.67
Fe	0.222	$p>.10$	1.35	0.295	15.8	0.632	0.261	0.815	Fe	0.839	$p>.10$	0.651	0.261	15.8	1.527	0.388	3.71
I	0.841	$p>.10$	5.96	2.41	21.9	5.09	1.97	12.7	*I	0.002	$p<.01$	5.525	1.97	21.9	85.85	55.4	423.0
*Li	0.008	$p<.025$	0.287	0.165	0.432	3.150	2.29	11.3	*Li	0.002	$p<.01$	1.361	0.165	11.3	316.0	96.5	880.0
Mo	1.000	$p>.10$	0.989	0.0468	1.12	0.367	0.136	1.010	Mo	0.539	$p>.10$	0.678	0.0468	1.12	0.341	0.27	0.59
Ni	0.548	$p>.10$	0.126	0.0929	2.69	0.123	0.0594	0.290	Ni	0.188	$p>.10$	0.1245	0.0594	2.69	1.584	0.11	5.28
Pb	0.151	$p>.10$	0.0366	0.0069	0.65	0.008	0.0048	0.0348	Pb	0.839	$p>.10$	0.0188	0.0048	0.65	0.039	0.0045	0.084
Rb	0.151	$p<.10$	0.314	0.266	0.36	0.897	0.238	2.080	*Rb	0.002	$p<.01$	0.346	0.238	2.08	19.125	3.45	72.0
Sb	0.421	$p>.10$	0.231	0.218	0.55	0.225	0.143	0.507	*Sb	0.004	$p<.025$	0.2295	0.143	0.55	0.732	0.514	0.87
Sc	0.032	$p<.10$	0.0262	0.0212	0.0385	0.0387	0.0325	0.0718	*Sc	0.004	$p<.025$	0.0347	0.0212	0.0718	0.129	0.0682	0.174
Se	0.310	$p>.10$	0.0876	0.0369	0.132	0.249	n.d.	0.352	Se	0.635	$p>.10$	0.0979	n.d.	0.352	0.079	0.0145	0.299
*U	0.008	$p<.025$	0.534	0.269	0.694	0.962	0.825	1.38	U	0.142	$p>.10$	0.7595	0.269	1.38	0.409	0.0852	0.707
V	0.841	$p>.10$	0.538	0.213	0.647	0.268	0.0441	1.01	V	0.188	$p>.10$	0.3075	0.0441	1.01	0.108	0.0599	0.576
Zn	0.421	$p>.10$	0.831	0.673	1.31	0.567	0.19	4.13	Zn	0.454	$p>.10$	0.8115	0.190	4.13	1.42	0.424	1.96
Zr	0.016	$p<.10$	0.0154	0.0065	0.0378	0.0055	0.0015	0.0076	Zr	0.054	$p>.10$	0.0071	0.0015	0.0378	0.476	0.0075	0.971
*TDS	0.008	$p<.025$	299.65	292.60	347.11	457.90	392.98	620.55	*TDS	0.002	$p<.01$	370.04	292.60	620.55	1828.43	867.86	3536.40

Note: p1 = M–W *U* test (2*1 sided *p* exact); p2 = K–S test (*p*-level); all tests are significant at $p<0.05$ (marked with asterisk); n.d. = not detectable.

hardness" on a diamond diagram (Hounslow, 1995). Characteristic differences, though, can be easily detected along the Ca–Mg axis of the cation diagram where the subtle split occurs between the Dinaric and Pannonian brands (Fig. 2). The latter are richer in Mg which in the case of CRO006-1 approaches almost ideal mixture very desirable for drinking purposes (50% Ca–50% Mg), with one exception (CRO011-1) sourcing in the Pannonian region that exhibits concentration of the major ionic constituents almost identical to its Dinaric counterpart (richer in Ca).

3.3. Statistical tests

The results of nonparametric statistical tests (Table 6) highlight a number of variables as the main source of variance between the groups in both divisions. Some of these, such as EC, K, F, HCO_3, Li, and particularly TDS, are strongly emphasized in separating mineral and spring water brands but also in separating the spring water brands sourcing in Pannonian and Dinaric regions. In both divisions major ionic constituents and trace elements seem to stand in equal discriminatory importance although the latter are slightly less accentuated. Irrespective of the concentrations far lower than tolerated by quality regulations (Table 4) these, however, must not be passed over as in both cases there are potentially toxic trace metals. For example, arsenic which is characteristic for Pannonian spring waters exceeds its Dinaric counterparts by order of magnitude (0.226–1.5 µg/l against 0.0472–0.108 µg/l), while differences are slightly lower for cadmium being more typical for Dinaric and mineral brands, respectively (Table 6, Fig. 3). Some trace metals do not show systematic variation across the groups despite their considerably elevated concentrations in some brands (Pb in CRO003-2, Co in CRO002-1, Cu in CRO007-1 and CRO0011-1 or, Fe in CRO008-1 also SO_4 in CRO002-1).

