



## Short communication

## Authenticity of bottled water chemical composition inferred from brand labels: example of the Lebanese market

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## ARTICLE INFO

## Keywords:

bottled water composition  
brand labels  
food analysis  
accuracy check  
charge balance  
calculated TDS  
Lebanon

## ABSTRACT

To date, no emphasis has been given to the quality of chemical composition of purchased bottled water as deduced from brand labels. Declared information ought to provide customers with facts and realistic figures to the best possible extent; however, contradiction is often oddly noticeable when hydrochemical data is screened for accuracy. This impeaches the authenticity of the brand and raises doubts about its credibility. Reviewing the truth of the water quality is quite easy based on the registered labels. Charge balance (CB) within a water sample and calculated total dissolved solids (TDS<sub>c</sub>) derived from major constituents announced on brand label are two straightforward proxies to the quality of water analyses. The example of the Lebanese market shows that 47% of the recognized local brands miss the CB of the water chemical analysis, and 65% declare significantly lower TDS values compared to TDS<sub>c</sub>. In addition, comparing lab measurements of Cl<sup>-</sup> and TDS to label concentrations reveal more than 25% variance for the majority of the studied brands, which confirms inaccurate announcements. These results criticize the reported labels, and call for more strict regulations in labeling procedures to ensure transparent, realistic and reliable claims.

## 1. Introduction

Water is a foundation of life and key to sustainable development. Plenty of water exists on Earth, but the major portion (around 99.4%) is either saline or trapped in ice caps. A very minor share is fresh, accessible, and suitable for domestic and drinking usages. This paucity is further stressed by population increase, and deterioration of water quality, usually associated with pathogen loading due to industrial and municipal wastewater often discharged without pretreatment. Consequently, around 1.8 billion people are currently using a drinking water source contaminated by faeces posing different health problems if not properly treated (UN-Water, 2018). In this context, citizens in many countries notably in Western Asia do not trust the quality of tap water, and hence rely on bottled water as a safer and healthier drinking source for both outdoor and indoor usage. For instance, Saudi Arabia and United Arab Emirates are two Arabian countries among the top countries in bottled water consumption per capita in the world.

Many papers have been published to deal with the quality of bottled waters originating from various countries worldwide (e.g. Fugedi et al., 2010; Varrica et al., 2013; Bulia and Enzweiler, 2018; Roje and Šutalo, 2019; Kilic, 2019; Pantelić et al., 2019; Lyubomirova et al., 2020). Some authors compared the analyzed chemical composition to those given on

the bottle labels (e.g. Demetriades, 2010; Khan and Chohan, 2010; Hussein et al., 2014; Ehya and Ghanavati, 2019; Vardè et al., 2019), or the quality of bottled water to tap water (e.g. Apollaro et al., 2019); others tackled the composition and the origin of the water from a hydrogeochemical perspective (e.g. Dinelli et al., 2010; Peh et al., 2010; Felipe-Sotelo et al., 2015; Versari et al., 2002). However, no emphasis has been given to the quality of the chemical analyses as deduced from the brand labels themselves. Contradiction is sometimes noticeable when hydrochemical data is screened for accuracy, which impeaches the authenticity of the brand and raises doubts about the quality of the product.

In Lebanon (an Eastern Mediterranean country), bottled water is the main drinking water source. It is becoming a growing market and a spreading business. Its consumption per capita is around 75 liters, exceeding the global average (Rodwan, 2018). The total annual consumption from licensed companies is nearly 700,000 to 800,000 m<sup>3</sup> (BLOM Invest Bank, 2016). By May 2020, the Ministry of Public Health (MoPH) had 44 valid permissions of bottled water brands active on its records (MoPH, 2020). The Lebanese legislation identifies different classes of bottled water based on origin. The two most prominent are: (1) natural mineral water (NMW, captured from a direct subsurface source with a nearly constant composition throughout the year), and (2)

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Received 28 May 2020; Received in revised form 2 August 2020; Accepted 4 August 2020

Available online 10 August 2020

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table/drinking water (TDW, clean drinkable water regardless of source and treatment activities) (Article 3, Decree Law 108/83, 1983). The legislative norms requests that bottled water quality comply with the standards set by the Lebanese Standards Institution (LIBNOR), but no regulations to control the quality of the data announced on the labels have been set yet. The current labeling regulations stress on the brand name, the source of water, the production date, and other general information (Article 7, Decree Law 108/83, 1983). Major elements are solely reported on labels, in line with other international regulations (e.g. in the European Union, EEC directive 2009/54/EC, 2009), but the information is in many instances outdated.

