Chemical composition of Chilean bottled waters: Anomalous values and possible effects on human health

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Chemical composition of Chilean bottled waters: Anomalous values and possible effects on human health

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HIGHLIGHTS

- Chilean bottled waters do not comply with national drinkable water regulations.
- As levels in some Chilean bottled waters exceed values established by WHO and EPA.
- Risk evaluation reveals As in bottled water (1 L/d) is not a threat for humans.

ARTICLE INFO

ABSTRACT

The Chilean bottled water market has experienced continuous growth since 2000, surpassing 500 million liters sold in 2015. Generally, consumers tend to associate the consumption of bottled water with a healthy lifestyle, but current Chilean law does not require the product to be labelled with the chemical composition, thus preventing consumers from making informed choices.

Our study focuses on determining the water quality of ten brands of bottled water available for sale in Santiago, Chile. All of the analyzed water was not carbonated and in plastic containers in the 1.5 L size when available and the closest size to this when not available. Thirty-two chemical elements were analyzed, including minor and trace elements, and the data have been evaluated with respect to the limits established by Chilean and international regulatory agencies.

Our results indicate that the quality of the analyzed water generally complies with Chilean law for bottled water. However, 30% of the analyzed samples exceed the values of arsenic (As) permitted by Chilean drinking water regulations, the World Health Organization and the United States Environmental Protection Agency. In 40% of the samples, the NO_3 content is higher than groundwater values suggesting that the source of the bottled water is superficial. The purified bottled water brands contain minimal amounts of dissolved elements but do not comply with all of the parameters (e.g., pH) established by Chilean drinking water regulations.

Our study highlights that there is an inconsistency between the Chilean norms that regulate bottled water and those that regulate drinking water. Some of the analyzed bottled waters do not comply with the drinking water regulations and paradoxically these brands should not be consumed by humans. However, risk assessment calculations for As ingestion show that the consumption of 1 L/day of bottled water does not pose a risk for human health.

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1. Introduction

The fundamental role of water in human health and in the performance of multiple functions of the human body is well known. Water regulates body temperature, helps with dissolution of vitamins and minerals, transports nutrients and oxygen to the cells, as well as the waste products of metabolism, and removes toxins to reduce the burden on the kidneys and liver (Montain et al., 1999; Jequier and Constant, 2010).

Several authors have reviewed the use of different types of water, underlying the importance of oligomineral and bicarbonate waters as these serve to treat a large number of disorders, including problems with the liver, intestine and digestive systems (Albertini et al., 2007; Marcussen et al., 2013; Rosborg et al., 2015a). Some oligomineral waters increase diuresis, normalize urinary pH and help with the elimination of

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uric acid, while magnesium bicarbonate waters intervene in the functioning of the digestive system (Lima et al., 2010; Kozisek et al., 2015; Rosborg et al., 2015b) and carbonate waters stimulate secretions and motility of the digestive tract (Schoppen et al., 2004; Gasbarrini et al., 2006).

The benefits associated with water consumption have led to a constant worldwide increase in the consumption (and sale) of bottled water. Establishing guidelines for drinking and bottled water is very difficult since the degree and time of exposure play an important role in the determination of the adverse health effects on humans.

Bottled water is a commodity of daily consumption for many people and has generated an active niche market offering consumers endless options. Consumers of this product also associate its consumption with a healthy lifestyle, and although for a long time the presence of trace elements in drinking water has not been considered important for human health, recent clinical and pharmacological studies have documented that trace elements can create adverse effects (Selinus et al., 2005). Recent studies on bottled water from different countries have revealed that some of the analyzed waters exceed permissible concentrations of potentially toxic elements (Birke et al., 2010; Güler and Alpaslan, 2009; Cicchella et al., 2010; Palomo et al., 2007). Legislation on bottled water varies widely across countries. For example, legislation in Europe provides the guidelines for labelling bottled waters (EC, 2003), with labels listing specific geochemical data on the contents that can be particularly harmful to a sector of the population (art. 4, paragraphs 1–2). Legislation 21 by the FDA (United States Food and Drug Administration) establishes quality standards for ninety chemical substances, classifies bottled water according to its origin (artesian, subterranean, spring, surface) and purification treatments (distilled, deionized, purified, reverse osmosis, etc.) and regulates what information must be contained on the label of each bottle (FDA, 2019).

In Chile, there has been more than a 400% increase in the consumption of bottled water between 2000 and 2013 (Fig. S1), with national consumption reaching approximately 393 million liters of bottled water (SERNAC, 2015). Although bottled water consumption in Chile does not reach that of the top 20 countries in the world (2012–2017, Beverage Marketing Corporation, 2018) and falls only in the middle of the list of Latin American countries (Fig. S2) (LABWA, 2015), consumption has increased significantly over the last 20 years. Between 2000 and 2009, the amount of bottled water consumed in Chile nearly doubled from 80 to 150 million liters, and in 2010 consumption nearly doubled again from 150 to 247 million liters, coinciding with the M 8.8 Maule earthquake that occurred on February 27, 2010 (Fig. S1). Following 2010, bottled water consumption has continued to increase sharply each year and is projected to follow this trend until at least 2020 (Bonatici, 2017).

