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Geochemical Characterisation and Health Concerns of Mineral Bottled Waters in Catalonia (North-Eastern Spain)

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Abstract: Spain currently produces around 7000 million litres of mineral water a year, of which about 20% is produced in Catalonia, and there is a need for greater regulation and research into bottled waters and their impact on human health. A total of 29 samples were analysed from different brands of commercially bottled water, and 71 chemical elements were determined in each sample. The aim was to classify each brand based on composition, compare lithological origins, verify compliance with international standards for drinking water, and report benefits for human health. More than 60% of the samples were of the calcium bicarbonate type, had a low mineral content, and were associated with granitic aquifers, ranging from leucogranites to granodiorites. In contrast, 17% were of the sodium bicarbonate type, had harder waters, and were related to thermal springs. The thermal springs of the bottled waters from the Montseny-Guilleres massif (Vichy Catalán, Malavella, and San Narciso) emerge at a temperature of 60 °C with their own natural gas. Two samples exceeded European standards for As and Hg concentrations in water for human consumption, while one showed a concentration of U greater than that set out in international recommendations.

Keywords: natural mineral waters; inorganic composition; trace elements; lithological association; health benefits; international standards; recommended daily intake (RDI)

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1. Introduction

In recent years, the consumption of bottled water has grown dramatically worldwide, even in countries where tap water quality is considered excellent. This is because consumers perceive bottled water to have better organoleptic and physicochemical properties and to be even healthier than tap water [1]. North America has the highest rate of bottled water consumption (30%), followed by Europe (29%) and Asia (27%), and, finally, 14% in other parts of the world. As a result, the bottled water industry has become a sector of considerable interest economically [2]. Nevertheless, bottled water, like any other industry, is not exempt from environmental impacts, either positive or negative. In particular, as plastic bottles are not readily biodegradable, the main challenge is their durability in the environment having a high potential environmental impact if not recycled sufficiently. In addition, since bottled water manufacturers mainly rely on fossil fuels, energy consumption is another major issue in production and distribution of bottled water. The amount of energy required for treating water, producing plastic bottles, and transporting bottled water to shopping centres can further aggravate the conditions [3].

In Spain alone, this industry boasts a yearly turnover of some EUR 900 million, with annual growth exceeding 5%. In 2018, bottled water production in Spain surpassed 8200 million litres for the first time [4]. In addition, Spain ranks third among European countries in the consumption of natural mineral waters [5], and Catalonia produces around a quarter of this volume. Given that some of the brands from this region, such as Font Vella, Fonter, Vichy Catalan, and Aquarel-Los Abetos [6], are the most sold in Spain, a thorough analysis of them is opportune [4,5].

Natural mineral waters have a constant flow rate and temperature of upwelling and a relatively stable physico-chemical composition [7]. The composition is unique for each water source, giving the water a characteristic taste and sometimes properties that can be beneficial for human health. The presence of dissolved natural components and trace elements in this kind of water depends heavily on its interaction with the predominant lithology of the aquifer [8], and it is essential in protecting mineral waters from springs, as they are considered vulnerable to contamination in all rock types [9,10].

Several studies have addressed the composition of bottled mineral water in Europe at different levels (local, national, or continental) and have compared its composition with that of tap water supply, but none of them addressed the Catalonia area [11–18].

Given the commercial importance of the brands of bottled water sourced in Catalonia, here we studied a wide range of natural mineral waters from the area. We addressed their hydro-chemical facies and described the relative abundance of the major elements. We also analysed the trace element content of each brand to determine the relationship between mineral content and geological origin.

To contribute to informing and protecting the consumer, we tested the water samples against international standards for human consumption (WHO, EPA, and Directive 2009/54/EC).

In addition, we report on the benefits of the samples tested for human health, concerning mineral content and recommended daily intake (RDI) of some trace elements [19–21], without forgetting the possible toxic effects of some elements present in bottled waters [22].

In Spain, a distinction is made between four bottled waters: natural mineral water (Agua Mineral Natural), medicinal mineral water (Agua Minero-medicinal), spring water (Agua de Manantial) and drinking prepared water (Agua Potable Preparada).

The exploitation of natural mineral waters in Spain has two legal obstacles. The extractive industry is regulated by the Mining Law of 1973 and the food industry by the Sanitary Technical Regulation of 1981. After Spain's admittance to the European Community, the regulations were adapted to the Council Directive 80/777/EEC, which aims to approximate the different regulations on natural mineral waters of all state members. Since the promulgation of this European Directive, four subsequent directives (96/70/EC, 2003/40/EC, 2009/54/EC, and 2015/1787) have updated the legal framework of the bottled water sector in the European Union. The government of Spain has applied the aforementioned directives through different Royal Decrees (R.D. 2119/1981; R.D. 1161/1991; R.D. 187/1998; R.D. 1074/2002; R.D. 1744/2003; R.D. 1798/2010; R.D. 1799/2010; 902/2018).

Regarding quality control, bottled water producers should analyse water samples every working day. Water producers analyse the finished product with, at least, the parameters indicative of microbiological pollution, as well as electrical conductivity and pH.

Moreover, the water of the finished product must be controlled, at least, quarterly, with all the microbiological determinations provided for in this Royal Decree, the main components (cations and anions) and those components that characterize such water, as well as nitrites, nitrates, pH, and electrical conductivity. Additionally, at least every five years, the water of the source must be controlled by means of an analysis that covers the parameters that are contemplated in the quarterly analysis.

Mandatory information on the labels should include the name of the spring or water source and the place of exploitation and the quantitative analytical composition of characteristic major elements must be included, and waters that have been subjected to treatment with air enriched with ozone must bear the indication "water subjected to an authorized oxidation technique with ozonated air" near the analytical composition of characteristic components. In the same way, waters that have been subjected to a technique with activated alumina must bear the indication "water subjected to an authorized adsorption technique" near the analytical composition of characteristic components.

2. Location and Geological Context of the Water Sources

Catalonia is composed of three major geological units: the Pyrenees to the north, the Catalan Coastal Ranges to the east and south, and the Catalan Central Basin in the centre and to the west (Figure 1).