After recording inconsistency in the labels of some marketed drinking water products in Lebanon, this study introduces charge balance (CB) within a water sample and calculated total dissolved solids (TDS<sub>c</sub>) as two proxies to accuracy check of water analysis. Its main purpose is to raise awareness on how to conduct an initial review of the authenticity of the bottled water brand based on the registered labels. It is a step to urge manufactures and water authorities to adopt better regulations in bottled water labeling in order to ensure more realistic claims. The Lebanese market is selected as a test case by targeting its most recognized 17 brands. Two physical and 5 chemical parameters were analyzed in the lab as well, and compared to the announced values on the labels as a double check to the alleged water quality. It is stressed that the main intention of this paper is not to assess the quality or origin of the bottled water in the Lebanese market, but it is to address the contradictions listed on some brand labels, which is considered odd and unacceptable.

## 2. Materials and methods

### 2.1. Accuracy check of water chemical analysis

A well-known method to check the accuracy of chemical analysis in water samples is to calculate the charge (or ionic) balance (CB) (Appelo and Postma, 2005; Khadra and Stuyfzand, 2014; Stuyfzand, 2017).

$$CB = \frac{(\Sigma C - \Sigma A)}{\Sigma C + \Sigma A} \times 100 \quad (1)$$

$$\Sigma C = \frac{Na}{22.99} + \frac{K}{39.01} + \frac{Ca}{20.04} + \frac{Mg}{12.15} + \frac{Fe}{27.92} + \frac{Mn}{27.47} + \frac{NH_4}{18.04} + \frac{Al}{9} + \frac{10^{(3-pH)}}{\gamma_1} \quad (2)$$

$$\Sigma A = \frac{Cl}{35.45} + \frac{SO_4}{48.03} + \frac{HCO_3}{61.02} + \frac{NO_3}{62} + \frac{PO_4}{94.97(1 + 10^{(pH-7.21)})} + A_{org} \quad (3)$$

where ions are given in mg/L;  $\Sigma C$  = sum of cations (meq/L);  $\Sigma A$  = sum of anions (meq/L);  $HCO_3^-$  = alkalinity as  $HCO_3^-$ ;  $PO_4^{3-}$  = orthophosphate [mg  $PO_4/L$ ];  $A_{org}$  = organic anions not included in the alkalinity analysis as  $HCO_3^-$  [meq/L];  $\gamma_1$  = activity coefficient for species with charge  $\pm 1$  [kg  $H_2O$ /mole], the activity coefficient is calculated based on the ionic strength, the concertation of an ion, and its charge number (Refer to Appelo and Postma, 2005 for details). Some components like  $PO_4^{3-}$  and  $A_{org}$  have a minor contribution, and hence could be dropped out when data is missing.

The charge balance is judged as good, moderate and bad if  $|CB|$  is  $< 6$ ,  $< 12$  and  $\geq 12$ , respectively (Stuyfzand, 2017).

Another accuracy check introduced here is the value of the total dissolved solids (TDS). Most bottled water brands record TDS as a major parameter, and they use it as a proxy to the quality of water. In fact, this parameter is a useful check to the authenticity as well when compared to the calculated TDS (TDS<sub>c</sub>) based on the major claimed constituents listed on brand labels. Any discrepancy between the calculated and the recorded TDS (TDS<sub>r</sub>) points to an error in either TDS<sub>r</sub> or the major analyzed ions, which either way harms the accuracy of the chemical

analysis and thereby the authenticity of the brand.

$$TDS_c = \Sigma \text{ major cations} + \Sigma \text{ major anions} + 10^{-(pH-3)} + \Sigma \text{ all trace elements (excluding gases)} + SiO_2 + 2.5 \text{ DOC [mg/L]} \quad (4)$$

where major cations =  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Al^{3+}$  [mg/L]; major anions =  $Cl^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $NO_3^-$ ,  $PO_4^{3-}$  [mg/L]

$$\Delta TDS = 100 (TDS_r - TDS_c) / TDS_r \quad (5)$$

### 2.2. Data collection

Seventeen different brands of still bottled drinking water (both natural mineral and table/drinking) were collected from the local market in Lebanon in August 2019. The names of the brands are kept anonymous and alternatively numbered for referencing herein. The main feed sources of water in Lebanon are the Jurassic and the Cretaceous (dolomitic) limestone aquifers. They have varying degrees of karstification, cover around 54% of Lebanon, and host most of the national groundwater reserves. They are either Ca-enriched with little Mg (e.g.  $Ca_{0.96}Mg_{0.04}CO_3$ ) or magnesium enriched approaching a dolomite like composition (e.g.  $Ca_{0.58}Mg_{0.42}CO_3$ ) (Khadra et al., 2017). The remaining aquifers at the national level are partially limestones as well. These are: the Eocene limestones, the Miocene limestones, the early Cretaceous sandstones, the Aptian and Albian terrigenous clastics and limestones, and the recent Quaternary deposits sometimes with calcareous fragments, quartz and kaolinite.