The decree N. 106/1997(DS106) by the Ministry of Health (MINSAL, 1997) in Chile contains the guidelines for the classification of mineral waters, lists the parameters that are monitored, and sets concentration limits for seventeen chemical elements (Table S1). However, the decree does not provide complete regulations on the labeling and presentation of the chemical composition of the bottled water. In the Chilean market, it is possible to find different types of bottled water: natural, mineral, carbonated, non carbonated and purified, with a wide range of prices and generally two types of packaging—plastic and glass. Over the past two decades, only two studies have been performed on bottled waters, both by the National Consumer Service of Chile (SERNAC). The first study compared physical properties and composition of bottled mineral waters sold in the city of Santiago with current regulations (SERNAC, 2001). The second study (SERNAC, 2015) performed an evaluation of prices and labeling of bottled water in 20-liter containers commercialized only in Iquique, Chile.

To determine the quality of Chilean bottled water, we analyzed the chemical composition of the ten best-selling brands in Chile and compared the results with the threshold limit values established by Chilean and international regulatory agencies (Table S1).

2. Material and methods

2.1. Characteristics of water sources

The chemical composition of water is affected by geological factors, such as the local geology of the spring source area and the composition of the rocks in contact with the water (Bhattacharya et al., 2014). Rock units that are most likely to interact with water are found upstream of the source area. In Fig. 1, we show the location of the springs where the samples have been bottled and summarize the main geological features related to the sampled waters (Table S2). According to the 1:1000000 geological map of Chile (SERNAGEOMIN, 2003), Jumbo and Jahuel waters flow through continental or transitional sedimentary rocks, andesitic to basaltic volcanic rocks, and granitic or granodioritic plutons. Porvenir water comes in contact with marine or continental sedimentary rocks, andesitic and basaltic volcanic rocks and granitic intrusive rocks. Cachantun water flows through marine and continental sedimentary rocks, rhyolitic to andesitic volcanic rocks, and granitic to granodioritic plutons. Vital water interacts with marine, transitional and continental sequences, andesitic to basaltic volcanic rocks, and granitic to granodioritic plutons. Tottus water flows through marine, transitional and continental sequences, andesitic to basaltic volcanic rocks, and granodioritic to tonalitic plutons. Waters from Andes Mountain are in contact with rhyolitic, andesitic and basaltic volcanic rocks, granitic to granodioritic plutons, and metamorphic rocks (metapelites, metacherts, metabasites, and ultramafic rocks). Puyehue water flows through rhyolitic, andesitic and basaltic volcanic rocks and granodioritic to tonalitic plutons.

Puyehue bottled water is thought to be influenced by the Puyehue-Aguas Calientes geothermal system, where the waters are extracted from a well at a depth of 143 m (Celis, 2012) in an area close to an active volcano (Puyehue Volcanic Complex). Jahuel and Jumbo waters have their source in a hydrothermal alteration system associated with the Pocuro Fault (Bustamante et al., 2012). The source of Tottus water is located in the thermal area of Panimávida, near the baths of Quinamávida where water springs have a temperature of 23 °C, a flow rate lower than 1 L/s, an alkaline pH of 9.2 and a total dissolved solids content of 170 ppm (Benavente, 2010).

About twenty brands of bottled water are commercialized in the Chilean market, twelve of which are mineral waters. Among those, four brands target the premium segment of the market (Brian, 2015): Andes Mountain (from the feeder river of Lake Colico, Araucanía Region), Aonni (from waters that originated on the shores of the Strait of Magellan), ICESWAN (Queulat River, Aysén Region) and Puyehue (Puyehue National Park, Los Lagos Region). The other mineral water brands are concentrated in the Valparaiso and Maule Regions. The purified water brands have little to no information about their spring sources.

Based on Internal Tax Service reports (SII, 2012 and SII, 2015), we analyzed the main economic activities that can affect the quality of the waters in the study areas. For example, agricultural activity has decreased in all areas of production of our samples (−20%), with only one area (where Tottus' spring is located) experiencing an increase in cultivation and farming. Mining activity has been relatively stable in the analyzed period, with only Tottus' spring location experiencing a significant decrease (−21%).