As shown by the tests, the most indicative variables among the ten regionally distributed spring water brands (REGION) are represented by EC, K, Mg, SiO_2, F and HCO_3 (major ionic constituents and physical parameters assemblage, Table 3a) as well as by Al, As, Cd and Li (trace elements assemblage, Table 3b). To some degree Ba and Zr could be also allowed to join this assembly of variables although it was determined only by the location-sensitive M–W test that the two observed groups (Dinaric and Pannonian) differ significantly (at $p<0.05$ level). A selection of variables is displayed on the box and whisker plots summarizing characteristic differences between the groups (Fig. 3). Characteristically, separation between the spring waters is shown in higher values for all variables in Pannonian brands except for Al and Cd (and Zr), which are more abundant in the Dinaric brands. For above mentioned variables of established significant

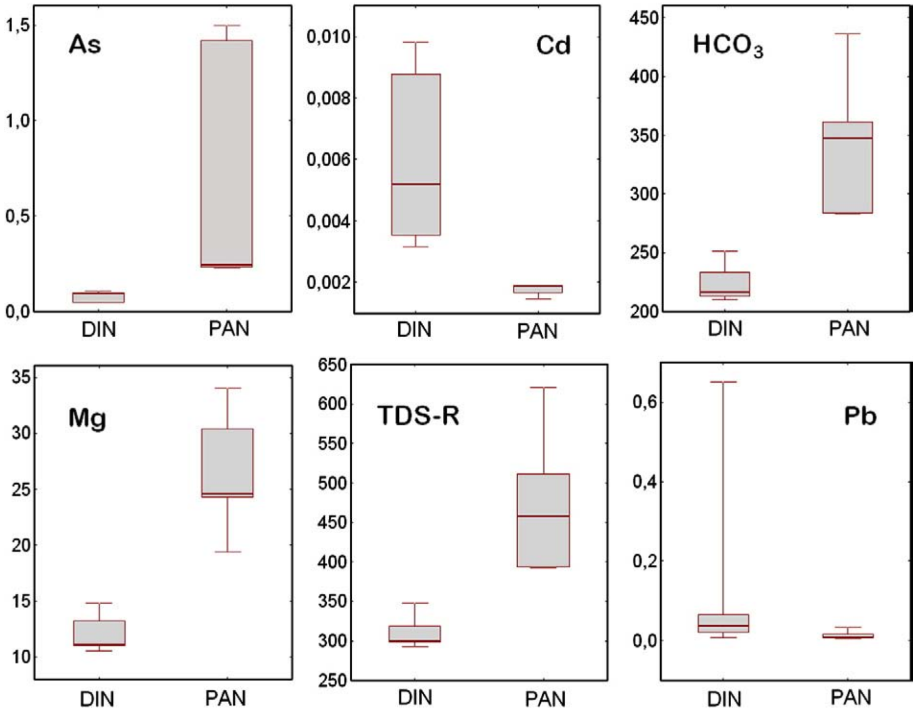

Fig. 3. Box and whisker plots of selected geochemical bottled water parameters in REGION division; the middle horizontal line is the median value; box covers the interquartile range (25th–75th percentile); whiskers are at minimum and maximum. Notes: DIN = Dinaric, PAN = Pannonian; TDS-R stands for total dissolved solids in REGION division.

differences no overlapping is shown between minima and maxima in either group, a strong reason to ponder on different origin of dissolved matter in the analyzed waters. To this effect, the variable most captivating is the total content of dissolved substances (TDS) which is not only the powerful indicator of mineral waters but also makes a substantial difference between the Dinaric and Pannonian spring waters, something that is not readily seen on the Piper diagram. The ten analyzed Dinaric and Pannonian spring waters (5 + 5) show TDS ranging from 292.6–347.11 mg/l to 392.98–620.55 mg/l, respectively. Typically, aside from total separation of values a considerably larger concentration range is also displayed for Pannonian brands, a result indicating again the major differences in rock types building the two geotectonic regions in Croatia. It shows that geological diversity represented by characteristic mineral assembly of the aquifer rock,