All of the collected samples were purchased as new sealed bottles and delivered to the American University of Beirut lab (Beirut, Lebanon) as such, and hence were not subjected to any treatment or preparation before chemical analyses. They were then analyzed for: (1)  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$  and alkalinity by titration, and  $NO_3^-$  by spectrophotometry at a minimum detection limit of 1 mg/L, and (2) electrical conductivity (EC) and pH using a SevenGo Duo pro water quality meter (Mettler Toledo) at a precision of 0.5% and 0.002 for EC and pH, respectively. Two duplicates were analyzed for quality control, and they showed acceptable results ( $< 5\%$  discrepancy).

The measured EC was then converted into measured TDS (TDS<sub>m</sub>) according to the following formula (Stuyfzand, 2017) to be used in comparison to TDS<sub>c</sub>:

$$TDS_m = 4.059 \times 10^{-21} EC^5 - 1.449 \times 10^{-15} EC^4 + 1.832 \times 10^{-10} EC^3 - 6.974 \times 10^{-6} EC^2 + 0.8365 EC - 0.5 \quad (6)$$

Two brands recorded dry residue instead of TDS, so the following conversion was applied:

$$TDS = \text{Dry residue} + 0.5 HCO_3^- \text{ (all in mg/L)} \quad (7)$$

## 3. Results

### 3.1. Accuracy check of water chemical composition

The chemical composition of 41% of the studied bottled water brands have a good charge balance, 47% have a moderate to bad charge balance, and 2 samples (i.e. 12%) are missing at least one major ion that hinders the possibility to calculate CB (Table 1). The significant shift in charge balance indicates analytical errors in the recorded concentrations, which renders the whole label not trustworthy. Moreover, around 65% of the brands record an inconsistent (i.e. wrong) TDS. The calculated value (TDS<sub>c</sub>) is more than 25% higher than that given on the label, which is considered a notable deviation from reality. Therefore, the results of most of the studied brands reflect unrealistic, and contradictory claims.

**Table 1**

Accuracy check of declared values on the studied bottled water brands labels.

Brand		Declared values on labels										Accuracy check		
#	Type	mg/L										%		
		pH	Ca	Mg	Na	K	Cl	SO <sub>4</sub>	NO <sub>3</sub>	HCO <sub>3</sub>	TDS <sub>r</sub>	TDS <sub>c</sub>	ΔTDS	CB
1	NMA	7.40	33	16	2.3	0.3	7	12	1.5	150	150	222	-48	2.3
2	NMA	7.10	50	12	10	2	10	40	0	230	345	354	-3	-10.3
3	NMA	7.90	31.3	5.2	3.5	0.5	5.1	10.9	1.8	105	130	164	-26	0.7
4	TDW	7.50	M	1	5.2	0.2	14.3	M	0.9	145	193	NA	NA	NA
5	NMA	7.30	21	9	6	1	9	4	4	81	135	136	0	8.2
6	NMA	7.40	33	16	2.3	0.3	7	12	1.5	150	150	222	-48	2.3
7	TDW	7.50	45	8.8	1.1	0.1	10	16	0.2	132	220	213	3	4.1
8	NMA	7.90	50	13	4	1	10	40	0.5	160	270	243	10	11.6
9	TDW	7.81	33.6	11.7	1.8	0.5	4	6	0.6	170	159	228	-44	-5.3
10	NMA	7.81	33.6	11.7	1.8	0.5	4	6	0.6	170	159	228	-44	-5.3
11	TDW	7.10	33.0	14	4.1	0.8	4	8.1	0	293	130	357	-174	-26
12	TDW	7.40	33.0	16	2.3	0.3	7	12	1.5	150	150	222	-48	2.3
13	TDW	8.41	93.8	67.2	7.0	1.2	10.7	4.2	M	152	165	336	-104	57.1
14	TDW	7.10	33.0	14.0	4.1	0.5	4.0	8.1	0.0	293	130	357	-174	-26.0
15	TDW	7.70	103.8	11.2	2.1	0.2	5.7	11.5	1.6	144	160	281	-75	37.8
16	NMA	7.90	50.0	13.0	4.0	1.0	10.0	4.0	0.5	160	190	243	-28	11.3
17	TDW	7.70	67.0	20.0	6.9	1.9	22.0	M	8.1	M	250	NA	NA	NA

M: missing data. NA: not applicable. NMA = Natural Mineral Water; TDW = Table/Drinking Water.

### 3.2. Declared vs. measured chemical composition

The measured values of pH, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and TDS for the 17 selected brands are shown in Table 2. A comparison of these values to the declared ones shows clear discrepancies. The lab measurements revealed a good match of NO<sub>3</sub><sup>-</sup> for the majority of the samples, lower values of Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, slightly higher values of Ca<sup>2+</sup>, and a significant difference in Cl<sup>-</sup> and TDS (Fig. 1). In fact, the measured values of Cl<sup>-</sup> and TDS show greater than 25% variance compared to the brand labels for 59% and 76% of the brands, respectively. The discrepancy in pH is significant for some brands especially for the brands # 13 and 17 (Table 2).

