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Characterization of Bottled Waters by Multielemental Analysis, Stable and Radiogenic Isotopes

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Received: 24 July 2020; Accepted: 27 August 2020; Published: 31 August 2020

Abstract: Multi-elemental (Ca, Mg, Na, K, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Ti, V, and Zn) and stable isotope (i.e., δ²H, δ¹⁸O, and δ¹³C(DIC)) analyses were performed on 13 (8 Slovenian and 5 imported) bottled mineral and spring waters from the Slovenian market. In addition, ⁸⁷Sr/⁸⁶Sr isotope ratios were determined for the first time. In all analyzed bottled waters, the majority of elements were present although in low concentrations, and according to EU legislation, all were suitable for human consumption. Also, concentrations of major elements (Ca, Mg, Na, and K) were in general agreement with the values reported on the bottle labels, and any differences were the consequence of the natural variability of the water source used for bottling. The exception was one spring water, for which the source location changed, which was confirmed by the δ²H, δ¹⁸O, and δ¹³C(DIC) data. Two mineral waters had distinctive elemental compositions due to the particular geology of their recharge areas. The δ¹³C(DIC) was also investigated to decipher the carbonate contribution in the bottled waters. The results suggest that dissolution of carbonates and non-equilibrium carbonate dissolution by carbonic acid produced from soil zone CO₂ are the predominant geochemical processes influencing the δ¹³C(DIC) values of bottled water.

Keywords: bottled waters; multielemental analysis; ⁸⁷Sr/⁸⁶Sr; δ²H; δ¹⁸O; δ¹³C(DIC); water quality; Slovenian market

1. Introduction

Bottled water is the most popular beverage in the world, and sales continue to grow year-on-year. Estimated global consumption in 2007 was 212 billion liters and 437 billion liters in 2017 [1]. More than 25% of the global bottled water production is located in the EU, where 52 billion liters of bottled water are consumed each year [2]. This increase in consumption of bottled water can be attributed to the claims about its higher quality compared to tap water and its health benefits. Bottled water is classified into mineral, spring, and table water according to the Council Directive 80/777/EEC [3]. Their properties are described in detail in EU Directive 2009/54/EC [4]. In both the Drinking Water Directive (98/83/EC) [5] and for bottled waters in more detail in Commission Directive 2003/40/EC [6] the quality requirements for water intended for human consumption with threshold levels for toxic substances are laid down. According to national legislation/regulations, only the concentrations of the major elements must be declared on the label.

Waters used for bottling originate from various parts of the hydrological cycle and have a distinctive hydro-geochemical fingerprint. The natural origin of the water is reflected in its hydrogen (δ²H), oxygen (δ¹⁸O), carbon as dissolved inorganic carbon (δ¹³C(DIC)) values, strontium isotope ratio (⁸⁷Sr/⁸⁶Sr), and elemental composition, among others. Additionally, its composition may be affected...
by handling operations after extraction from the source [7,8] and by leaching from storage containers (glass or plastic) [9–12].

Elemental composition and \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratio of water are linked to the geology of the recharge area. Both are traditional geochemical tracers and used mainly for defining lithological sources (silicate and carbonate rocks) and the percentage of silicate/carbonate fraction in groundwater [13,14] since they are controlled by water-rock interactions [15]. The isotopic composition of oxygen and hydrogen (i.e., \(\delta^{18}\text{O}\) and \(\delta^{2}\text{H}\)) in the water molecule changes as the water circulates through the water cycle. Significant variations in \(\delta^{18}\text{O}\) and \(\delta^{2}\text{H}\) values in precipitation (i.e., the ultimate water source for surface and groundwater) depend on latitude and altitude [16]. Therefore, determining \(\delta^{18}\text{O}\) and \(\delta^{2}\text{H}\) can help to characterize the origin of the bottled water and the natural conditions of the parent water body, recharge area and the influence of different processes during infiltration and the flow of water through the water body [7]. Dissolved inorganic carbon (DIC) is the main species in waters draining from carbonate rocks; therefore, carbon isotopes can be used to assess its origin. Changes in dissolved inorganic carbon concentrations result from the addition and removal of carbon from the DIC pool [17].

The importance of collecting different data on the elemental and isotopic composition of bottled waters is twofold. First, since the composition of natural waters varies even in the absence of pollution sources, the collected data can be used to create meaningful standardized limits for potentially toxic constituents. Secondly, due to the increasing consumption of bottled water and consequently, higher economic value, the data can help protect the quality and origin of bottled natural mineral and spring waters. Several studies investigating the chemical composition and origin of the bottled water using \(\delta^{2}\text{H}, \delta^{18}\text{O}, \delta^{13}\text{C}_{\text{DIC}}, \, ^{87}\text{Sr}/^{86}\text{Sr}\), and elemental analyses together or separately have been published. Frengstad et al. [18], Birke et al. [19], and Filipe-Sotelo et al. [8] characterized bottled water based on major and trace elemental composition, while Montgomery et al. [20], Voerkelius et al. [21], and Kim et al. [14] used multielemental and Sr isotope data for the geochemical assessment of bottled waters. Brenčič and Vreča [7,22], Redondo and Yélamos [23], and Raco et al. [24] used stable isotope composition of light elements (i.e., \(\delta^{2}\text{H}, \delta^{18}\text{O}, \text{and } \delta^{13}\text{C}_{\text{DIC}}\)) for the characterization and classification of bottled waters.