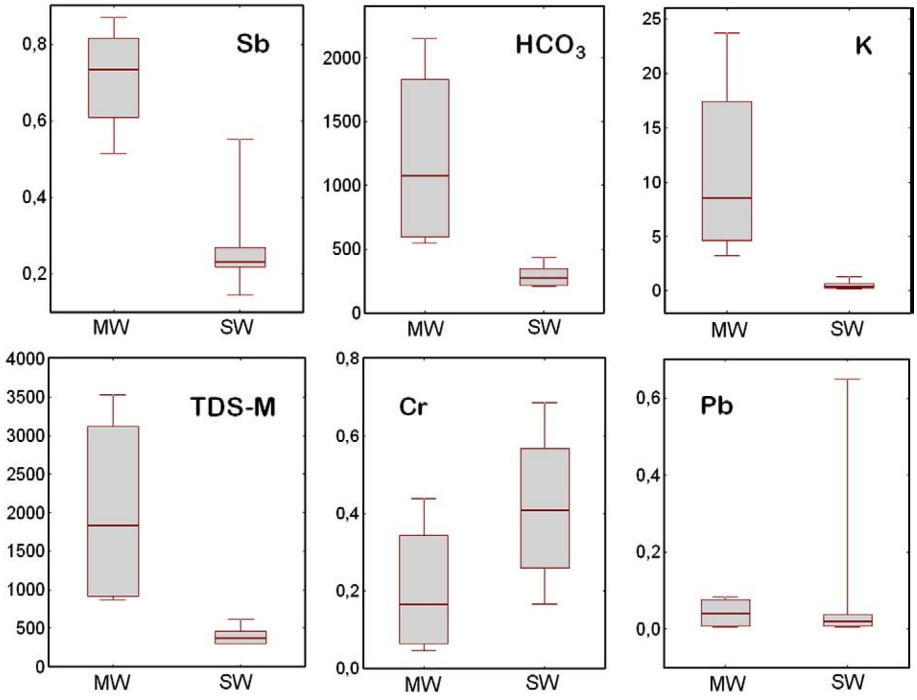

Fig. 4. Box and whisker plots of selected geochemical bottled water parameters in MINERALIZATION division; the middle horizontal line is the median value; box covers the interquartile range (25th–75th percentile); whiskers are at minimum and maximum. Notes: MW = mineral waters, SW = spring waters; TDS-M stands for total dissolved solids in MINERALIZATION division.

relative abundance of particular minerals and their solubility is the most influential factor on water quality (Edmunds et al., 2003).