Three brands (# 1, 6 and 12) have exactly the same values on labels (a perfect match), which questions the truth and the chance of just copying the labels, especially that the measured values show clear distinction. Brands # 9 and 10 have the same labels as well, but their measured values are very close, and hence the similarity of labels could be attributed to a rare coincidence.

The concentrations of the major chemical constituents of brand #17 are much higher on the label than in reality for all components. In fact, the measured value of TDS is significantly low (TDS =51 mg/L) reflecting oligohaline-fresh water. It has high pH (> 8.5), and lacks

buffer ions as manifested by low bicarbonate. Therefore, its chemistry probably testifies of re-mineralized reverse osmosis (RO) permeate water, and falsifies the claim on the label to be a naturally spring water.

## 4. Discussion

### 4.1. Authenticity of the studied brands

Most of the studied bottled water brands either miss the charge balance of the chemical analysis or present a significantly lower TDS value, which challenges the validity of the claimed values on labels. The doubts are further supported by the apparent discrepancies of Ca<sup>2+</sup>, Cl<sup>-</sup> and most importantly TDS between the measured values and the declared values. A *t*-test performed for Ca<sup>2+</sup> shows no statistically significant difference between the labeled and the measured values, contrary to Cl<sup>-</sup> where a statistically significant difference does exist. Similarly, the *Mann-Whitney U Test* performed for TDS revealed a statistically significant difference between the measured and the labeled values as well (Table 3), confirming the discrepancy between the two sets. The *Mann-Whitney U Test* is a nonparametric equivalent to the *t*-test (Mann and Whitney, 1947), and hence it is selected to analyze the TDS values after they showed a non-normal distribution.

**Table 2**

Labeled (L) vs. measured (M) chemical composition of the studied bottled water brands.

Brand #			mg/L											
	pH <sub>L</sub>	pH <sub>M</sub>	Ca <sub>L</sub>	Ca <sub>M</sub>	Mg <sub>L</sub>	Mg <sub>M</sub>	Cl <sub>L</sub>	Cl <sub>M</sub>	NO <sub>3L</sub>	NO <sub>3M</sub>	HCO <sub>3L</sub>	HCO <sub>3M</sub>	TDS <sub>L</sub>	TDS <sub>M</sub>
1	7.4	7.5	33	36	16	8.8	7	8	1.5	< 2	150	128	150	216
2	7.1	6.7	50	35.2	12	4.9	10	12	0	< 1	230	84	345	194
3	7.9	7.6	31.3	28.8	5.2	2	5.1	8	1.8	< 2	105.2	100	130	138
4	7.5	7.5	NA	44.8	1	2.4	14.3	12	0.9	< 1	145	140	193	220
5	7.3	7.6	21	27.2	9	12.7	9	11	4	< 2	81	96	135	209
6	7.4	7.6	33	40.8	16	3.9	7	8	1.5	< 2	150	120	150	208
7	7.5	7.5	45	56	8.8	3.2	10	10	0.2	< 2	132	128	220	280
8	7.9	7.5	50	48.8	13	14.1	10	11	0.5	< 1	160	164	270	271
9	7.81	7.6	33.6	40	11.7	10.7	4	11	0.6	< 1	170	128	159	245
10	7.81	7.5	33.6	40	11.7	11.2	4	11	0.6	< 1	170	142	159	235
11	7.1	7.3	33	40.8	14	2.4	4	12	0	< 1	293	120	130	210
12	7.4	7.4	33	40	16	13.2	7	11	1.5	< 1	150	128	150	226
13	8.41	7.4	93.8	35.2	67.2	12.7	10.7	20	M	< 1	152	120	165	243
14	7.1	7.5	33	38.4	14	3.9	4	16	0	< 1	293	118	130	216
15	7.7	7.9	103.8	20.8	11.2	7.8	5.7	12	1.6	< 1	144.4	64	160	137
16	7.9	7.6	50	47.2	13	12.2	10	16	0.5	< 1	160	156	190	295
17	7.7	9.0	67	9.6	20	5.9	22	16	8.1	< 1	M	20	250	66

M: missing data.