Slovenia has abundant water resources, with 272 km\(^{2}\) of Slovenia’s territory covered by water [25], and an extensive groundwater system. Due to climate change and extended periods of drought, the situation could change in the coming years. A detailed characterization of bottled water available on the Slovenian market based on their elemental and isotopic (\(\delta^{2}\text{H}, \delta^{18}\text{O}, \delta^{13}\text{C}_{\text{DIC}}\)) composition was performed in 2004 by Brenčič and Vreča [7,22,26], and in 2008 additional elemental investigations were performed by Brenčič et al. [27]. In the past, it was proposed that isotopic and elemental investigations of bottled waters should continue; however, according to our best knowledge, there have been no systematic follow-up studies. Moreover, there is no data on the \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratio available for any type of bottled water samples from Slovenia. Therefore, the main objective of the present study was to characterize Slovenian spring and natural mineral bottled waters as well as the most popular bottled waters from the EU available on the Slovenian market using multi-elemental and multi-isotope analyses. We aimed to (i) determine the \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratio in bottled spring and natural mineral waters, (ii) compare the data with data from previous investigations, (iii) compare label vs. analytical values, (iv) verify compliance with regulatory demands, and (v) evaluate the geochemical processes to determine, e.g., the type of aquifer (geological composition).

2. Materials and Methods

2.1. Samples and Sampling Procedure

Examples of the popular Slovenian mineral water brands (8 samples) and imported (5 samples) were collected from supermarkets across Slovenia in 2016. Table 1 lists the mineral waters by type, brand, and source/origin. The survey was focused only on still waters. All samples were stored in plastic (PET) bottles.
Table 1. List of natural mineral and spring bottled waters

| Bottled by      | Brand      | Type                      | Source         | Country of Origin |
|-----------------|------------|---------------------------|----------------|-------------------|
| Radenska Naturelle | Natural mineral water | Radenci          |                | Slovenia          |
| Dana Dana       | Natural mineral water | Mirna             |                | Slovenia          |
| Union Brewery Zala | Spring water | Ljubljana        |                | Slovenia          |
| Voda Julijana Julijana | Spring water | Tržič             |                | Slovenia          |
| Laško Brewery Oda | Natural mineral water | Rimske Toplice | Slovenia       | Slovenia          |
| Plasticna Kaplja | Natural mineral water | Radomlje        |                | Slovenia          |
| Voda 902 Voda 902 | Spring water | Črnievec       |                | Slovenia          |
| Costella Costella | Natural mineral water | Fara             |                | Slovenia          |
| Jamnica Jana     | Natural mineral water | Gorice Svetojanske | Croatia     | Croatia           |
| Vodavoda Vodavoda | Spring water | Gornja Toplica      | Serbia         | Serbia            |
| Aquamarque Laqueuille | Spring water | Pay-de-Dôme         | France        | France            |
| Danone Evian     | Natural mineral water | Evian-les-Bains   |                | France            |
| Coca-Cola HBC Römerquelle | Natural mineral water | Edelstal and Prellenskirchen | Austria | Austria |

2.2. Analytical Procedures

2.2.1. Determination of Major and Trace Elements

Dissolved trace elements were determined using an Agilent 7900x inductively coupled plasma mass spectrometer (ICP-MS, Agilent Technologies, Tokyo, Japan). Two surface water reference materials: SLRS-5 (National Research Council Canada, Ottawa, Ontario, Canada) and SPS-SW1 (Spectrapure Standards, Manglerud, Norway), were used for the accuracy check and analyzed multiple times during the measurements; recoveries varied between 97% and 102%. Repeatability was > 5%.

2.2.2. Determination of \(^{87}\text{Sr}/^{86}\text{Sr}\) Isotope Ratio

Samples (1–30 mL) for Sr isotope analysis were evaporated to dryness on a hot plate at 80–90 °C. Concentrated HNO\(_3\) (Supra-pure, Merck, Darmstadt, Germany) was then added and again evaporated to dryness. The dried residue was dissolved in 1 mL of 8 M HNO\(_3\) and loaded on pre-packed columns with 2 mL Sr specific resin Eichrom\(^\text{®}\) (SR-B50-S, Triskem International, France). The resin was pre-cleaned with 6 M HCl and 8 M HNO\(_3\). The Sr was eluted from the Sr specific resin with 10 mL of MilliQ water (Merck-Millipore Watertown, MA, USA). The final concentration of Sr in the samples was approximately 30–50 ng mL\(^{-1}\). Rb was efficiently removed, as its concentrations in the Sr fraction were <0.003 ng/mL. The Sr recovery from the resin was better than 95%.

The \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratio was determined using a Nu plasma II multi-collector ICP-MS (Nu Instruments Ltd., Wrexham, United Kingdom) fitted with an Aridus II™ Desolvating Nebulizer System (Teledyne Cetac, Omaha, Nebraska, USA). Instrumental mass discrimination was corrected by internal normalization using the ratio \(^{86}\text{Sr}/^{88}\text{Sr} = 0.1194\), and Rb and Kr interferences were corrected for mathematically using \(^{87}\text{Rb}/^{85}\text{Rb}\) and \(^{86}\text{Kr}/^{83}\text{Kr}\) ratios of 0.38567 and 1.50566, respectively. Measurements were performed following the standard-sample-standard bracketing method using a NIST SRM 987 SrCO\(_3\) (0.71034 ± 0.00026, National Institute of Standards and Technology, Gaithersburg, MD, USA) as the standard. All samples were prepared in triplicates. In Table 2, the ± values represent the reproducibility (expressed as 2 SD). The instrumental operation parameters are given in Supplementary Table S1.
### Table 2. $^{87}$Sr/$^{86}$Sr isotope ratios (mean, 2 SD, $n = 3$) of 13 bottled waters.