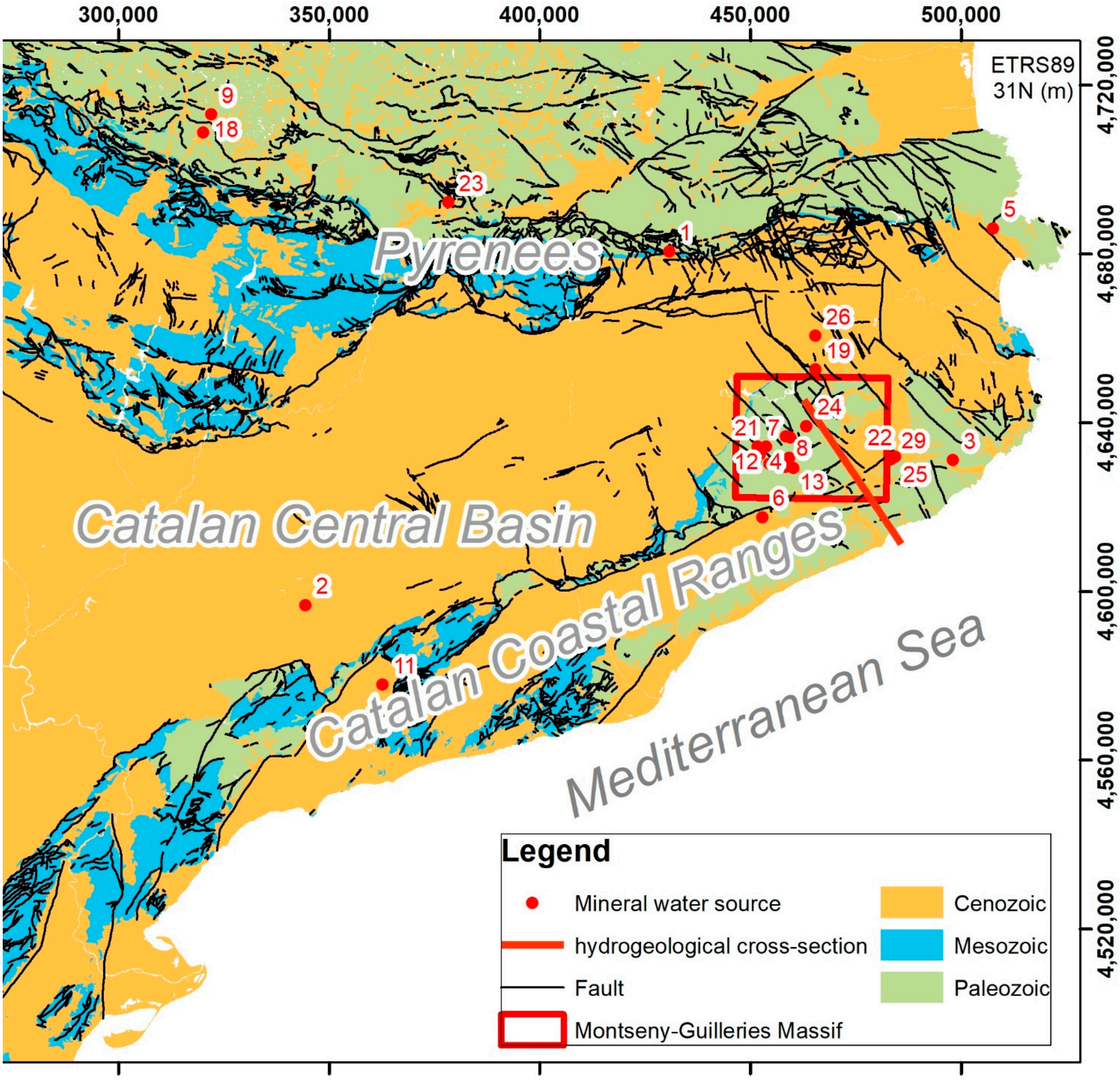

Figure 1. Simplified geological map showing the analysed mineral waters sources and the location of Figure 2 hydrogeological cross-section. Geological base map modified from [23].

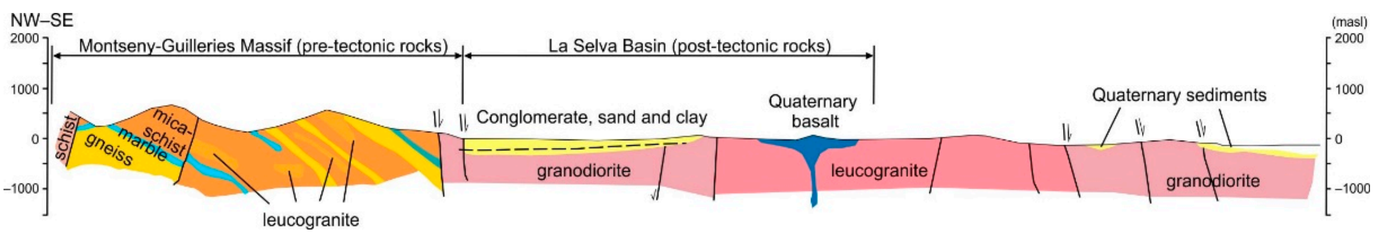

Figure 2. Hydrogeological cross-section of Montseny-Guilleries Massif–La Selva Basin. The dashed line shows the position of the water table. Modified from [24].

The Pyrenean Massif is one of the most extensive geological units in Catalonia, with approximately 250 km stretching across the region (435 km total length). This mountain range was formed during the Alpine Orogeny and was the result of the collision between the European and Iberian plates. It consists of a central core of igneous and metamorphic rocks that corresponds to the Hercynian basement (Axial Pyrenees), flanked to the north and the south by a folded cover of Mesozoic and Tertiary sedimentary rocks.

The Catalan Coastal Ranges consist of two parallel mountain ranges aligned in a NE–SW direction and comprise metamorphic and granitic rocks of the Cambro-Ordovician and Carboniferous age. The Montseny-Guilleries Massif is delimited by fractures in a NW direction [25]. Between the two mountain ranges, there is an elongated intermediate basin (Vallès Basin) filled by a thick (up to 3500 m) sequence of Tertiary and Quaternary sediments.

The Montseny-Guilleries Massif is an isolated block located at the northern end of the Catalan Coastal Ranges. The main geological units are as follows:

(a) Paleozoic rocks affected by an intermediate-to-high metamorphism (gneisses, schists, and marbles); (b) granite and porphyritic rocks; and (c) Triassic and Tertiary sediments covering the south-western edge.

La Selva Basin, located to the southeast of this massif, is a complex unit, with a metamorphic and granitic basement filled by arkosic sediments of the Pliocene age and Quaternary alluvial sediments associated with volcanic rocks, silicified deposits, and travertines (Figure 2). This depression is delimited by fractures aligned in a NW–SE direction, and it includes a set of alluvial terraces that form the largest aquifers in the region [26].

The Catalan Central Basin is part of the wide Ebro Basin depression, which occupies most of the northeast and northern territory of the Iberian Peninsula. This depression extends throughout almost the whole of inland Catalonia, from the southwest of the coastal mountain ranges to the pre-Pyrenees. It consists of Tertiary sedimentary materials, the morphology of which is strongly conditioned by tectonics and erosion. This wide depression is filled mainly by conglomerates and sandstone in the margins and by marls, limestones, clays, and evaporites in the centre.

The mineral water used by the bottling industry in Catalonia is extracted from various aquifers located in the three main geological units described above. The most productive units are the hydrogeological complexes related to plutonic or metamorphic rocks, especially granite-type rocks, such as those of the Montseny-Guilleries Massif, which produce 20% of the mineral water bottled in the Iberian Peninsula [27].

The second core of extraction is the thermal area of Caldes de Malavella (La Selva depression), followed by the springs associated with metamorphic rocks of the Paleozoic age, located in the fault areas separating the main mountain ranges of the border depressions. The mineral waters of the Pyrenees belong to this group and include the brands Pineo, Agua de Ribes, Fontboix, and Caldas de Bohi.

Finally, the aquifers located in the Catalan Central Basin are particularly productive, especially around its edges, where sandstone and conglomerates are the dominant lithologies interbedded with loamy and clayey sediments, which were deposited mainly at Oligocene localities.

3. Materials and Methods

Twenty-nine bottled natural mineral water samples, twenty-three still waters, one sparkling containing natural CO_2, and five with added CO_2 were analysed (Table 1). Twenty-one water samples were bottled in PET (polyethylene terephthalate) and nine in glass bottles. Three brands were bottled in glass and PET: Fonter, Sant Aniol, and Font d'Or.

Table 1. Sample sources, bottle type, classification and details of analysed mineral waters. Lithology: G: Granites; S: Sedimentary rocks; M: Metamorphic rocks.