Due to the small numbers of mineral water brands in Croatia as well as to their long-known beneficial quality as regards the human health the data on label of the bottle was easy and quite a self-evident criterion for their classification into the proper division (MINERALIZATION). However, it remains veiled what is exactly the content of the dissolved compounds accountable for the difference because at the market the bottle declaration labels usually contain only concentration of major ions and ionic complexes given by the water producers. The confusion becomes even greater as the criteria for the classification of mineral waters according to the EU mineral water directive tend to blur the boundary towards the spring waters (see van der Aa, 2003). If TDS is strictly applied as a standard, the majority of Croatian spring water brands would be properly classified as the mineral water types with low mineral concentration and some of these even with intermediate mineral concentration. In spite of this, since the Croatian regulations set the minimum limit of 1000 mg/kg of total dissolved solids for mineral waters (Croatian Official Gazette, 2009a), two of four analyzed mineral water brands from Croatia (CRO002-1 and CRO007-1) unquestionably fall into this class on the compositional basis. The remaining two (CRO001-2 and CRO009-1) that are slightly below this limit (TDS = 964 mg/kg and 867 mg/kg, respectively) are included into the group taking into account historical roots (long-known and renowned brands in the country). The tests conducted showed that more variables are significant concerning the differences between the mineral and spring waters (MINERALIZATION) than in the REGION division. These include EC, K, Na, Mn, Br, Cl, F, HCO_3, NH_4 among physical parameters and major ions, together with B, I, Li, Rb, Sb and Sc among the trace elements, and finally TDS (Table 6). All of these are present in higher concentrations in the mineral water brands. As in the REGION division (Dinaric vs. Pannonian) no overlapping occurs between the mineral and spring brands for variables of statistically significant difference save from F, Sb and Sc where minima of mineral intersect maxima of spring waters. As can be clearly seen from the box and whisker plots (Fig. 4) the mineral waters are characteristic for their very wide concentration range (including interquartile range). This is particularly distinctive for EC, TDS, HCO_3, K, Na and Li but also of Co, Cs and Zr which, however, are not significantly different. On the other side, some trace elements and ionic complexes (Cr, U, V and NO_3) in the treated dataset are generally more abundant in spring waters although, again, at a non-significant level. By the same token, trace elements such as Al, Fe, Pb and Zn have almost identical spread in both types of waters under the MINERALIZATION division with a single high value in the non-mineral realm and mostly from Dinaric region (except Zn) (example relative to Pb in Figs. 3 and 4). Also, it must be noted that some variables such as electrical conductivity (EC) and the quantity of the total dissolved solids (TDS) are so closely associated, whether in mineral or spring water brands, that their Spearman's rank (non-parametric) correlation coefficient reveals a practically functional relationship. In spring waters it is close to unity ($r = 0.988$) while in their mineral counterpart it actually assumes the unit value ($r = 1.000$). Considering that EC measurements often offer an advantage to analytical TDS as a relatively quick and reliable field method of determining the content of ionic species, particularly in continuous monitoring of water, soil and environmental chemistry (Hayashi, 2004), it is useful to determine the relationships between these variables (TDS mg/l $= A \times \mathrm{EC}_{25}$ µs/cm). Conversion factor A (according to Hem, 1985) varies between 0.55 and 0.75 and was found 0.65 as the best approximation for the European mineral waters (van der Aa, 2003). However, for Croatian mineral waters this value is found as 0.91 in average (0.86–0.96) while for spring waters it is slightly less and amounts to 0.89 (0.86–0.95). These data again point at generally increased mineralization even of the spring bottled waters of which some, such as CRO005-1 (TDS = 620.5 mg/l; EC = 656 µs/cm) and CRO011-1 (TDS = 510.8 mg/l; EC = 563 µs/cm) exceed the values set by standards and regulations.

3.4. Bottled water types and regional geology

In broad geochemical terms the results presented above are well in concordance with division of the entire territory of Croatia into two very distinct regions based on structural and regional geology. As recent results of geochemical mapping of Croatia show (Halamić and Miko, 2009) the lithology of Dinaric (Adriatic) carbonate platform and Pannonian Basin has strong impact on geochemical composition of the soil cover developed over the outcropping bedrock. Geochemical differences are so clear that virtually no room is left for possible confusion and the present research on the chemical characteristics of Croatian bottled waters confirm the two existing geochemical groundwater provinces, reflecting regional and structural division. Mineral water aquifers are present only in the Pannonian region and are associated with characteristic rocks rich in Na and K, namely basic volcanic rocks (basalt and spilite) and, sometimes, sedimentary siliciclastic rocks (sandstone and siltite). Prolonged existence of the currently active springs, some of which date back from Bronze Age (according to artefacts found nearby), together with more than 120 years of unchanged chemical composition and concentration of dissolved compounds (CRO002-1) (Bukovac and Šimunić, 2008) indicate that mineral waters in Croatia are not only of mixed origin (basically originating from fossil groundwater) but in some cases are also highly rechargeable (CRO002-1 and CRO007-1). This implies more or less constant rechargeable events allowing the meteoric water to penetrate deep into the aquifer, mix with fossil water of older age (Pannonian Basin natural brines found in oil wells) and be involved in the dissolution processes of the host volcanic or siliciclastic rock (hydrolysis) releasing major and trace element cations (Šimunić and Hećimović, 2002; Mraz et al., 2008). However, in other cases (CRO009-1) depletion in some anions and anion complexes such as iodine (from 17 mg/l during the period of 1839–1885, down to present 55.4 µg/l) suggests a steady loss of the fossil groundwater deriving its origin from the deep seated brines (Pannonian sea residue) due to exploitation (Czukor et al., 1995; Bukovac and Šimunić, 2008).