| Sample Name | $^{87}$Sr/$^{86}$Sr |
|-------------|---------------------|
| Radenska    | 0.71164 ± 0.00035   |
| Dana        | 0.70852 ± 0.00028   |
| Zala        | 0.70965 ± 0.00025   |
| Julijana    | 0.70832 ± 0.00034   |
| Oda         | 0.70921 ± 0.00021   |
| Kaplja      | 0.71194 ± 0.00020   |
| Voda 902    | 0.71942 ± 0.00026   |
| Costella    | 0.70795 ± 0.00020   |
| Jana        | 0.70833 ± 0.00022   |
| Vodavoda    | 0.70854 ± 0.00018   |
| Laqueuille  | 0.70400 ± 0.00015   |
| Evian       | 0.70885 ± 0.00024   |
| Römerquelle | 0.70901 ± 0.00025   |

2.2.3. Determination of the Isotope Composition of Hydrogen and Oxygen

The isotope composition of hydrogen ($\delta^2$H) and oxygen ($\delta^{18}$O) was determined using the H$_2$-H$_2$O [28] and CO$_2$-H$_2$O [29,30] equilibration technique. Measurements were performed on a dual inlet isotope ratio mass spectrometer (DI IRMS, Finnigan MAT DELTA plus, Finnigan MAT GmbH, Bremen, Germany) with an automated CO$_2$-H$_2$O and H$_2$-H$_2$O HDOeq 48 Equilibration Unit (custom built by M. Jaklitsch). The temperature of the water bath was 18 °C. The water vapor trap was cooled to −55 °C. Both CO$_2$ (Messer 4.5) and H$_2$ (IAEA) were used as working standards for water equilibration. Equilibration of H$_2$-H$_2$O and CO$_2$-H$_2$O was 2 and 6 hours, respectively. All measurements were performed together with laboratory reference materials (LRM) calibrated periodically against primary IAEA calibration standards: to VSMOW/SLAP scale. Samples of water were measured as independent duplicates. Results were normalized to the VSMOW/SLAP scale using the LIMS programme and expressed in the standard $\delta$ notation (in %). For independent quality control we used LRM W-45 with defined isotope values and an estimated measurement uncertainty of $\delta^2$H = −60.6 ± 0.7 % and $\delta^{18}$O = −9.12 ± 0.04 %. Commercial reference materials USGS 45 ($\delta^2$H = −10.3 ± 0.2 %, $\delta^{18}$O = −2.238 ± 0.006 %) and USGS 46 ($\delta^2$H = −235.8 ± 0.4 %, $\delta^{18}$O = −29.80 ± 0.02 %). The average sample repeatability for $\delta^2$H and $\delta^{18}$O was 0.3 and 0.02 %, respectively.

2.2.4. Determination of Alkalinity

In order to measure alkalinity, each sample was passed through 0.45 µm nylon filter into HDPE bottle and kept refrigerated until analyzed. First, the pH was measured in the lab with a pH meter (Mettler Toledo AG 8603, Schwerzenbach, Switzerland). The total alkalinity was then determined within 24 h of sample collection using the Gran titration method [31] with a precision of ± 1%. Approximately 8–10 g of the sample was weighed into a plastic container and placed on a magnetic stirrer. A calibrated pH electrode (7.00 and 4.00 ± 0.02) was placed in the sample, and the initial pH was recorded. Reagencon HCl 0.05N (0.05M) was used for titration. The titration performed using a CAT titrator (Ingenierbüro CAT, M. Zipperer GmbH Ballrechten-Dottingen, Germany). HCl acid was added, and the change in mV monitored. At 220 mV, the mV was recorded with the addition of acid until a value of 260 mV was reached. A Gran plot was then constructed and the intersection of the line estimated using linear regression. The intersection of the line represents the amount of acid required to reach the second endpoint of the carbonate equilibrium. From the volume of acid added with a known concentration, the alkalinity of the sample can be then calculated as

$$A_s = \frac{(C_a \times V_a)}{V_s} \quad (1)$$

where,
A_s – alkalinity of the sample  
C_a – concentration of acid  
V_s – sample volume  
V_a – the volume of acid added  

The result is expressed in mmol/l.

2.2.5. Determination of Stable Isotope Composition of Dissolved Inorganic Carbon (δ^{13}C_{DIC})

Samples were stored in glass serum bottles filled with no headspace and sealed with septa caps. The δ^{13}C_{DIC} values were then determined using continuous flow IRMS (Europa Scientific 20–20) with an ANCA-TG preparation module. Phosphoric acid (100%) was added (100–200 µL) to a septum-sealed vial which was then purged with pure He. The sample (1 mL to 6 mL, depending on alkalinity) was then injected, and the headspace CO_2 measured (modified after [32] and [33]). In order to determine the optimal extraction procedure for bottled water samples, a standard solution of Na_2CO_3 (Carlo Erba reagents, Val de Reuil, France) with a known δ^{13}C_{DIC} value of –10.8 ± 0.2‰ was used. The average sample repeatability was 0.2‰.

2.2.6. Thermodynamic Modeling

Thermodynamic modeling was used to evaluate the pCO_2 and the saturation state of calcite (SI_{calcite}) and dolomite (SI_{dolomite}) using the PHREEQC speciation program [34]. The inputs were pH, total alkalinity, and temperature (20 °C).