Brand	Locations	Sample ID	Bottle Type	Electrical Conductivity (μScm^{-1})	Lithology	R.D. 1798/2010 Classification
Aigua de Ribes	Ribes de Fresser	1	PET	334	M	Suitable for a low-sodium diet
Aigua de Rocallaura	Rocallaura	2	PET	1767	S	Contains sulphate calcium magnesium
Aigua de Salenys (sparking)	Llagostera	3	Glass	3320	G	Contains bicarbonate calcium magnesium
Aigua de Viladrau	Viladrau	4	PET	283	G	
Aigua Vilajuiga (sparking)	Vilajuiga	5	Glass	2730	G	Contains bicarbonate sodium chloride
Aigua del Montseny	Sant Esteve de Palautordera	6	PET	269	M	Suitable for a low-sodium diet
Aiguaneu	Espinelves	7	PET	284	G	Suitable for a low-sodium diet
Aquarel Los Abetos	Arbúcies	8	PET	267	G	Suitable for a low-sodium diet
Caldas de Bohi	Barruera	9	PET	176	G	
Font Agudes	Arbúcies	10	PET	465	G	
Font del Pla Nova	Aiguamúrcia	11	PET	730	S	Suitable for a low-sodium diet
Font del Regás	Arbúcies	12	PET	278	G	Suitable for a low-sodium diet
Font d'Or	Sant Hilari de Sacalm	13	Glass	192	G	Suitable for a low-sodium diet
Font d'Or	Sant Hilari de Sacalm	14	PET	175	G	Suitable for a low-sodium diet
Font Selva	Sant Hilari de Sacalm	15	PET	380	G	
Font Subirà	Osor	16	PET	248	G	Suitable for a low-sodium diet
Font Vella	Sant Hilari de Sacalm	17	PET	308	G	Suitable for a low-sodium diet
Font Boix	Barruera	18	PET	60	M	Suitable for a low-sodium diet
Fonter (sparking)	Amer	19	PET	279	S	Suitable for a low-sodium diet
Fonter (sparking)	Amer	20	Glass	295	S	Suitable for a low-sodium diet
Fuente Estrella	Arbúcies	21	PET	217	G	Suitable for a low-sodium diet
Malavella	Caldes de Malavella	22	Glass	4250	G	Contains bicarbonate sodium chloride
Pineo	Estamariu	23	Glass	433	M	Suitable for a low-sodium diet
Rocaigua	Osor	24	PET	261	G	Suitable for a low-sodium diet
San Narciso (sparking)	Caldes de Malavella	25	Glass	4773	G	Contains bicarbonate sodium chloride
Sant Aniol	Sant Aniol	26	PET	524	S	Suitable for a low-sodium diet
Sant Aniol (sparking)	Sant Aniol	27	Glass	576	S	Suitable for a low-sodium diet
Sant Hilari	Arbúcies	28	PET	315	G	Suitable for a low-sodium diet
Vichy Catalan (sparking)	Caldes de Malavella	29	Glass	4838	G	Contains bicarbonate sodium chloride

The bottles of mineral water were obtained directly from the supermarkets, ensuring that they were recent deliveries to avoid variations in the content due to poor storage of the samples. Before analysis, water samples were stored at 4 °C in the dark.

The geographical location of the points of emergence is identified on the label, as established by the Spanish regulations. In addition, the characteristics of each emission point have been reviewed through the technical reports for the legalization of the catchments.

Cations, trace elements, and rare earths were analysed by means of inductively coupled plasma (ICP) emission spectrometry/mass spectrometry, which was performed at Activation Laboratories in Ontario (Canada). The concentrations of the following 67 elements were determined: Ag, Al, As, Au, Ba, Be, Bi, Br, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, I, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, Os, Pd, Pb, Pt, Rb, Re, Ru, Sb, Sc, Se, Si, Sn, Sr, Ta, Te, Ti, Tl, U V, W, Y, Zn, and Zr, and rare earths Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Th, Tm, and Yb. Four major anions (Cl^-, HCO^{3-}, NO^{3-}, ${SO_4}^{2-}$) were analysed by ion chromatography at the Scientific and Technological Centres of the University of Barcelona. Electrical conductivity (EC) was also measured.

Careful quality control of analysis was undertaken by sample blanks to detect any contamination and to derive reliable detection limits, as well as frequent analysis of sample duplicates, to assess that the analytical error was less than 5% for major ions and less than 10% for trace elements. In addition, ion balance error for major elements was checked for each sample.

For univariate statistical analysis, we used the Sigma Plot software for Windows [28]. In the statistical calculations, the value of elements with concentrations below the limit of detection, a value equal to 50%, of the instrumental detection limit was considered.

For the purposes of multivariable statistical tests, we selected a total of 35 chemical elements and EC values, discarding those elements with a high proportion of data below the limit of detection. Of the rare earths (REE) tested, only Ce and Nd were included. Statistica for Windows [29] was used for the univariate and multivariate statistical analyses. Prior to the PCA (principal component analysis), the data were log-transformed to obtain a set of nearly normal distributed parameters.

We grouped the samples into the following three categories based on the dominant lithology where the springs emerged: granitic or plutonic rocks; metamorphic rocks; and sedimentary rocks. Given that some springs cannot be easily assigned to a single lithological type because of their geological complexity, this division simplified the classification of the distinct kinds of water.

4. Results and Discussion

Seventy-one elements were analysed in the sampled bottled mineral waters. The results for EC and the 35 elements with significant values in all samples are available in the Supplementary Material.

4.1. Chemical Composition—Hydrochemical Facies

4.1.1. Major Ions

The major ions (with concentrations above 1 mg L^{-1}) determine the type of water and allow its classification based on mineralisation (Table 1 and Figure 3). The ionic content of the samples ranged from low to medium (EC between 60 and 1767 μS cm^{-1} and geometric mean equal to 282 μS cm^{-1}), except for five sparkling water samples, which showed higher EC values (4250 μS cm^{-1} mean).

The chemical characteristics of the samples revealed that they were mainly calcium bicarbonate- or sodium-calcium-type water, although sodium bicarbonate- and calcium-sulphate-types were also present, as shown in the Piper diagram (Figure 4). We have also compared our analytical results with the chemical composition of major elements given on the bottle labels. As an example of the overall agreement, the correlation plots for HCO_3 (R^2 = 0.9975) and Na (R^2 = 0.9981) are shown in Figure 5.

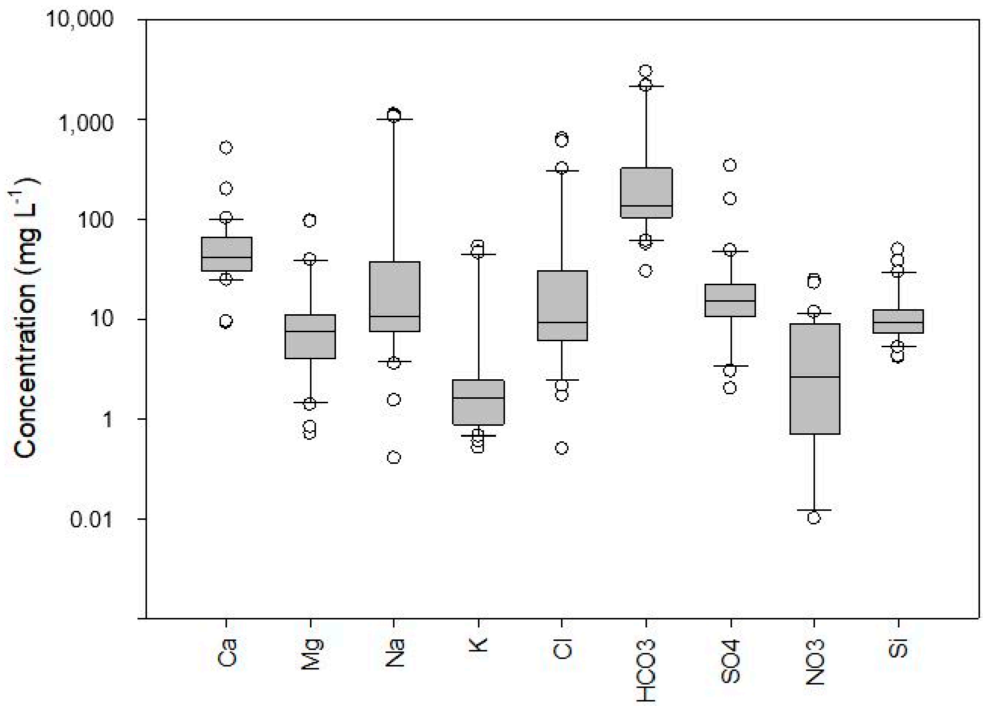

Figure 3. Box plots for major ions in the sampled mineral waters (n = 29 samples). Boxes correspond to the inter-quartile range of the distribution; whiskers correspond to no more than 1.5 times the inter-quartile range and outliers are shown as black open circles.