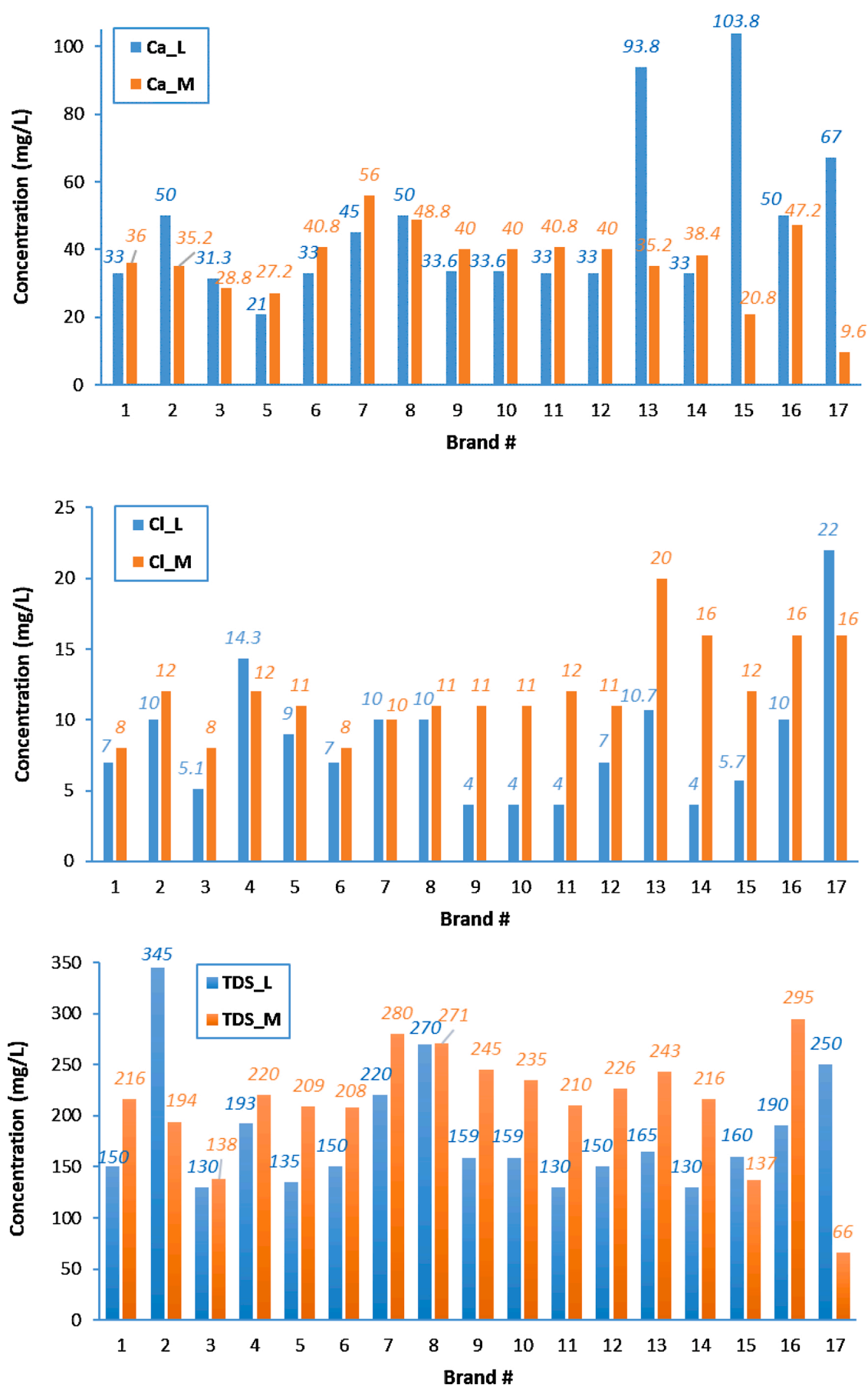


Fig. 1. Column charts showing labeled (<sub>L</sub>) vs. measured (<sub>M</sub>) values for Ca<sup>2+</sup>, Cl<sup>-</sup> and TDS.

**Table 3**

Results of paired sample statistics (t-test and Mann Whitney).

Test	Variables	Mean difference	p-value	Result	Conclusion
t-test	Ca_L vs. Ca_M	-3.8	0.22	> 0.05	No statistically significant difference
t-test	Cl_L vs. Cl_M	-2.8	0.01	< 0.05	Statistically significant difference
Mann Whitney	TDS_L vs. TDS_M	-38.4	0.03	< 0.05	Statistically significant difference

NB: Negative mean difference represents lower mean for the first variable, i.e. the labeled value.

The discrepancy between the declared and the measured values could be attributed to: (1) the fact that information reported on the labels goes back to a long time when licenses were issued, and since then significant changes in source water chemistry has occurred (note that controlling the stability of the chemical composition of bottled water is not a required condition), (2) inaccurate analytical methods when analyzing the major water constituents, (3) typo mistakes on the labels, and (4) possibly fabricated chemical results just to issue the license (e.g. the match among the labels of brands # 1, 6 and 12, and the discrepancies recorded in brand #17 sounds illogical).