2.2.7. Statistical Analysis

Correlations between determined parameters, descriptive statistics (i.e., mean, median, standard deviation, minimum, and maximum) were calculated and principal component analyses (PCA) were performed and visualized using the R language [35] and ggplot2 package in R [36]. Spearman’s correlation analysis was used to identify correlations between 24 elements. The significance level was  p < 0.05. General descriptive statistics were calculated (median, Q_1, Q_3) and presented as boxplots on a logarithmic scale. Two PCA analyses were performed, the first using element concentrations, and the second using stable isotopes, alkalinity, and pH. For both analyses, Z-scores were calculated to represent the relationship between the samples and the observed variables.

3. Results and Discussion

3.1. Content of Major and Trace Elements in Bottled Waters

The concentrations of major elements (Ca, K, Mg, and Na), potentially toxic elements (As, Cd, Cr, Ni, Pb) and trace elements (Al, Ba, Co, Cu, Fe, Li, Mn, Mo, P, Rb, Sb, Se, Sr, Ti, V, and Zn) in the samples of bottled spring and mineral waters are summarized graphically in Figure 1. The actual values are given in Table S2 and the descriptive statistics in Table S3.

The concentrations were in the range 4.92 to 120 mg L^{-1} for Ca 1.55 to 48.3 mg L^{-1} for Mg, 0.70 to 14.7 mg L^{-1} for Na and 0.18 to 2.20 mg L^{-1} for K. The highest variability between waters was observed for Ca and Mg, which differed by two orders of magnitude. In general, the determined concentrations were in good agreement with those reported on the labels (Table S4). The largest inconsistency was between labeled vs. determined values of Ca, K, and Na in Jana (bottled in Gorice Svetojanske, Croatia) and Mg, K, and Na in Voda 902, bottled in Črnivec, Slovenia. In both samples, the determined concentrations were higher than the label values. The levels of major elements in Dana (Mirna, Slovenia), Julijana (Tržič, Slovenia), Oda (Rimske Toplice, Slovenia), and Zala (Ljubljana, Slovenia) from this study were also compared to those reported by Brenčič et al. [26] where they analyzed the same bottled waters, among others, in 2004 and 2008. The most significant difference was for Ca in Dana (93.1, 73.2, and 66.0 mg L^{-1} in 2004, 2008, and 2016, respectively), and Julijana (42.5 and 51.9 mg L^{-1} in 2004 and 2016, respectively). Also, in Julijana, significant differences were observed for
K (0.292 mg L\(^{-1}\) in 2004 and 1.25 mg L\(^{-1}\) in 2016) and Na (0.661 mg L\(^{-1}\) in 2004 and 9.3 mg L\(^{-1}\) in 2016). These differences in major element concentrations can be explained by natural variability, except for Julijana, for which the location of the source was changed.

![Boxplots of element concentrations (major elements, potentially toxic elements and trace elements) in bottled mineral and spring waters.](image)

The trace elements—Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Ni, Mn, Mo, Pb, Sb, Se, V, and Zn—were detectable in all the water samples but were generally very low. The exception was As in Vodavoda spring water (bottled in Gornja Toplica, Serbia) where its concentration (8.86 µg L\(^{-1}\)) was just under the European drinking water standard of 10 µg L\(^{-1}\). In the same bottled water, also Li (45.9 µg L\(^{-1}\)), Cr (2.13 µg L\(^{-1}\)), and Tl (0.731 µg L\(^{-1}\)) concentrations were much higher than in other waters, suggesting that this is a consequence of geology rather than contamination of the aquifer. The water comes from a limestone aquifer situated at the bottom of Neogene sediments. Its chemical composition is altered by the presence of pegmatite, as reported by Petrović et al. (2010) [37]. Spring water Laqueuille was characterized by higher As, V, and K concentrations, where K may be related to the occurrence of alkaline rocks, especially near volcanic centers, and V confirming the presence of volcanism and basaltic rocks [38]. Indeed, the Laqueuille spring water is captured near Parc Naturel Regional des Volcans d’Auvergne in France.

The median values for the PTE determined in bottled waters from the present study were, in general, lower than those of the British and continental EU (Czech Republic, Slovakia, Finland, France, Germany and Italy) bottled waters analyzed by Felipe-Sotelo et al. (2015) [8]. The median values for As (0.293 µg L\(^{-1}\)), Cd (0.015 µg L\(^{-1}\)), and Cr (0.257 µg L\(^{-1}\)) from the present study were slightly higher compared to German and other EU mineral bottled waters as reported by Birke et al. [19] (0.190 µg L\(^{-1}\) for As, 0.0032 µg L\(^{-1}\) for Cd, and 0.121 µg L\(^{-1}\) for Cr) and Demetriades et al. [38] (0.235 µg L\(^{-1}\) for As and <0.2 µg L\(^{-1}\) for Cr). Frengstad et al. [18] determined the elemental composition (58 elements) of bottled mineral and spring waters from Norway, Sweden, Finland and Iceland. Their median values for most elements were mostly lower than the values in the present study, except for Cu, Fe, Mn, Ni, and Zn that were higher.

In the present study, the element concentrations in all the mineral and spring bottled waters were well below the limits set by Slovenian regulation [39], the EU Drinking Water Directive [6], US EPA [40], and WHO guidelines [41] for drinking water (Table S3).
3.2. $^{87}\text{Sr}/^{86}\text{Sr}$ Isotope Ratio

The concentrations of Sr, Rb, and $^{87}\text{Sr}/^{86}\text{Sr}$ values of the studied bottled waters are presented in Table 3.