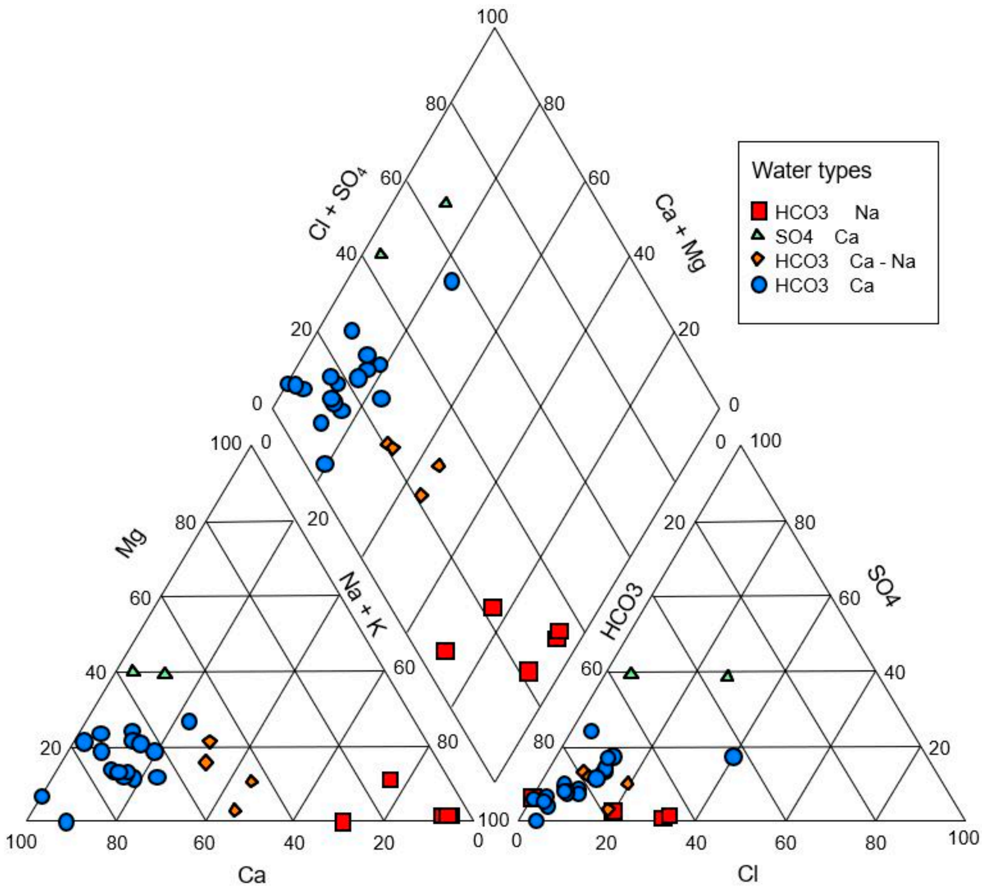

Figure 4. Piper diagram of all the bottled mineral waters showing the different water types.

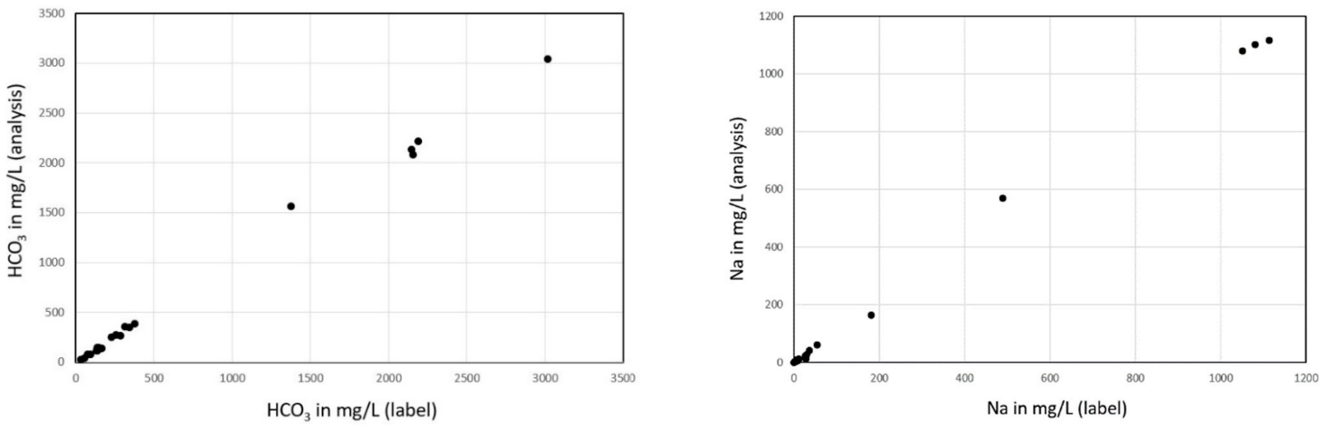

Figure 5. Comparison of our analytical results with the data given on the bottle labels for HCO_3 and Na.

According to the Spanish Regulations, the name of the spring or underground catchment and the place of exploitation shall be included. If the origin of the water is national, the municipal term and province in which the spring or underground collection is located must also be added. In the case of natural mineral waters, the quantitative analytical composition listing its characteristic components must be included.

Waters that have been subjected to treatment with air enriched with ozone must bear the indication "water subjected to an authorized oxidation technique with ozonated air" near the analytical composition of characteristic components. In the same way, waters that have been subjected to a technique with activated alumina must bear the indication "water subjected to an authorized adsorption technique" near the analytical composition of characteristic components.

Major ions, together with nitrate and Si, determined the variations in the chemical character of the samples. These values usually appear on commercial labels.

Calcium bicarbonate-type waters comprised the largest group (more than 60% of samples), which corresponded to water associated with granitic rocks located in the Montseny-Guilleries Massif. Grouped around a cluster to the left of the central diamond of the Piper diagram (Figure 4), these water samples were highly homogeneous from a geochemical point of view. In addition to Ca, these samples had a high content of Mg (Aquarel-Los Abetos, Font Vella-Sacalm, Fonter, and Sant Aniol) or Na (Aigua de Viladrau, Font Selva, Font Agudes, Font del Regás, and Font D'Or).

Water samples with the highest mineralisation are the sodium bicarbonate-type, corresponding to sparkling waters (San Narciso, Vichy Catalan, Vilajuiga, and Malavella) and associated with thermal springs. These springs are located in zones of fracture, predominantly in granite rocks, but also in other kinds of lithology, such as volcanic or metamorphic rocks [26]. This group of samples comprised water from Caldes de Malavella (Malavella, San Narciso, and Vichy Catalán) and the eastern Pyrenees (Aigua de Vilajuiga). In addition, their concentration in silica is between 21 and 38 mg L^{-1} and the chloride content (ranging from 200 to 640 mg L^{-1}) was remarkable in comparison with the rest of the samples, most with less than 15 mg L^{-1}. The chemical character of these sparkling waters suggests long residence times and, therefore, higher rates of reaction with the minerals that form aquifers, even for the waters of calcium bicarbonate facies with a chloride content below 30 mg L^{-1}. Spanish legislation establishes that for spring water to have the denomination of mineral water, it is necessary to prove the stability of its chemical composition with periodic chemical analysis for a period of 5 years. These conditions are achieved when there is a water–rock equilibrium in the aquifer without being affected by periodic variations during rainwater recharge.

Calcium-sulphate-type water samples were characterised by a high or intermediate ionic content (EC ranging from 730 to 1767 µS cm^{-1}). This observation may indicate that original calcium bicarbonate waters later mixed with sulphated waters or were in contact with lithologies containing oxidised sulphides or sulphates, thus, acquiring a sulphated profile. These water samples, therefore, showed a sulphate content exceeding 150 mg L^{-1}, reaching 339 mg L^{-1} in some cases (Aigua de Rocallaura and Font de). In contrast, the rest of the samples had a sulphate content under 50 mg L^{-1}. Calcium-sulphate-type waters corresponded to springs located in Tertiary sedimentary materials (clays, sandstones, marls, conglomerates) in the Catalan Central Basin. Another characteristic of these samples was their high Sr content (between 1700 and 4090 μg L^{-1}).