The first three aforementioned reasons could be justifiable to explain the discrepancy between measured and recorded values; however, it is very odd to license a brand without proper screening of chemical accuracy (i.e. with a bad CB), or while embedding contradictory results (e.g. in TDS). Recall that TDS is visualized by most people as the main representative of water quality, and hence any underestimation of its value is misleading and inauthentic.

#### 4.2. Hydrochemistry of the selected brands

The chemical water type was determined based on the scheme of [Stuyfzand \(1989\)](#). It combines in one code the chlorinity, the alkalinity, the dominating member of the strongest pair of cations and anions within a geohydrochemical family ([Table 4](#)). The water type of each of the 17 studied brands is shown in [Table 5](#) (e.g. based on Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup> and the dominant ion).

Most of the measured brands (both natural mineral and table water) have CaHCO<sub>3</sub> type, moderate alkalinity, and oligohaline-fresh water ([Fig. 2](#)) that is very suitable for drinking. They reflect the dominating limestone hosting rocks in Lebanon, from which all bottled waters are extracted. This is in line with hard water as well, due to dissolution of CaCO<sub>3</sub>, which increases Ca<sup>2+</sup> (Mg<sup>2+</sup> also in case of dolomitic limestone like in brand #13) and HCO<sub>3</sub><sup>-</sup>. Ca<sub>x</sub>Mg<sub>y</sub>CO<sub>3</sub> dissolution is the main

**Table 4**Chemical scheme of water type, combining into a code like F4CaHCO<sub>3</sub> (Adapted from [Khadra and Stuyfzand, 2014](#)).

Code	Parameter	Description / Criterion
<i>Chlorinity (main type)</i>		
		Chloride concentration in sampled water [mg/L]
G	Oligohaline	< 5
G	Oligohaline-fresh	5-30
F	Fresh	30-150
F	Fresh-brackish	150-300
<i>Alkalinity (type)</i>		
		Alkalinity as HCO <sub>3</sub> [mg/L]
*	Very low	< 31
0	Low	31-61
1	Moderately low	61-122
2	Moderate	122-244
3	Moderately high	244-488
<i>Dominant Cation and Anion (Subtype)</i>		
		Most important cation and anion
Ca	Calcium	The strongest family members discovered to date are placed in the appropriate fields inside two triangles constructed for this purpose ( <a href="#">Stuyfzand, 1989</a> )
Mg	Magnesium	
Na	Sodium	
HCO <sub>3</sub>	Bicarbonate	
Cl	Chloride	
Mix	No anion family > 50% of anions sum	

geochemical process in such setting, and the major hydrochemical difference between limestone and dolomitic limestone aquifers is defined by the contrasting Ca/Mg ratio in groundwater ([Table 5](#)). The HCO<sub>3</sub>/Ca ratio is nearly 2 (on mol basis); it indicates that calcite dissolution in limestones is mainly due to the presence of CO<sub>2</sub> rather than strong acids from atmospheric inputs. The origin of water is calcareous freshwater as suggested by a nearly fixed value of HCO<sub>3</sub>/ΣA, and confirmed by the Wirdum Ion Ratio (WIR) ([Van Wirdum, 1980](#)).

$$WIR = 100 \times \frac{1}{2}Ca^{2+} / (\frac{1}{2}Ca^{2+} + Cl^{-}) [\%] \text{ (with } Ca^{2+} \text{ and } Cl^{-} \text{ in mmol/L)} \quad (8)$$

WIR is > 75% for the majority of the brands ([Table 5](#)), indicating a lithocline calcareous groundwater origin, i.e. fresh groundwater that dissolved much calcite ([Fig. 3](#)).

Brand #17 is exceptional. It shows CaCl and MgCl water type, based on the values recorded on the label and measured in the lab, respectively, which either way points to a groundwater origin probably mixed with seawater. The WIR is low (51.5%), which when is combined with low EC reflects a mixture of lithocline and atmocline (rain) origin. The Ca/Mg, HCO<sub>3</sub>/Ca and HCO<sub>3</sub>/ΣA ratios are all low as well, which asserts that this brand isn't purely natural. It is either treated as previously mentioned (e.g. via a RO system), and/or mixed with other chemical components to fine tune its composition. In both cases, the water quality declared on the brand label is not realistic.

Hierarchical agglomerative clustering analysis of Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and TDS (using the Centroid method for clustering, and the Squared Euclidean Distance for similarity measure) reveals that all brands fit into one cluster whereas brand #17 forms another. Moreover, brands # 3 and 15 form a sub-cluster of the former group, which points to their distinctively lower measured TDS values.