2.2. Bottled water preparation

During the month of August 2016, ten samples of bottled water available on the Chilean market were purchased in randomly selected shops in the city of Santiago. The selected bottled waters did not contain added gas and were purchased in the 1.6 L (Cachantun, Jahuel, Jumbo, Tottus, Vital), 1.5 L (Benedictino, Nestlé, Puyehue), and 1 L (Andes Mountain) sizes. All of the analyzed waters were contained in plastic bottles made of polyethylene therephtalate (PET) with a polyethylene
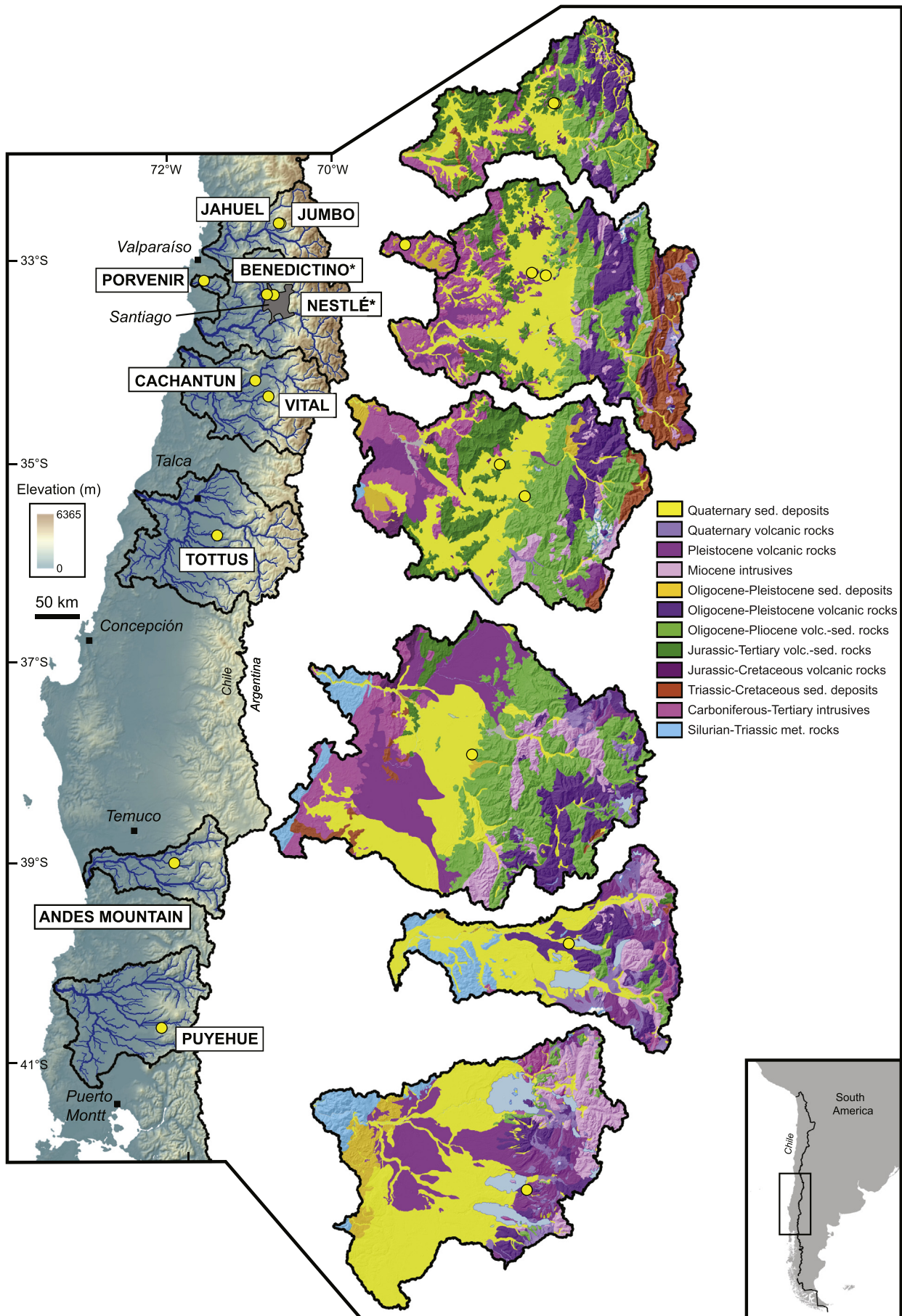
(PE) cap. Eight samples were mineral water and two were purified water, with all samples being from different brands.

2.3. Bottled water analysis

Each water sample was analyzed for 32 chemical elements and ions (Ag, Al, As, B, Ba, Be, Ca, Cd, Cl, Co, Cr, Cs, Cu, F, Fe, HCO₃, Hg, K, Li, Mg, Mn, Mo, Na, Ni, NO₃, Pb, Rb, Se, SO₄, Sr, U, Zn).

The bottled waters were all analyzed at the Fluid Geochemistry Laboratory of CEGA (Andean Geothermal Centre of Excellence) in the Department of Geology at the University of Chile. The anion content (F, Cl^-, Br^-, SO_4^{2-}, NO_3^-) was obtained by using a Thermo Scientific Dionex ICS-2100 Ionic Chromatographer. Cations (Na^+, K^+, Ca^{+2}, Mg^{+2}) were analyzed by a Perkin Elmer Optima 7300 V ICP-OES, and trace elements (Li, Be, B, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Ag, Cd, Cs, Ba, Hg, Pb, U) were obtained by a Thermo Scientific iCAP Q ICP-MS. Electrical conductivity (EC, 0–200 mS/cm^{-1}) and pH (0–14) were measured using a multi-parameter Hach HQ40d for each water sample immediately after opening the bottles in the laboratory. Carbonates and bicarbonates were measured by applying the method of Giggenbach and Goguel (1989). Tables 1 and 2 summarize all of the results.

To determine the sample water type, we used pH, hardness, electrical conductivity data and ionic concentrations. Hardness was evaluated using the classification of the U.S. Geological Survey (USGS, 2016). Major ions have been used to classify the waters using Stiff diagrams (Fig. 2). Trace and minor ion concentrations were compared with legal values established by Chilean and international regulations (Table S1).