Nitrate concentrations were generally low (<10 mg L^{-1}) in all samples, except Aigua de Rocallaura and Aigua del Montseny, which showed concentrations ranging between 23 and 25 mg L^{-1}, probably derived by anthropogenic activities The most widespread impact and probably the one that is most difficult to solve in Catalonia today comes from the high nitrate concentration in groundwater. This is essentially the result of fertilisation practices and, in particular, of the application of livestock manure [30]. The two samples of bottled water that have the highest nitrate content are Rocallaura and Aigua del Montseny, with values of 22.9 and 24.5 mg L^{-1}, respectively, corresponding to areas of the predominance of agricultural activity. However, both values are below the maximum concentration of nitrates in water for public consumption in EU countries, which is 50 mg L^{-1}.

The correlation between the major components of the waters is consistent and shows that the electrical conductivity, has high coefficients with Cl^-, HCO^3, Na^+, and Si, which are the constituents, while Ca^{+2} presents a high correlation with magnesium. Nitrate has no significant correlation with the other elements and only slightly with sulphates (Table 2).

Table 2. Correlation matrix of mayor elements. Coefficients higher that 0.75 are highlighted in bold.

	Ce	**Cl**	**HCO_3**	**NO_3**	**SO_4**	**Ca**	**Mg**	**Na**	**Si**
Ce	1.000	0.895	0.938	−0.176	0.177	0.380	0.374	0.934	0.809
Cl	0.895	1.000	0.754	−0.106	0.176	0.069	0.141	0.950	0.527
HCO_3	0.938	0.754	1.000	−0.275	0.023	0.604	0.464	0.806	0.918
NO_3	−0.176	−0.106	−0.275	1.000	0.580	−0.006	0.303	−0.234	−0.331
SO_4	0.177	0.176	0.023	0.580	1.000	0.248	0.671	0.032	−0.118
Ca	0.380	0.069	0.604	−0.006	0.248	1.000	0.853	0.046	0.616
Mg	0.374	0.141	0.464	0.303	0.671	0.853	1.000	0.049	0.433
Na	0.934	0.950	0.806	−0.234	0.032	0.046	0.049	1.000	0.653
Si	0.809	0.527	0.918	−0.331	−0.118	0.616	0.433	0.653	1.000

Principal component analysis (PCA) has been conducted to reduce the high dimensional data of cases and variables in the few dimensional spaces consisting of principal components (PC's) that are linearly independent to each other (Figure 6). Two PCs with eigenvalues of 5.48 and 2.40 were extracted, which explained 73.22% of the total variance. The first PC (PC1), accounting for 50.78% of the total variance, is significantly correlated with EC (−0.99), HCO_3 (−0.97), Na (−0.95), K (−0.90), Cl (−0.87), and Si (−0.85) and also with relative high loadings for Ca (−0.44) and Mg (−0.4). This factor is associated with increasing mineralization independently of the origin.

The second factor (PC2), accounting for 22.44% of the total variance, is significantly correlated with Mg (0.89), SO_4 (0.74), and Ca (0.70). This factor is interpreted in terms of water mineralization, where Ca and HCO_3 derived from calcite dissolution and partially from the weathering of Ca-bearing plagioclase. Gypsum dissolution has also an effect on Ca concentrations. Generally, Ca and HCO_3 are dominant in naturally recharging groundwater affected by the rapid dissolution of carbonates and calcium-bearing silicates (e.g., Ca-rich plagioclase). Mg can complement Ca in groundwater, since both elements are originated from the dissolution of Mg-bearing carbonates. On the other hand, NO_3 has no significant loadings for both factors, indicating an external or non-lithologic origin.

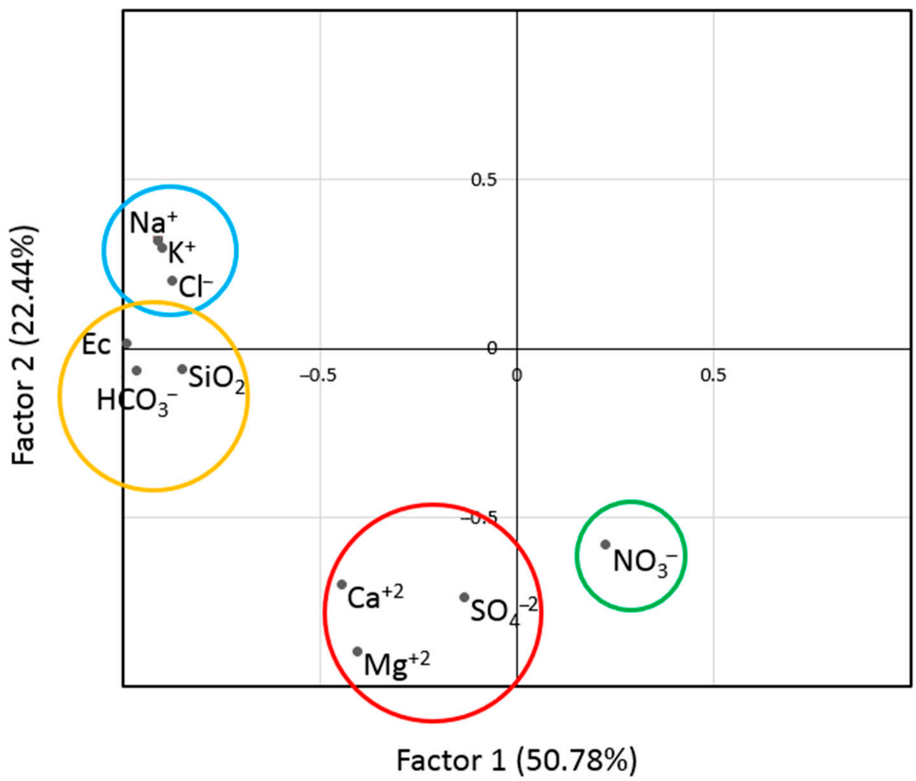

Figure 6. Plot of the principal component analysis results for major elements.

4.1.2. Minor Ions

Although the concentrations of the main constituents determine the mineralisation classification of water, the content of certain trace elements is essential for vital functions [7], while others are toxic [31].

The differences in concentration for each trace element ranged from one up to six orders of magnitude (values between 0.001 and 4400 µg L^{-1}). The low content of these elements partly explains but does not justify their omission from the information provided on the product labels.

The following trace elements showed high concentrations (between 0.1 mg L^{-1} and 4.4 mg L^{-1}) in most of the samples: Sr, Li, Ti, V, Mn, Fe, Cu, Zn, As, Br, Rb, Y, Mo, Sb, I, Cs, Ba, W, Pb, U, A, Sc, Ce, Nd, and Cr. In addition to these elements, high concentrations of others (e.g., Co, Ni, Cd and Be) were found only in some samples.

Figure 7 show the distribution of the selected trace elements through box and whisker diagrams of 29 water samples. The boxes show the interquartile ranges, the whiskers, the 10 to 90 percentiles, and the atypical values (outliers). Values below the limit of detection were set to half of the limit of detection. The diagrams show the concentration limits specified in the EC Directive (Directive 2003/40/EC) for bottled water and water intended for human consumption (Directive 98/83/EC) and also include the recommendations of the Environmental Protection Agency [32] and the Guidelines for Drinking-Water Quality [31] (see also Table 3).