Characteristic richness of anionic complexes in some bottled mineral waters, for example SO_4 (109 mg/l) in CRO002-1, can be explained by migration of fluids (gases and brines) from the oil reservoir caps along the deep reaching faults that cut the groundwater aquifers. In the case of CRO009-1, elevated concentrations of SO_4, NH_4, Cl and F ions probably follow the same destiny as iodine mentioned above pointing at isolation of the aquifer with fossil groundwater and/or constant dilution with meteoric waters from above. The origin of HCO_3 is especially interesting, as the elevated quantity of CO_2 is not characteristic only for mineral waters, such as CRO002-1 and CRO007-1 in particular. According to some models the relationship between Ca, Mg and bicarbonate ions in mineral waters (CRO007-1) indicates that abundance of bicarbonates results from dissolution of limestones and dolomites as well as dissolution of CO_2 already present in the aquifer (Mraz et al., 2008). Older works (Miholić, 1952) explain the genesis of CO_2 in the process of silicification of carbonate rocks — Triassic–Jurassic carbonate complex usually underlying Cretaceous volcanic-sedimentary formation in the Pannonian region — at the great depths and its subsequent migration to the (mineral) aquifer or to the surface along the deep rooted faults. These discontinuities can also explain the great capacity of some springs (up to 30 l/s in the case of CRO002-1), which suggests still another possible origin of mineral waters in the parts of Pannonian Basin, namely, their close association with thermal waters. Such considerable spring capacity requires an extensive karstic aquifer, supplying, for example, a number of spas in the northwest Croatia. Thus, a greater but poorly mineralized body of hot thermal water together with gases wells up from the karstified carbonate rocks into fractured and crushed volcanic-sedimentary complex above and mixes with its strongly mineralized but smaller body of water. High concentrations of Ca (105 mg/l) and Mg (39.6 mg/l) in CRO002-1 in spite of the absence of carbonate rocks in volcanic-sedimentary series support this model (Bukovac and Šimunić, 2008).

The origin of spring waters in the Pannonian region that are suitable for exploitation is associated with various types of unconfined aquifers allowing constant recharging by vadose waters from the surface except in the case of artesian waters such as CRO006-1 (Jana) which is by now one of the most popular and rewarded natural spring waters. This water is exceptionally hydrogeologically protected from any pollution as it derives from the Triassic dolomite rocks overlain at the depth of 800 m by the Neogene siliciclastic deposits. The long journey from the surface and dissolution of carbonate aquifer ensured the well-balanced relationship of Ca and Mg (http://www.finewaters.com/Bottled_Water/Croatia/Jana.asp). Impermeability here is not as high as in the case of other, non-artesian, natural waters springing in the Pannonian region. For example, the natural spring water from the Kalnik Mt. (CRO011-1) is found in aquifers potentially vulnerable in the hydrogeological sense due to their shallow emplacements — Upper Miocene porous “lithothamnium” limestones. Its high quality has been, however, supported until now by low population density and the absence of potential contaminating agents (witnessed by very low NO_2, NH_4 and PO_4). Typically, all natural spring waters originating in the Upper Miocene limestones, including CRO011-1, are distinguished by lower Mg and HCO_3 compared with those in older Palaeogene sedimentary rocks, mostly breccias (Mraz et al., 2008) ranking them closely to the waters from the Dinaric region (Fig. 2). The water samples CRO004-1 and CRO004-2 accumulate within vadose zone in the crushed and cavernous Triassic dolomites being recharged most probably from the northern slopes of the Medvednica Mt. The water is bottled from several springs and a single deep well (Marković et al., 2008). Sample CRO005-1 is also sourcing inside the Triassic dolomites. Based on its slightly increased mineralization (TDS>620 mg/l) it is assumed that the main body of water originates from the Neogene deposits (Jamičić and Crnko, 2008).