Although toxins found in bottled water are primarily from the water source itself, the plastic bottle may also be a source of contamination. A study of bottled water from nine different countries revealed that 93% of the bottled water contained micro fragments of plastic believed to originate from the plastic container or bottling facility (Mason et al., 2018). Analysis of water bottles from 28 countries showed that the polyethylene terephthalate (PET) used to make water bottles can release concentrations of antimony (Sb) after being stored for 6 months at room temperature (Shotyk and Krachler, 2007). Water bottles from China stored at high temperatures (max. 70 °C) over several weeks yielded high amounts of Sb as well as bisphenol A (BPA) (Fan et al., 2014). These water bottle plastics are also believed to create endocrine disruptors (Wagner and Oehlmann, 2009), which in high amounts can have adverse effects on humans (Diamanti-Kandarakis et al., 2009). Although water bottles from this study should also be tested, the wide range of elements found suggests that the water, not the bottles, has been the primary source of the elements measured.

2.4. Statistical analysis

A deterministic approach was used to assess the non-carcinogenic risks from As, which has a toxicity threshold value (or reference dose RfD) that is available in the literature (EPA, 1993). The carcinogenic risk has not been calculated since the values of As are significantly lower than the established RfD values for ingestion (TOXNET database).

We calculated the risk by using an average adult human weight of 70 kg and an average mineral water consumption rate of 1 L/day. In order to calculate the average daily dose, we considered the dose to be only dependent on the water ingestion and trace element concentration, and therefore normalized the values with body weight as a function of time. We have assumed that ingestion of 1 L of bottled water occurred every day over a 30-year period.

The health risk assessment was calculated using the equation developed by the United States Environmental Protection Agency (EPA) for non-carcinogenic metals as shown by Naughton and Petróczi (2008):

$$THQ = \frac{EF * FD * DIM}{RfD * W * T} \quad (1)$$

where THQ is the target hazard quotient, EF is the exposure frequency (day ∗ years^{-1}), FD is the exposure duration (years), DIM is the daily metal ingestion (mg ∗ day^{-1}), RfD is the reference dose (mg ∗ kg^{-1} ∗ day^{-1}), W is the adult average body weight (kg) and T is the average exposure time for non-carcinogens (number of days ∗ year^{-1} ∗ FD). The parameters used for the calculations are summarized in Table 3.

3. Results

3.1. Major elements and water classification

The average value of electrical conductivity (E.C.) of all of the samples is 341.0 μS/cm. The Cachantun sample has the highest E.C. value of the study (807.6 μS/cm) while the Benedictino sample, which is purified bottled water, has the lowest value (22.7 μS/cm). In general, the pH of the samples is basic with an average value of 7.7, but the Tottus and Nestlé samples have pH values of 9.3 and 5.7, respectively.

Andes Mountain (unpurified water) and Benedictino (purified water) stand out for having low mineralization values. Stiff diagrams (Fig. 2) show that the sampled water belong to different hydrogeochemical types: Andes Mountain, Porvenir, Vital and Tottus are bicarbonate waters, Jahuel, Jumbo and Cachantun are sulfate waters, and Benedictino, Puyehue and Nestlé are chlorate waters.

Hardness calculations (Table 2) indicate that four samples (Andes Mountain, Benedictino, Puyehue and Tottus) are classified as soft water while Jumbo, Jahuel y Cachantun are classified as very hard water. The rest of the samples are between hard (Porvenir) and moderately hard water (Vital and Nestlé).

The Porvenir sample has the highest bicarbonate concentration of the study (168.5 ppm), while the Jahuel sample has the highest sulphate concentration (191.3 ppm). The highest chloride value was measured in the Nestlé sample (58.3 ppm). Calcium, sodium, magnesium and potassium are present in concentrations that progressively decrease in the order listed. The maximum nitrate content from this study is 44.3 ppm (Cachantun) but the majority of the samples have concentrations below 10 ppm.

To visualize the ionic concentrations, values are shown in box-and-whisker plots (Fig. 3). The results indicate that the data have a strong dispersion with standard deviation values greater than the average.

3.2. Minor and trace elements

In this study, twenty-four minor and trace elements were analyzed, with most values found below detection limits (e.g., Ag, Cd, Pb, Be, Cr and Zn).

The results show that Sr content is low in almost all of the samples except for Porvenir (130 ppb), Jahuel and Jumbo (>300 ppb), and Cachantun (526 ppb).

All of the samples have Al, Fe and Mn values below detection limits except for the Tottus sample, which is the only one from this study that has concentrations of Fe (128.1 ppb), Al (114.2 ppb) and Mn (3.3 ppb). Puyehue is the only sample that has a detectable amount of Hg (0.09 ppb), and U, Cs, Co and Ni have also been measured in at least half of the samples. As concentrations are found in all of the samples except for Andes Mountain, with a range between 0.13 (Nestlé) and 18.97 ppb (Puyehue). The Jahuel and Jumbo samples have a similar As concentration of 12.5 ppb and 12.8 ppb, respectively.