All brands have pH above 7 except for brand #2 (measured pH = 6.71). This exception is probably due to high SO<sub>4</sub><sup>2-</sup>, and manifested by the highest contribution of strong acids to TDS. Strong acids in groundwater mainly consist of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HNO<sub>2</sub>, and HF. The contribution of strong acids to TDS (%TDS<sub>Acid</sub>) for most samples is < 5%; however, it is 10.9% for brand #2. %TDS<sub>Acid</sub> is estimated based on the following relation ([Stuyfzand, 2017](#)):

$$\%TDS_{Acid} = 100 (H^{+} + SO_4^{2-} + NO_3^{-} + NO_2^{-} + F^{-}) / TDS, \text{ where } H^{+} = 10^{3-pH} \text{ (mg/L)} \quad (9)$$

## 5. Conclusions

The way to reliable hydrochemical data is full of pitfalls, and hence water quality data should be always examined carefully. Many existing data contains errors that are easily overlooked. Ignoring such errors may be reasonable in some instances where water quality difference is not a key factor, but it is alarming when it comes to drinking water. Different tests exist for checking the accuracy of water chemical analyses, the easiest and most reliable rely on charge balance (CB) and total dissolved solids (TDS).

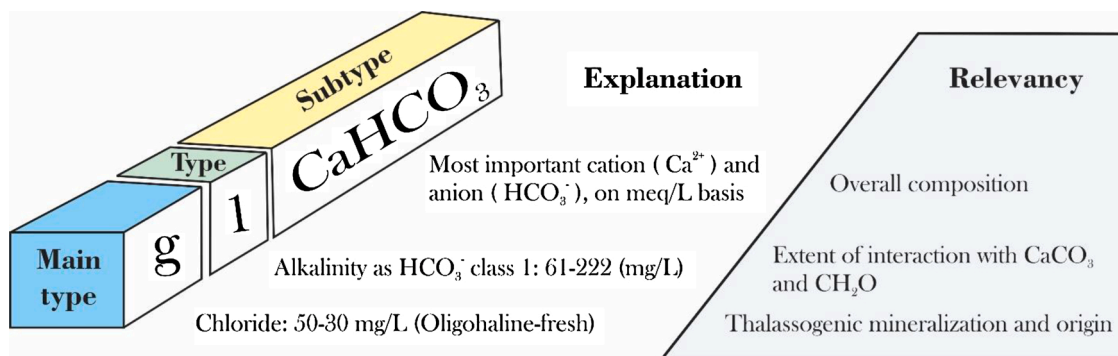
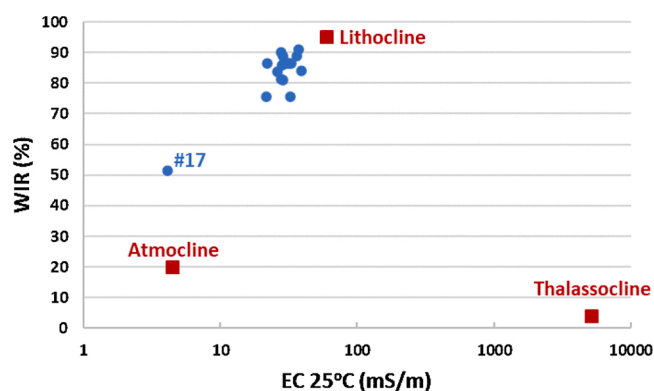
The main purpose of this paper is to instruct stakeholders about the importance of hydrochemical screening in an attempt to raise awareness about this issue. The information recorded on brand labels should provide consumers with facts and realistic figures to the best possible extent. One way to assess the authenticity of bottled water is to refer to



**Table 5**

Water types and ion ratios of the studied bottled water brands based on label/measured composition.