Table 3. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios (mean, 2 SD, n = 3) of 13 bottled waters

| Sample Name | $^{87}\text{Sr}/^{86}\text{Sr}$          |
|-------------|---------------|
| Radenska    | 0.71164 ± 0.00035 |
| Dana        | 0.70852 ± 0.00028 |
| Zala        | 0.70965 ± 0.00025 |
| Julijana    | 0.70832 ± 0.00034 |
| Oda         | 0.70921 ± 0.00021 |
| Kaplja      | 0.71194 ± 0.00020 |
| Voda 902    | 0.71942 ± 0.00026 |
| Costella    | 0.70795 ± 0.00020 |
| Jana        | 0.70833 ± 0.00022 |
| Vodavoda    | 0.70854 ± 0.00018 |
| Laqueuille  | 0.70400 ± 0.00015 |
| Evian       | 0.70885 ± 0.00024 |
| Römerquelle | 0.70901 ± 0.00025 |

The Rb concentrations were low (0.162 to 8.75 μg L$^{-1}$), while Sr concentrations ranged widely between 17.2 and 502 μg L$^{-1}$. On average, the Sr and Rb concentrations were lower in Slovenian compared to imported bottled waters. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ranged from 0.70400 up to 0.71942. Most waters had a ratio between 0.708 and 0.710, suggesting that in most cases the carbonate fraction prevails. The most radiogenic was Voda 902 (0.71942), while the least radiogenic was Laqueuille (0.70400).

Laqueuille has the highest Rb/Sr ratio and the lowest Mg/Na and Sr/Na ratios (Figure 2) confirming its volcanic origin. Alternatively, Voda 902 spring water is characterized by having the lowest Sr/Na ratio and low Mg/Na and Ca/Na (Figure 2) ratios while the Sr isotope composition is the most radiogenic indicating silicate weathering within the aquifer. The Oda spring water has the highest Ca/Sr, Mg/Na, and Ca/Na ratios, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70921, Such data are indicative of carbonate weathering in the aquifer which is confirmed by the hydrogeological conditions in the area [42].

![Figure 2. (a)](image-a)

![Figure 2. (b)](image-b)
Figure 2. (a) Plot of 87Sr/86Sr isotope ratio vs. Rb/Sr; (b) Mg/Na; (c) Sr/Na; (d) Ca/Na.

3.3. Hydrogen ($\delta^2$H) and Oxygen ($\delta^{18}$O) Analysis

The variability in the $\delta^2$H and $\delta^{18}$O values in the present study, together with some literature data, is presented in Figure 3. All results are reported in Table S4. The reported isotope data vary between $-77.9 \%_\text{o}$ and $-53.3 \%_\text{o}$ for $\delta^2$H and between $-10.84 \%_\text{o}$ and $-8.20 \%_\text{o}$ for $\delta^{18}$O. Variations in $\delta^2$H ($-65.5 \%_\text{o}$ and $-56.6 \%_\text{o}$) and $\delta^{18}$O values ($-9.44 \%_\text{o}$ and $-8.32 \%_\text{o}$) in Slovenian bottled water were smaller compared to literature values, and are typical for groundwater in shallow aquifers where precipitation is the primary recharge source [7]. In Slovenia, such values are also characteristic for karstic and fissured carbonate aquifers and are an important water resource (Figure 3).
According to the authors’ knowledge, there have been no long-term isotope studies of source waters (Figure 4a). Romerquille has the highest mineralization and alkalinity (6.75 mM), while Laqueuille (weathering of feldspars, e.g., albite/anorthite) lines. Only Voda 902 falls on the 1:1 line. Both cations (Ca$^{2+}$, Mg$^{2+}$) originate in carbonate and clastic rocks, which is indicated by an excess of divalent cations (Figure 4a). Romerquille has the highest mineralization and alkalinity (6.75 mM), while Laqueuille

Figure 3. Plot of $\delta^{2}H$ versus $\delta^{18}O$ of bottled waters from this study in comparison to data from the literature: still and sparkling waters from Slovenian market [7], springs from Northern Slovenia [43], groundwater from Pliocene and Triassic aquifers from the Velenje coal basin [44], groundwater from karst fissured aquifers in central Slovenia [45], and Italian bottled waters [24].

Furthermore, we compared Naturelle, Dana, Zala, Oda, Kaplja, Julijana and Costella with results from previous Slovene investigations [7,11,12]. A general trend to more positive values of $\delta^{2}H$ and $\delta^{18}O$ was observed for Dana, Zala, Oda, and Kaplja, with an average increase of 2.5‰ and 0.28‰, respectively, since 2004. A similar positive shift was also observed for foreign bottled water Jana and Evian since 2004. For Naturelle, Dana, Zala, and Costella an increase of 0.3 ‰ for $\delta^{2}H$ and 0.24‰ for $\delta^{18}O$ were detected since 2009. In general, those changes are small and can be attributed either to the variation and changes of the isotope composition of the source water or to changes related to storage conditions. As reported by Ferjan [12], the oxygen isotope composition in the source water used for bottling of brand Costella monitored in the period 2006–2011 was on average $-9.03 \pm 0.12‰$. According to the authors’ knowledge, there have been no long-term isotope studies of source waters for the bottled waters included in the study. In addition, a >1‰ positive shift in $\delta^{18}O$ was observed for Costella when stored under laboratory conditions while in a closed, dark room and outdoors a much smaller increase (up to 0.36‰) was observed [11,12]. A similar positive shift in $\delta^{18}O$ values was observed for Naturelle, Dana, and Zala. The most significant difference between our and previous results [7] was observed for Julijana. This increase of 9.7‰ for $\delta^{2}H$ and 1.44‰ for $\delta^{18}O$ results from a change in the source water from near Jesenice to Tržič. The $\delta^{2}H$ and $\delta^{18}O$ values indicate a change in the recharge area, which was in the past higher and near the tree limit [7]. Therefore, caution is needed when comparing results with past observations.