Fig. 1. Bottled water brands and water source locations. Shaded relief map created in ArcGIS using 90 m SRTM elevation data. Geology maps created in ArcGIS based on 1:1000000 geological map of Chile (SERNAGEOMIN, 2003). *Benedictino and Nestlé are purified water, so map locations represent bottling facilities.

Table 1
Concentrations of cations, anions, trace elements, values of conductivity and pH, and statistical results for the sampled bottled water. ND = Not determined; (*) = Purified Water. Cation and anion threshold limits = Limit of Detection (LOD). Trace element threshold limits = Limit of Quantification (LOQ).

	Units	Tottus	Andes Mountain	Jumbo	Vital	Jahuel	Cachantun	Porvenir	Puyehue	Nestlé*	Benedictino*	MIN	MAX	AVG	SD	LOD
pH		9.3	7.4	7.3	8.1	8.3	7.7	7.5	7.4	5.7	8.1	5.7	9.3	7.7	0.9	
Conductivity	(µS/cm)	333	35	644	203	642	743	380	185	233	23	23	743	349	257	
Bicarbonates	mg/L	150.19	10.01	149.82	93.28	123.17	140.71	168.49	38.32	4.27	1.02	1.02	168.49	87.93	67.77	–
Carbonates	mg/L	8.62	ND	ND	ND	ND	ND	ND	ND	ND	ND	–	–	–	–	–
Fluoride	mg/L	0.41	0.04	0.14	0.15	0.16	0.04	0.22	0.21	0.08	BDL	0.04	0.41	0.16	0.11	0.03
Chloride	mg/L	3.64	1.76	5.18	1.15	5.39	42.28	14.15	25.23	58.29	2.64	1.15	58.29	15.97	19.87	0.03
Sulphate	mg/L	11.99	0.44	185.84	16.79	191.3	118.34	28.74	10.57	0.68	1.02	0.44	191.3	56.57	77.82	0.03
Bromide	mg/L	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	–	–	–	–	0.03
Nitrate	mg/L	0.34	0.25	8.1	2.5	8.57	44.26	5.93	0.39	2.21	2.05	0.25	44.26	7.46	13.3	0.03
Sodium	mg/L	79.35	2.46	29.44	19.46	31.41	23.23	24.07	32.05	4.61	4.27	2.46	79.35	25.04	22.24	0.094
Potassium	mg/L	0.8	0.32	1.92	0.17	1.96	3.64	1.07	1.17	0.17	0.1	0.1	3.64	1.13	1.12	0.044
Calcium	mg/L	1.37	2.59	75.4	21.11	78.8	114.3	32.76	3.47	27.04	0.24	0.24	114.3	35.71	40.11	0.014
Magnesium	mg/L	0.02	1.11	21.76	2.45	21.58	12.19	17.05	0.63	5.02	<0.001	<0.001	21.76	8.18	9.08	0.001
Li	µg/L	9.51	0.11	6.6	1.33	6.58	21.91	1.55	3.7	<0.06	0.45	<0.06	21.91	5.18	6.73	0.02
Be	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	–	–	–	–	0.002
B	µg/L	294.18	2.46	124.21	10.19	118.35	264.84	5.42	1449.69	103.72	209.77	2.46	1449.69	258.28	431.47	0.07
Al	µg/L	114.2	5.9	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	114.2	–	–	0.06
Cr	µg/L	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	–	–	–	–	0.02
Fe	µg/L	128.1	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	128.1	–	–	0.9
Mn	µg/L	3.31	0.27	<0.01	<0.01	0.06	<0.01	<0.01	0.08	<0.01	<0.01	<0.01	3.31	0.38	1.03	0.004
Co	µg/L	0.02	<0.02	0.1	0.03	0.1	0.16	0.04	<0.02	0.04	<0.02	<0.02	0.16	0.06	0.05	0.005
Ni	µg/L	<0.1	0.16	1.2	0.42	1.26	1.91	0.64	0.19	0.55	<0.1	<0.1	1.91	0.65	0.61	0.03
Cu	µg/L	<0.2	4.14	<0.2	<0.2	<0.2	0.96	0.72	<0.2	<0.2	<0.2	<0.2	4.14	0.72	1.23	0.05
Zn	µg/L	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	–	–	–	–	0.2
As	µg/L	7.09	<0.06	12.76	6.18	12.54	2.46	0.3	18.97	0.13	1.04	<0.06	18.97	6.15	6.64	0.02
Se	µg/L	<0.3	<0.3	2.06	0.3	2.15	<0.3	1.03	<0.3	<0.3	<0.3	<0.3	2.15	0.73	0.76	0.08
Rb	µg/L	0.73	0.77	4.42	0.19	4.43	5.09	0.06	1.75	0.08	0.07	0.06	5.09	1.76	2.06	0.001
Sr	µg/L	0.75	21.35	305.09	54.42	305.74	525.91	129.98	16.68	11.08	0.59	0.59	525.91	137.16	181.27	0.001
Mo	µg/L	2.91	0.03	3.99	2.98	3.68	0.72	2.3	3.12	<0.006	0.08	<0.006	3.99	1.98	1.60	0.002
Ag	µg/L	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	–	–	–	–	0.001
Cd	µg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	–	–	–	–	0.001
Cs	µg/L	0.02	0.025	0.189	0.018	0.197	<0.001	<0.001	0.125	<0.001	<0.001	<0.001	0.197	0.06	0.08	0.0004
Ba	µg/L	0.63	2.55	15.68	0.11	15.43	25.4	3.54	1.84	0.29	<0.02	<0.02	25.4	6.55	8.96	0.01
Hg	µg/L	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004	0.09	<0.004	<0.004	<0.004	0.09	–	–	0.002
Pb	µg/L	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	–	–	–	–	0.002
U	µg/L	<0.001	<0.001	0.215	<0.001	0.245	0.648	0.642	0.01	<0.001	<0.001	<0.001	0.648	0.18	0.26	0.0002