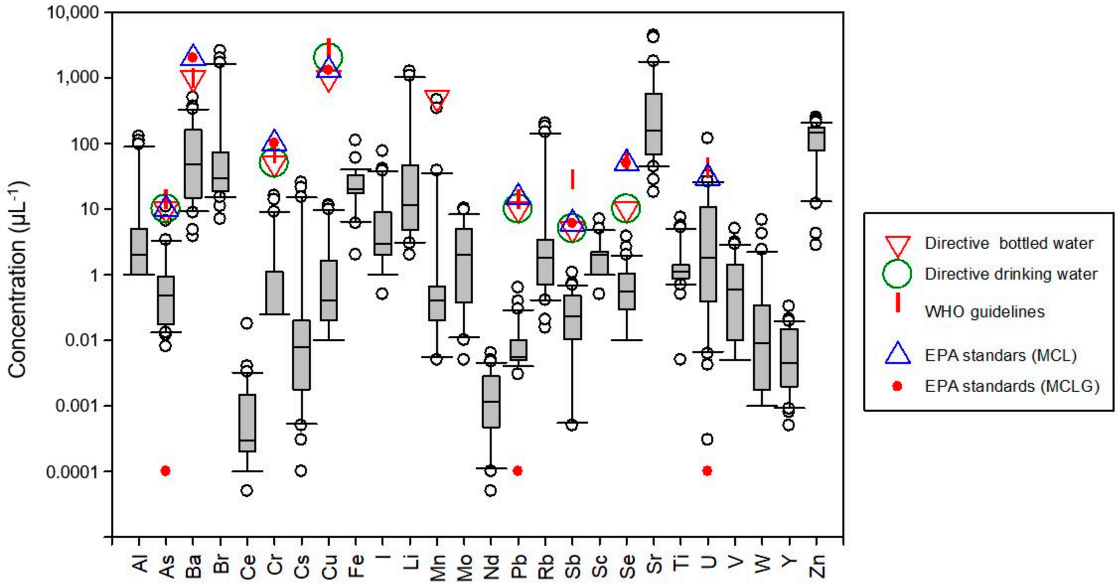

Figure 7. Box plots for trace elements in the sampled mineral waters (n = 29 samples). Boxes correspond to the inter-quartile range of the distribution, whiskers correspond to no more than 1.5 times the inter-quartile range, and outliers are shown as black open circles. EPA standards (MCL) are the maximum concentration level, and (MCLG) represents the maximum concentration level goal.

Table 3. Comparison between the concentration limits, according to the Commission Directive 2003/40/EC, the Drinking-Water Directive, WHO guidelines, and EPA standards (units in micrograms per litre/µg L^{-1}).

Parameter	Guidelines (WHO, 2011)	Guidelines (EPA, 2012)	Max Level (EPA, 2012)	Directive 2003/40/EC	Directive 98/83/EC	Sample Content
Antimony	20	6	6	5	5	All < 1.07
Arsenic	10	0	10	10	10	All < 6.6 No. 9 (10.8 µg L^{-1})
Barium	700	2000	2000	1000	-	All < 500
Beryllium		4	4			All < 1.3
Cadmium	3	5	5	3	5	All < 0.54
Chromium	50	100	100	50	50	All < 16
Copper	2000	1300	1300	1000	2000	All < 11.5
Manganese				500		All < 460
Mercury	6	2	2	1	1	All < 0.2 No. 19 (2 µg L^{-1})
Nickel	70			20	20	All < 6
Nitrate	50,000	50,000	50,000	50,000	50,000	All < 24,500
Lead	10	0	15	10	10	All < 0.63
Selenium	40	50	50	10	10	All < 3.8
Thallium		0.5	2			All < 0.019
Uranium	30	0	30			All < 22.2 No. 24 (32.4µg L^{-1})

4.2. Relationship between Lithology and Physico-Chemical Composition of Waters

There is a clear correspondence detected between the physico-chemical composition and the lithological provenance of the samples. Thus, waters that circulated through granitic rocks (Table 1) showed low mineralisation (except those with a thermal origin), and the dominant major ions were bicarbonate, Ca, and Na. Furthermore, these waters had a high concentration of silica (6–14 mg L^{-1}). In contrast, that of chloride and sulphate was, in general, low. Some samples showed high concentrations of U, Ba, and Mo, correlating with a granite origin (samples Rocaigua, Aquarel Font Selva, and Font del Regás). U, an element whose origin is associated with granitic rocks, was found at high concentrations (32.4 μL^{-1}) in the Rocaigua sample only.

Likewise, bottled waters from the area of Caldes de Malavella (La Selva) had the highest concentrations of As, but they were within the legal limits (6.60 $\mu g\ L^{-1}$ in Malavella sparking water and 3.35 $\mu g\ L^{-1}$ in Vichy Catalan sparkling water). According to the authors of [26], As concentrations of the groundwater in this aquifer exceed 10 $\mu g\ L^{-1}$. It is, therefore, likely that this element is removed prior to bottling. The groundwater around Caldes de Malavella can be considered potentially rich in As because it flows through a geothermal aquifer, with geochemical facies of high salinity (4250–4838 $\mu S\ cm^{-1}$) and high concentrations of Li, B, F, and Si. Local geological sources seem to cause the high As concentrations because arsenic in groundwater is mostly derived from the oxidation of As-bearing pyrite. The Royal Decree 1798/2010, which regulates the exploitation and marketing of natural mineral waters and spring waters packaged for human consumption in Spain, allows the removal of arsenic in some natural mineral waters and springs by air enriched with ozone. In such conditions, the composition of the essential properties of the water will not be altered, and the operator will take all necessary measures to ensure its effectiveness and safety under the control of the competent health authorities.

Waters from the Tertiary sediments (shales, marls and limestones) found in the Central Depression and other Neogene basins are characterised by having a high mineral content (an average EC of almost 1200 $\mu S\ cm^{-1}$), with relatively high sulphate, chloride, Mg, and Ca concentrations and to a lesser extent Na. In terms of the content of certain trace elements, the samples showed an elevated Sr concentration, with a high correlation with Ca and Mg from the original sedimentary material, as well as with Se, which is associated with sulphides [31]. The waters flowing through these materials correspond to the samples Aigua de Rocallaura, Font del Pla Nou, Aigua de Salenys, and Fonter.

Paleozoic rocks (schists, slates, gneisses), which comprise the basement of the Montseny-Guilleries Massif [27], often provide a characteristic composition of the circulating waters, which have bicarbonate as the dominant anion; are relatively low in Na, K, and chloride; and have a high content of Li and Si.

4.3. Meeting Quality Standards

In the European Community, bottled waters are regulated by directives on the exploitation and marketing of natural mineral waters (Directive 2009/54/EC) and bottled water (Directive 2003/40/EC). These standards have been transposed into Spanish legislation (R.D. 1798/2010).

We compared our results with the concentrations provided in the European Water Directive (Directive 98/83/EC), which coincides with the limits laid down by Spanish legislation (R.D. 140/2003).

Virtually all the parameters analysed in this study were lower than those stipulated in European regulations (Table 3).

The As concentration of the samples ranged between 10.8 and 0.080 $\mu g\ L^{-1}$. The sample from Caldes de Bohi was the only one to exceed the limit set by the regulations (10 $\mu g\ L^{-1}$). However, the As content of 90% of the samples was less than 2.75 $\mu g\ L^{-1}$, while for 75%, it was less than 0.10 $\mu g\ L^{-1}$.

As is one of the elements in drinking water that poses the greatest risk to human health. Most groundwater has a concentration of less than 10 $\mu g\ L^{-1}$ of As (WHO, maximum concentration established by the EPA and EC guideline values for natural mineral, spring, and drinking water). However, all the samples exceeded the content recommended by the EPA for water consumption (0 $\mu g\ L^{-1}$).

The U content of samples ranged between 0.003 $\mu g\ L^{-1}$ and 32.4 $\mu g\ L^{-1}$. A maximum concentration of 32.4 $\mu g\ L^{-1}$ (Rocaigua) of this trace element was detected, both values exceeding the limit recommended by the WHO and EPA (<30 $\mu g L^{-1}$). The samples Font del Subirà (26) and Font de les Agudes (22.1), associated with granite aquifers, were also close to this limit. Of the samples, 90% had U concentrations lower than 22.5 $\mu g\ L^{-1}$, while

75% had a U content under 10.6 μg L^{-1}. However, the EPA recommends zero μg L^{-1} for this element. Thus, all the samples analysed exceeded this value.