Brand #	Based on label composition					Based on measured composition				
	Chemical water type	Ca/Mg (mg/L)	HCO <sub>3</sub> /Ca (mmol/L)	HCO <sub>3</sub> /ΣA (meq/L)	Wirdum Ion Ratio (%)	Chemical water type	Ca/Mg (mg/L)	HCO <sub>3</sub> /Ca (mmol/L)	HCO <sub>3</sub> /ΣA (meq/L)	Wirdum Ion Ratio (%)
1	g2CaHCO <sub>3</sub>	2.1	2.99	0.84	89.3	g2CaHCO <sub>3</sub>	4.1	2.34	0.90	88.8
2	g2CaHCO <sub>3</sub>	4.2	3.02	0.77	89.8	g1CaHCO <sub>3</sub>	7.2	1.57	0.80	83.8
3	g1CaHCO <sub>3</sub>	6.0	2.21	0.81	91.6	g1CaHCO <sub>3</sub>	14.8	2.28	0.86	86.4
4	g2NaHCO <sub>3</sub>	–	–	0.84	–	g2CaHCO <sub>3</sub>	18.4	2.05	0.86	86.9
5	g1CaHCO <sub>3</sub>	2.3	2.53	0.75	80.5	g1CaHCO <sub>3</sub>	2.1	2.32	0.82	81.4
6	g2CaHCO <sub>3</sub>	2.1	2.99	0.84	89.3	g1CaHCO <sub>3</sub>	10.5	1.93	0.88	90.0
7	g2CaHCO <sub>3</sub>	5.1	1.93	0.78	88.8	g2CaHCO <sub>3</sub>	17.7	1.50	0.87	90.8
8	g2CaHCO <sub>3</sub>	3.8	2.10	0.88	89.8	g2CaHCO <sub>3</sub>	3.4	2.21	0.89	88.7
9	G2CaHCO <sub>3</sub>	2.9	3.32	0.92	93.7	g2CaHCO <sub>3</sub>	3.7	2.10	0.87	86.5
10	G2CaHCO <sub>3</sub>	2.9	3.32	0.92	93.7	g2CaHCO <sub>3</sub>	3.6	2.33	0.88	86.5
11	G3CaHCO <sub>3</sub>	2.4	5.83	0.94	93.6	g1CaHCO <sub>3</sub>	16.7	1.93	0.85	85.7
12	g2CaHCO <sub>3</sub>	2.1	2.99	0.84	89.3	g2CaHCO <sub>3</sub>	3.0	2.10	0.87	86.5
13	g2MgHCO <sub>3</sub>	1.4	1.06	0.87	93.9	g1CaHCO <sub>3</sub>	3.8	2.24	0.77	75.7
14	G3CaHCO <sub>3</sub>	2.4	5.83	0.94	93.6	g1CaHCO <sub>3</sub>	9.8	2.02	0.81	80.9
15	g2CaHCO <sub>3</sub>	9.3	0.91	0.85	97.0	g1CaHCO <sub>3</sub>	2.7	2.02	0.75	75.4
16	g2CaHCO <sub>3</sub>	3.8	2.10	0.87	89.8	g2CaHCO <sub>3</sub>	3.9	2.17	0.85	83.9
17	gCaCl	3.4	–	–	84.3	g*MgCl	1.6	1.37	0.41	51.5

**Fig. 2.** Hydrochemical classification of water types. The example is representative of most of the studied bottled water brands with CaHCO<sub>3</sub> type, moderate alkalinity, and oligohaline-fresh water.**Fig. 3.** Van Wirdum diagram of analyzed samples. Atmocline is atmospheric water (rainwater); lithocline is calcareous fresh groundwater; and thalassocline is seawater.

the registered labels.

The example of the Lebanese market with its 17 most recognized brands show that most of them bear the same signature of bicarbonate lithological origin, which is typical for the Lebanese (dolomitic) limestone aquifers with Ca<sub>x</sub>Mg<sub>y</sub>CO<sub>3</sub> composition. According to hierarchical agglomerative clustering analysis of measured Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and TDS, most of the brands belong to the same cluster. Their origin is calcareous freshwater as suggested by a nearly fixed value of HCO<sub>3</sub>/ΣA,

and confirmed by a Wirdum Ion Ratio (WIR) > 75%. One brand is exceptional, and has been subject to major treatment activities falsifying the claims on labels.

It is very surprising that many brands show inconsistent information on their labels (e.g. TDS < HCO<sub>3</sub><sup>-</sup>). In fact, 47% miss the charge balance (CB > 6), which indicates possible analytical errors in the recorded concentrations and renders the whole label not trustworthy, and 65% have significantly lower TDS values that contradict the calculated total dissolved solids (TDS<sub>c</sub>) derived from declared major constituents. In addition, a comparison of the lab measurements of Cl<sup>-</sup> and TDS to label concentrations reveal more than 25% variance for the majority of the studied brands thus raising further doubts about the accuracy of the announcements.

These results urge manufacturers and water authorities to adopt more professional acts to assure transparency and credibility. It is recommended that the Lebanese labeling procedure of bottled water be amended, and all currently licensed brands be reviewed accordingly. Future efforts are also encouraged to conduct a wider chemical scan that includes trace elements and organic compounds for all brands of bottled waters at the Lebanese market in an attempt to draw a coherent pattern of their natural variation, and uncover the hydrogeochemical processes and/or other influences controlling their composition.

#### Author statement

After recording inconsistency in labels of some marketed drinking water products in Lebanon, this manuscript aims at raising awareness on

how to conduct an initial review of the authenticity of the bottled water brand based on the registered labels. It is also an attempt to encourage manufactures and water authorities to adopt more strict regulations in bottled water labeling in order to ensure more realistic claims.

### Declaration of Competing Interest

No potential conflict of interest was reported by the author.

### Acknowledgements

The efforts of the handling editor Prof. Dr. Percy Onianwa and four anonymous reviewers are highly appreciated. Their constructive comments contributed to essential improvements of this manuscript.

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