As a rule, the natural spring waters bottled from karstic springs in the Dinaric region are considerably less mineralized (TDS = 292.6–347.1 mg/l) relative to their Pannonian counterparts (TDS = 393.0–621.5 mg/l) (Tables 5 and 6; Fig. 3). Almost purely carbonate (limestone) bedrock of the Dinaric carbonate platform gives rise to specific hydrogeochemical facies. However, the natural chemistry of the karst groundwater is generally highly liable to change due to anthropogenic impacts. If unprotected, the Dinaric karst aquifers, particularly the spring zones, respond to the slightest change in environmental conditions (Biondić et al., 1998). Trace elements in such aquifers are obvious tracers of surface water–groundwater interaction and total metal transport to the karst springs is usually performed after the storm surface events (flows) either by particulates controlled by physical processes, or by colloids controlled by coagulation processes (Vesper and White, 2003 and references therein). As most of the karst aquifers in the Dinaric region are recharged by the surface flow after heavy precipitations at the high altitudes (up to 4000 mm per year; Bonacci, 1987) part of the dissolved material is expected to come from the soil cover. Topsoil in the high mountainous ranges of the Dinaric region, stretching along the Adriatic coast (Velebit Mt.) and farther in the hinterland (Dinara Mt.) is considerably loaded with trace metals such as Pb, Ni, V, Co, Cr, Cd, Zn and Zr in particular, originating from anthropogenic, atmospheric pollution (Miko et al., 2004; Halamić and Miko, 2009). However, all sampled waters bottled at five karst springs in the Dinaric region (Lika and Dalmatia) show very low content of trace elements, which is significantly lower with respect to the Pannonian brands except in few cases — almost a perfect symmetry to the topsoil geochemistry. Thus, one of the functions of soils (particularly the forest soils) acting as filter in capturing the contaminants as the water percolates downward is fully accomplished. Higher content of Pb (0.65 µg/l), which is still well under the permissible limit, found in CRO003-2 bottled from a spring situated at the southern foot slopes of the Dinara Mt., can result from pollution at unknown distance and moved to the spot through the intricate karst system of interconnected fractures and conduits. Also, an increased content of Al and Fe, considerably higher relative to all other spring water brands, is found in CRO008-1 and CRO008-2 (Table 3b) indicating that Al and Fe in adjacent aquifer might have been dissolved in water as inorganic colloidal species (from the Lower Triassic clayey siliciclastic sedimentary rocks) but with minimum trace element absorbents. Therefore, a spring unaffected by the heavy metal content present in the soil cover distributed over the wider area must deserve its present status (natural spring water of high quality) as a result of favorable geomorphologic, lithologic, stratigraphic and structural controls protecting the aquifer from contamination.

4. Concluding remarks

The results obtained in this study show that stratigraphic, lithological and structural constraints on the aquifer placement rather than human impact dictate the water chemistry in the analyzed set of bottled spring and mineral waters in Croatia. Although concentrations observed for single elements can encompass about three orders of magnitude (e.g. Na, B, Br, Li), depending largely on the aquifer lithology from which investigated water originate, not a single one out of 14 bottled waters from Croatia exceeds the Croatian water standards. All substantially increased and thus potentially problematic concentrations observed for Na, Cl, B, Br, NH_4 and PO_4 belong to the mineral waters. However, no drinking water standards for this set of elements in mineral waters were established in Croatian legislation so that their content is tacitly accepted as passing without observable health effects.

According to the statistical analysis the water chemistry is found in high concordance with regional distribution of springs and associated aquifers from which the analyzed bottled waters originate. Actually, an á priori established regional division in the statistical testing (Pannonian vs. Dinaric) is commensurable with provisional (set for exploratory purposes) speculative geochemical groundwater provinces being highly dependent on the lithological hosts of investigated waters. A closer look at the data allows the several conclusions to be made:

- All analyzed natural bottled waters from Croatia belong to the bicarbonate (HCO_3) type with well balanced Ca–Mg relationship in the spring water realm and dominant Na–K signature characterizing the mineral water types. However, the spring waters from the Pannonian region show the trend of increased concentration of Mg, whereas mineral waters tend to be enriched in Cl.
- Mineral waters are spatially confined to the Pannonian region due to the characteristic geological, particularly lithological, features and structural placements of their aquifers. Geochemistry of mineral waters is characterized by considerably higher values in comparison with their spring complements. This is particularly evident in the case of EC and TDS, then K, Na, Mn, Br, Cl, HCO_3 and NH_4 among the major ionic species as well as among B, I, Li and Rb among the trace elements, where no overlapping occurs between the maximum values of spring waters and minimum values of mineral waters. Elemental concentrations in mineral waters are from three to over 200 times higher for elements of statistically significant difference (3.19 for Sb–232.18 for Li; expressed as median ratios) than in spring waters indicating great difference in mineralization.
- Spring waters from the two investigated regions – Pannonian and Dinaric – are chemically substantially different by means of the values of EC and TDS as well as concentration of K, Mg, SiO_2, Al, As,

Cd, Ba and Zr. All of these constituents are present in higher quantities in Pannonian spring waters except in the case of Al, Cd and Zr which are more abundant in their Dinaric counterpart (from 1.50 for EC to 10.98 for Li, expressed as median ratios for elements of statistically significant difference).

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