Significant concentrations of U have been detected in groundwater from granite aquifers in the Catalan Coastal Ranges that are exploited for domestic supply and bottling. In particular, in the Montseny-Guilleries Massif groundwater exceeds 140 μg L^{-1} for this trace element, and in the La Selva Basin it reaches 37.7 μg L^{-1} (at a depth of more than 100 m) [26].

Neither European directives nor Spanish regulations currently define a concentration limit for U in bottled water. In 2009, the European Food Safety Authority (EFSA) assessed the risk of U to human health and concluded that it would be recommendable to fix a guide value for European legislation [33].

Aigua de Vilajuiga has a Mn concentration of 460 μg L^{-1}, close to the limit set by European regulations (500 μg L^{-1}). This element is found throughout the Earth's crust and is usually associated with the presence of Fe. Higher concentrations of Mn are related to aquifers. Moreover, the occurrence of anaerobic conditions may increase the content of this element [34]. The Mn content of 90% of the samples was less than 6.55 μg L^{-1}, while for 50% it was under 0.40 μg L^{-1}.

None of the samples exceeded the maximum concentrations permitted for Sb, Ba, Cd, Cr, Cu, Ni, Pb, Se, and Tl for natural mineral water, spring water, or drinking water (Table 3). We found that 80% of the samples had a Pb concentration that could be considered low or very low (less than 0.1 μg L^{-1}) and were, therefore, below the EU Directive, 2003/40/EC. Two samples far exceed these values: Font Vella (0.63 μg L^{-1}) and Aigua de Salenys (0.39 μg L^{-1}). Nevertheless, EPA recommends that the MCLG (maximum contaminant level goal) for lead in drinking water is zero because lead is a toxic metal that can harm human health, even at low exposure levels. Lead is persistent and can bioaccumulate in the body over time.

Regarding Al and Fe, some samples, such as Aigua de Vilajuiga (128 μg L^{-1} of Al) and Aigua de Rocallaura (110 μg L^{-1} of Fe), had significant concentrations of these elements. However, the standards for natural mineral water and spring water do not include restrictive limits for these metals. Of the mineral water samples analysed, 75% showed concentrations of Al and Fe that can be considered low, concerning the regulations on drinking water (200 μg L^{-1}).

Font del Regás exceeded the concentration of Hg of 2 μg L^{-1}, which marks the European regulations for natural mineral water, spring water, and drinking water of 1 μg L^{-1}. The EPA recommends a concentration of 2 μg L^{-1} and the WHO 6 μg L^{-1} for water for human consumption. The Hg content for all the remaining samples was less than 0.2 μg L^{-1}. This heavy metal is often found in an inorganic form in groundwater (Hg^{2+}), and its concentration can be determined by sulphide mineralisation [31].

4.4. Composition Related to the Kind of Bottle

We have analysed the chemical composition of three brands made saleable in both glass and PET containers (Table 4). The concentrations of Al, Cu, and Fe were found to be higher in the glass containers than in PET containers, except in the Fonter samples. This was also the case for Zn, which was significantly higher in Font d'Or, Sant Aniol, and Fonter glass bottles. Another meaningful result is that concentrations of Sb were greater in water bottled in PET than in glass, particularly for the Font d'Or and Sant Aniol samples.

Table 4. Comparison between 3 water samples bottled in glass and PET.

Brand	Bottle	Ca	Mg	Na	K	Cl	HCO_3	SO_4	NO_3	Si	Al	Sb	As	Ba	Br	Ce	Cs	Cr	Cu
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Font d'Or	PET	24.6	6.20	19.6	2.47	8.47	63.0	13.1	11.7	9.80	2,00	0.24	0.13	18.7	59,0	0.002	0.016	1.20	0.20
Font d'Or	Glass	27.4	3.08	6.48	1.83	7.90	75.4	14.5	8.90	8.00	17.0	<0.01	0.14	13.6	32.0	0.019	0.078	<0.5	0.80
Fonter	PET	35.1	7.75	8.45	0.59	6.02	126	9.86	0.44	6.40	5.00	0.57	0.16	15.7	27.0	0.009	0.005	1.10	4.10
Fonter	Glass	35.9	8.55	7.74	1.59	9.00	135	11.0	5.60	10.0	3.00	0.69	0.17	26.7	27.0	0.033	0.017	2.50	0.20
Sant Aniol	PET	85.4	17.1	6.23	1.63	6.60	316	18.1	2.00	7.20	<2	1.07	0.23	14.9	19.0	0.001	0.003	<0.5	<0.2
Sant Aniol	Glass	102	17.4	3.53	1.55	6.50	343	16.3	2.00	14.3	5.00	<0.01	0.41	14.5	16.0	0.177	0.008	9.00	0.80
Brand	**Bottle**	**I**	**Fe**	**Pb**	**Li**	**Mn**	**Mo**	**Nd**	**Rb**	**Sc**	**Se**	**Sr**	**Ti**	**W**	**U**	**V**	**Y**	**Zn**	
		µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	
Font d'Or	PET	6.00	2.00	0.05	4.00	0.10	1.20	0.034	1.42	2.00	1.00	62.5	<0.1	0.11	8.00	2.90	0.069	2.80	
Font d'Or	Glass	3.00	10.0	0.10	4.00	0.30	2.00	0.012	1.87	2.00	0.90	44.0	1.40	0.12	9.53	2.10	0.027	115	
Fonter	PET	38.0	40.0	0.30	9.00	1.90	0.10	0.013	0.407	1.00	<0.20	105	0.07	<0.02	0.112	0.10	0.029	23.1	
Fonter	Glass	3.00	20.0	0.05	12.0	38.5	<0.10	0.064	1.12	2.00	0.30	99.1	1.10	<0.02	0.062	<0.1	0.131	210	
Sant Aniol	PET	2.00	30.0	0.04	4.00	<0.1	0.10	0.004	0.500	1.00	0.50	340	1.00	<0.02	0.524	0.60	0.005	96.0	
Sant Aniol	Glass	3.00	60.0	0.11	4.00	0.40	0.20	0.008	0.546	2.00	0.70	320	1.00	<0.02	0.549	0.60	0.014	151	

When comparing the metal contents of water bottled in PET and glass, the authors of [18,35] found that the former showed higher concentrations of Sb than the latter. Conversely, water bottled in glass showed higher values of Al, Cu, La, Ce, Mn, Sn, W, Zn, Zr, and Nd than that bottled in PET [35]. In addition, the author of [18] reported higher concentrations of Bi, Cr, Fe, Nb, Th, Ti, and Y in water bottled in glass. The presence of Sb in PET bottles has been associated with the inclusion of this element in PET production, thus, explaining a residual concentration of this metal in PET bottles, which is then transferred to drinking water.

4.5. Health Effects of Some Elements Present in Water

Water is essential for many vital processes of the human body, so much so that, on average, 60% percent of the body weight of an adult can be attributed to water.

The effects of consuming bottled water on health will depend on the frequency of consumption and the health status of the individual. In this study, we considered various types of physico-chemical parameters, principally the content of the main ions but also some trace elements of relevance for human health.

According to Directive 2009/54/EC, bottled waters can be classified as containing bicarbonate ($HCO_3{}^{-1}$ > 600 mg L^{-1}), containing sulphate ($SO4^{-2}$ > 200 mg L^{-1}), containing chloride (Cl^{-1} > 200 mg L^{-1}), containing Ca (Ca^{+2} > 150 mg L^{-1}), containing Na (Na^{+} > 200 mg L^{-1}), and suitable for low-sodium diets (Na^{+} < 20 mg L^{-1}).