Table 2
Classification of sampled water, values of hardness, TDS (Total Dissolved Solids), and pH. (*) = Purified water. (**) = ppm CaCO₃. (***) = ppm.

Sample	Water type	Hardness**	TDS***	pH
Tottus	Na-Bicarbonate	3.5 soft	218.5 very low mineralization	9.3
Andes Mountain	Mixed-Bicarbonate	11.0 soft	22.7 oligomineral	7.4
Jumbo	Ca-Sulphate	277.7 very hard	422.7 low mineralization	7.3
Vital	Ca-Bicarbonate	62.8 moderately hard	133.0 very low mineralization	8.1
Jahuel	Ca-Sulphate	285.5 very hard	421.2 low mineralization	8.3
Cachantun	Ca-Sulphate	335.7 very hard	487.7 low mineralization	7.7
Porvenir	Ca-Bicarbonate	151.8 hard	249.2 very low mineralization	7.5
Puyehue	Na-Chloride	11.3 soft	121.2 very low mineralization	7.4
Nestlé*	Ca-Chloride	88.2 moderately hard	146.4 very low mineralization	5.7
Benedictino*	Na-Chloride	0.6 soft	14.9 oligomineral	8.1

The analytical errors in the measured dataset were determined using standard solutions and are found to be negligible, thereby reinforcing the reliability of the dataset and interpretations.

4. Discussion

The analyzed bottled water samples belong to different hydrogeochemical types, ranging from Ca and Na-HCO₃ to Ca and Na—Cl types. All of the samples have low E.C. values and therefore can be considered as low mineralized waters.

Andes Mountain, Puyehue, Tottus and Benedictino have very low hardness values (0.6–11.3 ppm CaCO₃), while the Cachantun, Jahuel and Jumbo samples are classified as very hard (277.7–335.7 ppm CaCO₃). Extremely soft or hard drinking water is considered to be not good for human health or even liked by people primarily for its taste (WHO, 2011; Verma and Kushwaha, 2014). Kozisek (2005) also shows that human kidney stone formation can be related to soft and hard drinking waters.

The low mineral content of these samples seems to be related to the water-rock interaction processes that occur along the flow path from the recharge to the outflow area.

In general, the major ions have normal concentration values, but samples with the highest NO₃ content are somewhat concerning as these can be related to pollution processes primarily linked to the intense use of fertilizers and sewer seepage practices. The link between agriculture, NO₃ use in fertilizers and the worsening of water quality is well known (Wauchope, 1977; Dudka and Adriano, 1997; Zalidis et al., 2002; Pimentel et al., 2004; Kumar et al., 2005). As suggested by WHO (2017 and references therein), concentrations of up to 9 ppm
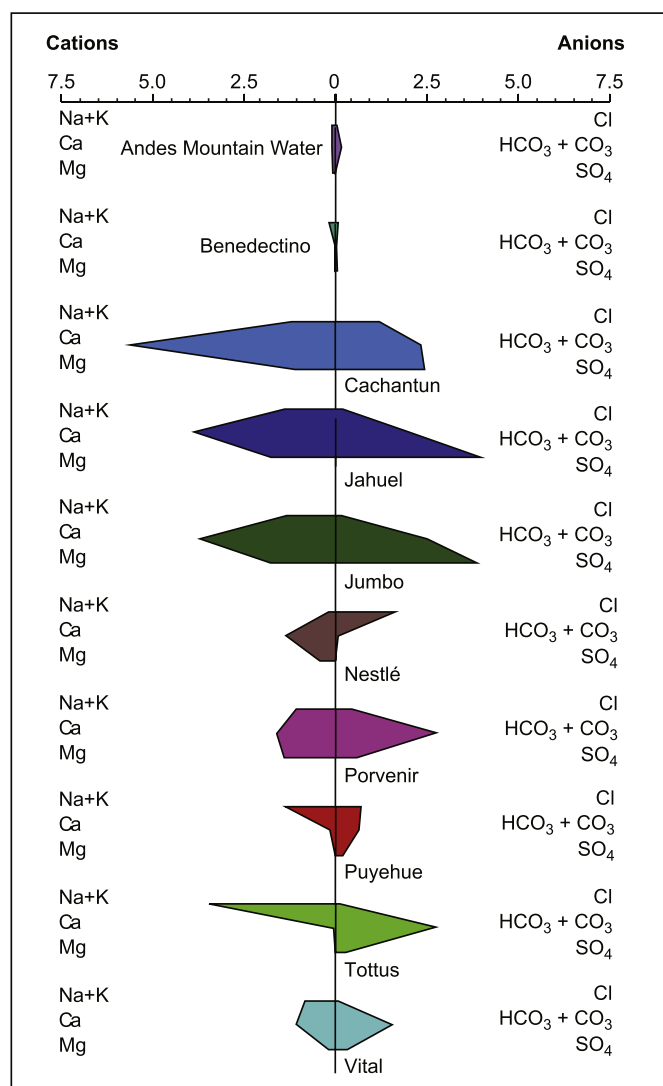
Fig. 2. Stiff diagram for sampled bottled water.