3.4. Evaluation of Geochemical Processes with Geochemical Parameters ($Ca^{2+}/Mg^{2+}$ Ratios, Total Alkalinity) and $\delta^{13}C_{DIC}$ in Bottled Waters

3.4.1. Geochemical Processes

Figure 4a shows how most of the cations originate from clastic rocks (sandstone, claystone, and marls) and carbonate rocks since they deviate from the 1:2 (weathering of carbonate) and 1:1 (weathering of feldspars, e.g., albite/anorthite) lines. Only Voda 902 falls on the 1:1 line. Both cations ($Ca^{2+}$, Mg$^{2+}$) originate in carbonate and clastic rocks, which is indicated by an excess of divalent cations (Figure 4a). Romerquille has the highest mineralization and alkalinity (6.75 mM), while Laqueuille
(alkalinity 0.66 mM) and Voda 902 (alkalinity 0.45 mM) have the lowest mineralization (Table S5). Also, most of the samples have a Mg$^{2+}$/Ca$^{2+}$ ratio of over 0.5 (Figure 4a). In Oda, dolomite prevails, while in Vodovoda calcite prevails. Laqueuille and Voda 902, have low alkalinity concentrations suggesting that Mg$^{2+}$ originates from mafic minerals (e.g., amphiboles and pyroxenes) and not from carbonate minerals like dolomite.

![Figure 4a](image1.png)

**Figure 4.** Plot of (a) Ca$^{2+}$+Mg$^{2+}$ ratio versus alkalinity with lines 1:2 indicating weathering of carbonates and 1:1 indicating weathering of albite of bottled waters, and (b) Mg$^{2+}$ vs Ca$^{2+}$ indicating the dominance of dolomite/calcite in the bottled waters.

All the samples were oversaturated with CO$_2$ (Figure 5a). Calculated pCO$_2$ ranged from 851.1 to 17378 ppm (average 6881 ppm) and is 2.36 to 48.3 fold higher than atmospheric CO$_2$ (360 ppm). A lower pCO$_2$ was observed in Voda 902, which has low alkalinity (0.45 mM). The calcite/dolomite saturation indexes (SI$_{\text{calcite}} = \log ([\text{Ca}^{2+}][\text{CO}_3^{2-}])/(K_{\text{calcite}})$, where $K_{\text{calcite}}/K_{\text{dolomite}}$ is the solubility product of calcite and dolomite and was generally well above equilibrium (SI$_{\text{calcite}} = 0$, SI$_{\text{dolomite}} = 0$), indicating that calcite and dolomite were supersaturated and carbonate precipitation was thermodynamically favored in the majority of the bottled waters (Figure 5b). Laqueuille (sample with low Ca$^{2+}$, Mg$^{2+}$, and total alkalinity) was undersaturated with respect to calcite and dolomite, while Voda 902 and Naturelle (Radenska) were undersaturated with respect to dolomite (Figure 5b). This data is consistent with
Figure 4A; Voda 902 and Laqueuille have low total alkalinitities meaning that the origin of cations in both bottles is in mafic alumosilicate minerals. In contrast, Oda has high mineralization (Ca$^{2+}$+Mg$^{2+}$), alkalinity, and pH, and therefore the highest $SI_{\text{calcite}}/SI_{\text{dolomite}}$ (Figure 5b).

![Figure 4A](image)

**Figure 5.** Plot of (a) pCO$_2$ versus pH in bottled waters and (b) saturation index of calcite ($SI_{\text{calcite}}$) versus dolomite ($SI_{\text{dolomite}}$) in bottled waters.

3.4.2. Origin of Carbon in the Dissolved Inorganic Carbon ($\delta^{13}$C$_{\text{DIC}}$) in Groundwater

Inorganic carbon in natural water consists of gaseous CO$_2$(g), dissolved CO$_2$(aq), dissolved carbon acid (H$_2$CO$_3$), dissolved hydrogen carbonate (HCO$_3^-$), and solid calcium carbonate (CaCO$_3$). All the $\delta^{13}$C$_{\text{DIC}}$ depends on the contribution of these multiple sources of carbon [23]. All these species represent the carbonate system in dynamic equilibrium. Concentrations of DIC and $\delta^{13}$C$_{\text{DIC}}$ are governed by processes occurring in the soil-aquifer system with time, depending on the contribution of multiple sources and sinks. Changes in DIC concentrations result from addition or removal from
the DIC pool, while changes of $\delta^{13}C_{\text{DIC}}$ result from fractionation accompanying the transformation of carbon or from mixing of carbon from different sources. The major sources of carbon to aquifer DIC loads are dissolution of carbonate minerals, and soil derived from root respiration and microbial decomposition of organic matter [43]. The primary removal mechanism of DIC in the aquifer system is carbonate mineral precipitation [17]. Redondo and Yélamos (2005) [23] found that naturally carbonated waters had $\delta^{13}C_{\text{DIC}}$ values between $-8$ and $-7\%$. The industrial carbon dioxide injected into mineral bottled water is produced from hydrocarbons by chemical processing leading to low $\delta^{13}C$ values of $-35.0$ to $-21.7\%$ [23].