Following this directive, the samples Aigua de Vilajuiga, Malavella, San Narciso, and Vichy Catalan can be classified as containing bicarbonate, chloride, and Na, respectively. The sample Aigua de Salenys falls into the calcium bicarbonate category, Aigua de Rocallaura is classified as calcium sulphate, and the samples Aigua de Ribes, Aigua del Montseny, Aiguaneu, Aquarel-Los Abetos, Font del Pla Nova, Font del Regás, Font d'Or, Font del Subirà, Font Vella-Sacalm, FontBoix, Fonter, Fuente Estrella, Pineo, Rocaigua, Sant Aniol, and Sant Hilar are classified as suitable for low-sodium diets.

Bicarbonate-type waters (samples Aigua de Salenys, Aigua de Vilajuiga, Malavella, Sant Hilari, and Vichy Catalan) regulate the acid-base balance of organic liquids [36]. The combination of this anion with other major ions, as is the case of water containing bicarbonate (usually sparkling), Mg, and Ca, promotes many vital body functions. In this regard, such combinations, as in the case of the Aigua de Salenys sample, protect against digestive and hepatobiliary diseases and appear to decrease the concentration of membrane cholesterol in cases of dyslipidemia [37].

Bicarbonate-type water with a high content of Na and chloride balance secretions contributes to fixing the water in tissues, thus, preventing dehydration. In addition, such water facilitates gastric motility, since it stimulates peristalsis in the first intestinal segments, encourages the secretion of bile, and contributes to neuromuscular transmission, due to the Na [37]. This cation acts as a reservoir in the bones where it maintains the pH of the blood [38,39]. The samples Aigua de Vilajuiga, Malavella, San Narciso, and Vichy Catalan were found to meet these criteria.

Given the recommended daily intake (RDI) for chloride (800 mg) according to the R.D. 1669/2009 [40], which establishes and regulates product labelling), the intake of Malavella or Vichy Catalan waters would fulfil requirements for an adult without causing health issues, before taking into account the additional contribution of this anion from the diet. In contrast, water low in Na is recommended for patients with urinary calculi (because of its diuretic effect) and child nutrition [38]. Most of the samples included in this study met this criterion, except for the most mineralised water samples mentioned above.

Waters rich in Ca and Mg contribute to neuromuscular transmission, blood clotting, and gastric motility. Ca also plays a key role in vascular and muscular contraction [21]. Given that the RDI for Ca for adults is between 800 and 1000 mg per day, the ingestion of two litres of certain brands of mineral water every day, such as the sample Aigua de Salenys with 513 mg L^{-1} of Ca, would cover the nutritional needs of this element [41].

Mg is the fourth most abundant cation in the human body and the second most abundant in intracellular fluid. Many studies show a negative relationship between a high concentration of Mg in drinking water (hard water) and the occurrence of cardiovascular diseases, thus, indicating that Mg is protective for human health. This element is also a cofactor enzyme involved in the metabolism of proteins and nucleic acids. In contrast, Mg deficiency has been associated with hypertension, coronary heart disease, diabetes mellitus type 2, and metabolic syndrome [21].

Given that the RDI for Mg for an adult is in the 265–420 mg per day range [40,41], the ingestion of two litres of some brands of mineral water every day, particularly the brands Aigua de Rocallaura (96 mg L^{-1} of Mg) and Aigua del Subirà (94 mg L^{-1} of Mg), would cover 45–70% of the nutritional recommendations for this element.

Finally, sulphate-type waters, such as the sample Aigua de Rocallaura, have an osmotic effect that stimulates gastric motility and improves gastric pH. This type of water, which has high concentrations of Mg, may also have laxative effects [21].

In terms of the trace elements, Li protects against mortality from cardiovascular disease in humans and increases the excretion of Na [37]. Additionally, this element is effective for the treatment of bipolar disorder by moderating and even preventing severe manic episodes. Li has also been found to reduce the high suicide rates associated with mood disorders [42]. The samples Malavella, Vichy Catalán, San Narciso, Aigua del Subirà, and Aigua de Vilajuiga (between 500 and 1300 mg L^{-1}) showed the highest concentrations of Li in the order listed. However, no RDI has been established for this element.

Iodine deficiency has caused nearly 750 million cases of endemic goitre or oedematous cretinism worldwide. This element is a fundamental component of the thyroid hormone, as approximately 60% of the total body I concentrate is on the thyroid gland. Therefore, to ensure proper growth and cellular differentiation and to preserve general cellular metabolism [37], adults should fulfil an RDI of 95 µg of this element. In descending order, the samples Font del Subirà, Vichy Catalan, Fonter, and San Narciso showed high I concentrations (between 37 and 76 µg L^{-1}). The Font del Subirà sample surpassed the RDI, while the other three brands covered almost 80%.

5. Conclusions

We have shown that bottled waters have distinctive geochemical characters (major and trace elements), which are determined mainly by the geology of the point of emergence, as well as by the residence time and the depth of the aquifer. All these factors have given rise to four facies of water hydrochemistry and degrees of mineralisation.

Most of the water samples analysed showed a characteristic low mineral content, which coincides with waters that have calcium bicarbonate facies. In contrast, the samples San Narciso, Vichy Catalan, Malavella, and Vilajuiga showed a sodium bicarbonate composition, with a high ion content, and they were associated with geothermal conditions.

In contrast, 17% were of sodium bicarbonate-type, harder waters, and related to thermal springs.

Although most of the samples met international standards (WHO and EPA, and European and Spanish regulations), with respect to the allowed concentrations of trace elements, some approached or exceeded these limits. Fonter sparking water and Caldes de Bohi exceeded European regulations for Hg and As concentrations, respectively.

Regarding uranium, some years ago, mineral bottled water from Font del Regás had U contents up 100 μg L^{-1}, but our last analysis found content of 2.24 μg L^{-1}. Not all chemicals present in water are regulated in European legislation, partly because they are not considered a public health risk. However, for many years the European Union has been debating the need to establish a limit for U, which is contemplated by the WHO and EPA (30 μg L^{-1}). Although Hg, As, and U are of natural origin, it would be pertinent to monitor their content in bottled water periodically and to include their concentrations on the product label.

Furthermore, the EPA has established a limit of 0 μg L^{-1} for Pb, a concentration exceeded by almost all the samples included in this study.

In three water brands that are marketed both in glass and PET bottles (Fonter, Font d'Or, and Sant Aniol), the concentrations of Al, Cu, Fe, and Zn were between two and seven times higher in glass than in PET bottles. Conversely, the concentration of Sb was 214 times greater in waters bottled in PET than in glass. Given these observations, we propose that bottled water producers be encouraged to use glass bottles, which have the additional advantage of being easily recycled.

The consumption of 2 L a day of some of the bottled waters tested here would cover the RDI of some of the elements necessary for health, such as Mg, Ca, Na, chloride, and sulphate, as well as Li and I.

In accordance with the Directive 2009/54/EC, Aigua de Vilajuiga, Malavella, San Narciso, and Vichy Catalan can be classified as chloride-sodium bicarbonate-type water. With this profile, these kinds of water contribute to regulating the acid–base balance of organic liquids.

The Aigua de Salenys sample, labelled as calcium-magnesium bicarbonate-type, protects from affections of the digestive and hepatic biliary apparatus. Aigua de Rocallaura was found to be a calcium-magnesium-sulphate-type water. This type stimulates gastric motility and improves gastric pH. Most of the samples analysed (Aigua de Ribes, Aigua del Montseny, Aiguaneu, Aquarel, Font del Pla Nova, Font del Regás, Font d'Or, Font del Subirà, Font Vella, Font del Boix, Fonter, Fuente Estrella, Pineo, Rocaigua, Sant Aniol, and Sant Hilari) were found to be suitable for diets low in Na. Given the finding that trace element concentrations in the bottled water samples approached or exceeded the maximum concentrations permitted, we conclude that it would be opportune to establish a stricter periodic control of these elements, particularly Li, Mn, Hg, and U. Additionally, we recommend that suppliers of bottled water include information about these elements on the labels.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w14213581/s1, Table S1: Results for EC and the 35 elements with significant values in all samples.

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