Mining is often reported as an activity that worsens water quality because soil and rock movements facilitate the leaching of potentially toxic metals and metalloids from the material extracted from the mines while also generating pollution from the metallurgic industry (Helios, 1996; Razo et al., 2004; Younger and Wolkersdorfer, 2004; Ochieng et al., 2010; Parra et al., 2011). Several studies on the correlation between mining activity and water quality have been conducted worldwide (Helios, 1996; Thornton, 1996; Razo et al., 2004; Younger and Wolkersdorfer, 2004; Ochieng et al., 2010; Palmer et al., 2010), including Chile (Oyarzún et al., 2006; Parra et al., 2011; Carkovic et al., 2016). Chile, like many other countries, faces a big problem with anomalous As concentrations in waters (Mukherjee et al., 2014; Raychowdhury et al., 2014), especially in the northern part of Chile where a legally higher value is permitted. Thus, special attention must be made for the presence of As, even in minor and trace amounts, to determine possible sources.

The water samples from this study have very low concentrations of minor and trace elements. In fact, most of these elements are below detection or quantifiable limits. However, As has been quantified in all of the samples, with 30% having values higher than 10 ppb.

For the risk assessment evaluation of As, THQ values <1 indicate that there is a reduced health hazard, while values between 1 and 5 represent a human health hazard (Gergen and Harmanescu, 2012). All of the analyzed waters from this study have THQ values <1, suggesting that the consumption of 1 L/day of bottled water should not be hazardous for human health.

As is the case for the major elements, the minor and trace element concentrations of the ten samples can be attributed to natural water-rock interactions. The small chemical differences detected between the samples are associated with the differences in the geological and hydrogeological settings of the springs. In fact, samples from Jahuel and Jumbo, bottled in the same area, have a very similar chemical composition, thereby highlighting the relevance of water–rock processes. In addition, these two water samples have a similar As content that fits with published values of As in the area (Hauser, 1997; Benavente, 2015).

All bottled waters analyzed in this study have concentrations below the thresholds established by DS106, but if drinking water regulations (NCH409/1) are applied, then some bottled water samples do not comply with the Chilean national limits, especially samples with high values of pH and As. Values of pH for the Tottus (9.3) and Nestlé (5.7) samples do not fit with the permissible pH range of NCH409/1 (6.5 to 8.5), although there is no scientific evidence for the possible negative health effects of water consumption with these high pH values (WHO, 2011).

Regarding As content, the Puyehue (19.0 ppb), Jahuel (12.5 ppb) and Jumbo (12.8 ppb) samples contain between 25% and 90% more As than that permitted by drinking water regulations (NCH409/1). The permitted value for As in DS106 is 50 ppb, while the permitted value by NCH409 is 10 ppb, which coincides with that suggested by the EPA (2009) and WHO (2011). In Chile, the threshold value for As in drinking water was changed with NCH409/1 as a result of an actualization of the law, while DS106 that regulates bottled water has not been changed

could be considered to be naturally occurring in groundwater. Most of the samples from this study have NO_3 concentrations below 8 ppm except for the Cachantun sample, which has a NO_3 concentration that is almost 5 times higher than the other samples (44.3 ppm). We suggest that the source of NO_3 for the majority of the bottled water in this study is natural, while the source for the Cachantun sample is most likely from agricultural and mining activity in the area (SII, 2012 and SII 2015). The Cachantun bottling facility is located in the Coinco valley (Cachantun location, Fig. 1), which is an area with intense agricultural activity that may explain the high NO_3 concentration.

Table 3
Parameters used for risk assessment calculations. (*) = Purified water. (**) = Actual values less than those shown but threshold limits used for calculations.