$\delta^{13}C_{\text{DIC}}$ in our study is on average, $-11.7\%$ and range from $-17.3$ to $-6.2\%$ (Figure 6a). A summary of all $\delta^{13}C_{\text{DIC}}$ values is presented in Table S5. In a study by Brenčič and Vreča, (2007) of domestic and foreign bottled waters randomly collected from the Slovene market (58 brands and 16 replicates), the $\delta^{13}C_{\text{DIC}}$ values varied between $-63.1\%$ and $+1\%$ with an average of $-12.3\%$, while average values of naturally sparkling, artificially sparkling, still and flavored waters were $-3.3\%$, $-36.5\%$, $-10.0\%$, and $-11\%$, respectively [22]. The lowest values are characteristic of artificial sparkling waters because of the injection of industrial CO$_2$ [22]. Carbon isotopic values of effervescent bottled waters vary from $-35.0$ to $-2.7\%$ [23]. Figure 6a shows that most of the DIC in bottled waters falls between lines 1 and 2 indicating the dissolution of carbonates according to the average $\delta^{13}C_{\text{CaCO}_3}$ (2.2\% predicted value for carbonate rocks) [43] and non-equilibrium carbonate dissolution by carbonic acid produced from soil zone CO$_2$ [43]. Only Laqueuille with a value of $\delta^{13}C_{\text{DIC}}$ $-17.3\%$ falls close to the equilibration line 3, indicating more soil CO$_2$. Vodovoda had the highest carbonate contribution with $\delta^{13}C_{\text{DIC}}$ value of $-6.2\%$. The low alkalinity of Voda 902 meant that the $\delta^{13}C_{\text{DIC}}$ could not be measured.

A plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\delta^{13}C_{\text{DIC}}$ (Figure 6b) confirms our presumption that for the majority of analyzed samples the carbonate fraction prevails. The low alkalinity Voda 902, suggest it is undersaturated with respect to dolomite (Figure 5b) and has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Vodovoda has high $\delta^{13}C_{\text{DIC}}$, low $^{87}\text{Sr}/^{86}\text{Sr}$ and is supersaturated with calcite and dolomite (Figure 5b), meaning it is of carbonate origin. Laqueuille has low alkalinity, low $\delta^{13}C_{\text{DIC}}$, low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and is undersaturated with calcite and dolomite and is the lowest mineralized bottled water in our study (Figure 5b). The $\delta^{13}C_{\text{DIC}}$ and total alkalinity results reveal that samples from our study fall between karst fissured and igneous aquifers (Figure 6c). Figure 6c also represents values of $\delta^{13}C_{\text{DIC}}$ and alkalinity of some previous studies [43–45] of groundwater in Slovenia and Italian bottled waters [24].
Figure 6. Cont.
Figure 6. Plot of (a) $\delta^{13}$C$_{\text{DIC}}$ values in bottled waters, with lines indicating biogeochemical processes. These include (1) dissolution of carbonates according to the average $\delta^{13}$C$_{\text{CaCO}_3}$ (2.2‰) value—predicted value \[43\], causing 1‰ ±0.2‰ enrichment in $^{12}$C in DIC \[46\]; (2) non-equilibrium carbonate dissolution by carbonic acid produced from soil zone CO$_2$ \[43\] and (3) open system equilibration of DIC with soil CO$_2$ originating from degradation of organic matter with $\delta^{13}$C$_{\text{soil}}=-27.2$‰ \[43\]; (b) $^{87}$Sr/$^{86}$Sr vs $\delta^{13}$C$_{\text{DIC}}$ in bottled waters with a figure indicating silicate/carbonate fraction \[47\]. (c) Comparison of $\delta^{13}$C$_{\text{DIC}}$ versus total alkalinity of bottled waters from this and other studies \[43\], tap water from central Slovenia \[45\] and mining groundwater wells (Pliocene and Triassic) from Slovenia \[44\] and Italian bottled waters \[24\].

3.5. Statistical Analysis

None of the observed correlations between elements had a correlation coefficient >0.8, although Sr-Se, Sr-Ca, Se-Ca, Se-Ni, Ca-Na, Na-K, and Cu-Al had correlations of 0.75 or above, with Sr-Ca and Li-Na having the highest (0.8). Figure 7 shows a Spearman correlation matrix for all elemental combinations where dark blue colors present higher positive correlation values and light green colors higher negative values. Crossed-out values are not significant.

The first PCA analysis, for elements only (Figure 8), shows that there is no clear and evident clustering of the samples. In this case, PC1 explains 27.3% of the variance, and PC2 explains 21.7% of the variance, which combined is only 49%, suggests observing more principle components to evaluate further the relationships of the elements and samples. Although there are no apparent clusters, two samples stand out—Vodavoda and Romerquelle—the former being characterized by As, Cr, and Tl, and the latter by Se, Ca, Sr, and Mn.
Figure 6. Plot of (a) $\delta^{13}$CDIC values in bottled waters, with lines indicating biogeochemical processes. These include (1) dissolution of carbonates according to the average $\delta^{13}$CCaCO$_3$ (2.2‰) value—predicted value [43], causing 1‰ ±0.2‰ enrichment in 12C in DIC [46]; (2) non-equilibrium carbonate dissolution by carbonic acid produced from soil zone CO$_2$ [43] and (3) open system equilibration of DIC with soil CO$_2$ originating from degradation of organic matter with $\delta^{13}$Csoil=$-27.2$‰ [43]; (b) $\delta^{13}$CDIC versus total alkalinity of bottled waters from this and other studies [43], tap water from central Slovenia [45] and mining groundwater wells (Pliocene and Triassic) from Slovenia [44] and Italian bottled waters [24].