|	As ppb	As ppm	DIM (mg d^{-1})	EF (d y^{-1})	FD (y)	RdF (mg kg^{-1} d^{-1})	W (kg)	T (d)	THQ
Tottus	7.09	0.00709	0.01418	365	30	0.0003	70	10,950	0.338
Andes Mountain	0.06**	0.00006	0.00012	365	30	0.0003	70	10,950	0.003
Jumbo	12.76	0.01276	0.02552	365	30	0.0003	70	10,950	0.608
Vital	6.18	0.00618	0.01236	365	30	0.0003	70	10,950	0.295
Jahuel	12.54	0.01254	0.02508	365	30	0.0003	70	10,950	0.598
Cachantun	2.46	0.00246	0.00492	365	30	0.0003	70	10,950	0.118
Porvenir	0.30**	0.00030	0.00060	365	30	0.0003	70	10,950	0.015
Puyehue	18.97	0.01897	0.03794	365	30	0.0003	70	10,950	0.903
Nestlé*	0.13	0.00013	0.00026	365	30	0.0003	70	10,950	0.006
Benedectino*	1.04	0.00104	0.00208	365	30	0.0003	70	10,950	0.050
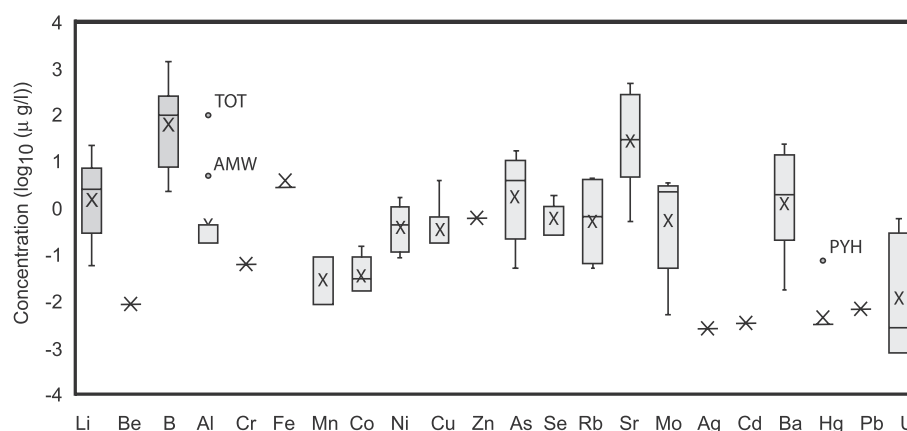
Fig. 3. Box-and-whisker plot of ionic concentrations for sampled bottled water.

since 1997. This means that three of the bottled water samples analyzed in this study and available for sale to the Chilean population are not considered suitable for consumption according to drinking water standards.

When comparing Chilean and international water regulations (EPA, 2009; WHO, 2011), some differences exist relating to the element type and amount considered. For example, there are no regulations in Chile for Sb, asbestos, Be, BrO$_3$, Ni, U, and Tl and DS106 establishes higher limits for As and Pb. Acceptable values of Cd and Pb in mineral and drinking water are higher in Chile than values accepted by the EPA (2009) and WHO (2011), although all sampled waters from this study comply with the international standards of these two elements.

With regard to elements not considered by the Chilean regulatory agencies (e.g., U), five of our samples have U concentrations between 0.01 and 0.65 ppb. The maximum concentrations were found in the Cachantun and Porvenir samples, but the values are approximately fifty times lower than the limit (30 ppb) established by the EPA (2009) and WHO (2011).

5. Conclusions

This paper has analyzed the physicochemical composition of ten different brands of bottled water available for sale in the Chilean market. This study aims at starting a discussion in Chile about the importance of bottled water quality and the right of the consumer to buy a healthy and safe product with contents clearly labelled on the bottle. The results of this study should be used as an aid to know the composition of Chilean bottled water, which has become a product commonly bought by numerous Chileans over the last five years.

It is also important to note that different brands do not always have different water sources. This means that water from the same source can be bottled with different brand names, as is the case for the Jahuel and Jumbo water brands that are both extracted from the Termas de Jahuel (about 100 km north of Santiago).

Our results indicate that Chilean bottled waters have different chemical compositions with different pH, hardness and mineralization values. Ionic contents indicate that water-rock interactions are the main source of the physicochemical composition of the waters.

To regulate water chemistry, Chile has established regulations for bottled (DS106; MINSAL, 1997) and drinking water (NCH409/1; INN, 2005). All of the water samples analyzed in this study have values below limits established for bottled water (DS106), but the difference between these regulations has shown that some of the bottled waters could not be used for consumption as drinking water.

Among the analyzed parameters and ions, pH and As are found in concentrations that exceed the drinking water limits (NCH409/1). Two samples, Tottus and Nestlé, have pH values that do not fit within the range established by Chilean drinking water regulations. The

Puyehue, Jahuel and Jumbo samples have between 20% and 90% more As than the amount permitted for drinking water (10 ppb). In addition, the Cachantun sample has a NO$_3$ content that is very close to the maximum limit allowed by the EPA (2009) for human consumption, especially for newborn babies.

DS106 (MINSAL, 1997) is outdated and particularly permissive for As, Pb and Cd. We suggest that the permissible values should be changed in order to comply with those established for drinking water by international regulatory agencies. Furthermore, the current labelling of Chilean bottled waters does not reveal the content of the product, as it lacks information about organoleptic properties (water type, hardness, pH, cations and anions).

Risk assessment calculations of the analyzed water did not reveal any carcinogenic or non-carcinogenic effects on humans, but a slight increase in daily consumption could result in values exceeding acceptable limits for non-carcinogenic effects, and therefore could increase the potential risk for human health. The preliminary results from this study have already sparked an intense debate about the quality of water that many Chileans drink (Daniele et al., 2018), showing there is a need to continue analysis of all brands of bottled water available in the Chilean market.

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