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Figure 7. Spearman correlation matrix for all analyzed elements with significance model set at $p < 0.05$ and insignificant values crossed-out. Blue colors represent higher correlation factors, while green values show negative correlations.

The first PCA analysis, for elements only (Figure 8), shows that there is no clear and evident clustering of the samples. In this case, PC1 explains 27.3% of the variance, and PC2 explains 21.7% of the variance, which combined is only 49%, suggests observing more principle components to evaluate further the relationships of the elements and samples. Although there are no apparent clusters, two samples stand out—Vodavoda and Romerquelle—the former being characterized by As, Cr, and Tl, and the latter by Se, Ca, Sr, and Mn.

Figure 8. Biplot of the first two principal components axes from a PCA of elemental concentrations in bottled waters.

The second PCA analysis (Figure 9), which includes stable isotope values, alkalinity and pH shows higher values for the first two principal components (PC1: 46.8%, PC2: 23.6%) which combined explain 70.4% of the variance. Again, no apparent clustering is observed, although Julijana, Voda
902 and Jana show a strong positive relationship with $\delta^{13}C_{\text{DIC}}$. The reverse is evident for Laqueuille. Moderate clustering could be interpreted for Kaplja and conditionally Zala with positive relationships with $\delta^2H$ and $\delta^{18}O$.

**Figure 9.** Biplot of the first two principal component axes of the PCA of stable isotopes, alkalinity, and pH in samples of bottled water.

4. Conclusions

Multi-elemental and stable isotope analyses were performed on 13 (8 Slovenian and 5 foreign) bottled mineral and spring waters from Slovenian market. The majority of the elements studied were present in the samples in low concentrations. According to EU legislation, all waters were suitable for human consumption. Concentrations of major elements were in good agreement with the data on the labels, while compared to data from previous studies, some differences were observed. Most differences were a consequence of the natural variability, except for Julijana spring water where the source changed. Vodavoda and Laqueuille had the most distinctive elemental compositions due to the particular geology of their recharge areas. Laqueuille also had a distinctive $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio, since its recharge area has a volcanic origin. With combining Sr isotope ratio data and ratios of major elements (i.e., Mg/Na, Ca/Na, and Ca/Sr), the prevailing mineral weathering was identified. Although differences in the elemental and Sr isotope composition of the samples were observed, it was not possible to provide a clear division according to their geographical origin.

The study also showed how $\text{HCO}_3^-$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$ dominate the solute chemistry of bottled mineral and spring water. According to the calculated pCO$_2$ values, bottled waters are saturated with CO$_2$. Also, saturation indexes of calcite and dolomite indicated saturation with both minerals, except for Voda 902 (undersaturated with dolomite) and Laqueuille (undersaturated with calcite and dolomite) that are low in mineralization. Vodovoda is Ca enriched, while Oda is the most saturated
with calcite/dolomite and Mg enriched. Voda 902 is also Mg enriched. $\delta^{13}$C$_{\text{DIC}}$ values indicate that Laqueuille has the most soil CO$_2$ contribution, while Vodovoda has the most carbonate contribution.

General geochemistry together with O, H, C, and Sr isotope data indicates that analyzed bottled waters originated mostly from shallow aquifers in clastic and carbonate rocks. A general trend towards more positive values of $\delta^{18}$O and $\delta^2$H for Naturelle, Dana, Zala, Oda, Kaplja, Costella, Jana, and Evian in comparison to previous investigations were observed. However, it was not possible to confirm whether the changes are related to climate change and isotope composition variability of the source water or storage conditions.

Therefore, in future studies, a systematic approach for bottled water characterization, including trace element and isotope monitoring, of source water prior to bottling would be necessary. Also, these data would be of value in raising consumer awareness about the quality of bottled water.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4441/12/9/2454/s1, Table S1: Instrumental and operation parameters of MC-ICP-MS; Table S2: Elemental compositions of the analyzed bottled mineral and spring waters; Table S3: Summary of elemental concentrations, basic statistics and recommended maximum levels by SI and EU legislation, US EPA and WHO; Table S4: Data from the declarations on the bottles; Table S5: Data for $\delta^2$H, $\delta^{18}$O, $\delta^{13}$C$_{\text{DIC}}$, total alkalinity, pH, pCO$_2$, SI$_{\text{calcite}}$ and SI$_{\text{dolomite}}$.

**Author Contributions:** Conceptualization, T.Z.; Software, T.K. and R.N.; Formal analysis, T.Z., T.K., and P.V.; Resources, T.Z., T.K., and P.V.; Data curation, T.Z., T.K., and P.V.; Writing—original draft preparation, T.Z.; Writing—review and editing, T.Z., T.K., P.V., and R.N.; Visualization, T.Z., T.K., and P.V.; Supervision, T.Z., T.K., and P.V.; Project administration, T.Z.; Funding acquisition, T.Z., T.K., and P.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** The Slovenian Research Agency funded this research through the ARRS Programme P1-0143, MASSTWIN – Spreading excellence and widening participation in support of mass spectrometry and related techniques in Health, the Environment and Food Analysis (H2020, GA No. 621329) and bilateral project BI-US/19-21-079.

**Acknowledgments:** Special thanks go to S. Žigon for his valuable help with H, O, and C isotope analysis.

**Conflicts of Interest:** The authors declare no conflict of interest.

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