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Drinking Bottled and Tap Water for Healthier Living in Volcanic Areas: Are All Waters the Same?

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Abstract: In most volcanic areas, the population considers the use of bottled waters as a healthier and safer option. This study aimed to (i) assess the fluoride concentrations in tap and bottled water consumed on São Miguel Island, (ii) confirm the accuracy of the labeling of fluoride levels on bottled water, and (iii) assess the fluoride daily intake and risk exposure and discuss the possible health effects in adults and children. Fluoride concentrations were measured in tap water (49 samples) and bottled water (23 samples) with a fluoride ion-selective electrode. The fluoride concentration was above the recommended limit in tap water from Sete Cidades (1.71 mg/L), in bottled waters nº 5 and 7 from category C (2.05 ± 0.04 mg/L and 2.36 ± 0.14 mg/L, respectively), and in bottled water nº 5 from category D (1.92 ± 0.03 mg/L). Fluoride daily intake in children reached a maximum value in gasified water nº 7 (0.059 mg F/day/kg). The risk assessment evidenced that all the brands with over 1.2 mgF/L might be a concern for potential non-cancer health effects, especially in adults. The most recognized brands of gasified and gasified flavored waters represent a higher risk of exceeding fluoride daily intake when compared to tap and mineral bottled waters.

Keywords: fluoride; bottled water; daily intake; risk exposure assessment; volcanic regions; fluorosis

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1. Introduction

Fluoride is a naturally occurring element that is found in water, food, soil, air, and several minerals, such as fluorite and fluorapatite [1,2]. Although fluoride is not an essential element for human growth, the daily ingestion of small amounts, in the order of 1mg/L through water, is beneficial because its incorporation in bones and teeth prevents the occurrence of dental caries [3–6]. An excessive intake of fluoride can be harmful, resulting in the development of dental and skeletal fluorosis [7]. To prevent the development of these fluoride manifestations, the World Health Organization has specified that the tolerance limit of fluoride in drinking water is 1.5 mg/L [8,9]. However, in temperate climates where, because of temperature and humidity, the water consumption is higher, the tolerance limit of fluoride in water decreases to 1 mg/L [10,11].

Water is the most popular drink in the world; as it is essential to sustain life, there are several guidelines for drinking-water quality to ensure an adequate, safe, and accessible supply [8,12,13]. Still, as drinking water supplies continue to be a major source of human disease and death globally because many of them remain unsafe and vulnerable, populations are changing their drinking habits [14,15]. Worldwide, water consumption is being subject to changes, with tap water losing ground compared to bottled water. This change in habits arises essentially for three reasons: (i) health and safety concerns regarding the quality of tap water in several parts of the world [16,17], (ii) organoleptic properties (e.g., sensorial information such as taste and odor) that play a major role in water type consumption [16,18], and (iii) a busy lifestyle that privileges the use of water that is easy to transport and with additional nutritional attributes that help to promote a healthier lifestyle [19,20].

In countries such as Mexico and Thailand, where tap water is considered unsafe for consumption, bottled water consumption reaches 265 L per capita/year [21]. However, even in countries where people have easy access to cheap and safe potable tap water, bottled water consumption has been increasing on a global scale [22,23]. In a study by the Flanders Environment Agency (2018) [23], 66% of the participants showed they drink bottled water at least half of the time, averaging 0.4 L per day. Portugal follows the same tendency. The consumption of bottled water has seen sustained growth over the past few years, gaining a prominent place in the beverage sector. The per capita consumption of bottled water increased from 57.9 L/year in 2010 to 68.7 L/year in 2019 [24] with still water (non-gasified water) leading the consumer's preferences, followed by gasified water and gasified flavored water. In Portugal, the Regulatory Entity for Water and Waste Services controls the quality of the supply water as recommended by the WHO with a maximum limit for the concentration of fluorides in the water of 1.5 mg/L (DL 306/2007), while for bottled water, as it occurs in the rest of the EU, the available commercial brands are only obliged to put a "clearly visible" label on the bottle when the fluoride concentration is greater than 1.5 milligrams per liter, allowing a maximum limit of five milligrams per liter (Directive 2003/40/CE). Bottled waters are legally allowed to have fluoride concentrations above the recommended values for tap water. It is important to assess if the change in habits of water consumption contributes to better health in the country.

In the Azorean framework where geogenic fluoride contamination in groundwater is a representative major concern [25], allied with the public general concern regarding the safety of tap water, most of the inhabitants tend to consider bottled water a better and safer option.

Because of the archipelago-specific geological formation context, with aquifers formed by volcanic rocks, high fluoride concentrations are often found in the water [26]. Fluorides in these aquifers can result from the rock leaching processes and from the release of fluoride into the atmosphere by active volcanoes. Other factors, such as soil buffering through adsorption, also influence fluoride concentration, as in the case of andosols, typically found in volcanic regions. As about 98% of the archipelago's water supply comes from underground sources, the aquifers in these islands are subjected to increasing pressure, which is sometimes reflected in the deterioration of groundwater quality, mainly due to salinization in coastal areas and, inland, due to the high levels of nitrogen and associated microbiological parameters, resulting from agricultural activity and the lack of wastewater treatment systems. Some past studies identified sources of tap water with very high concentrations of fluoride, up to 9.9 mg/L, with the highest values observed in the villages of Furnas and Ribeira Quente, in the vicinity of the Furnas volcano [27] and evidenced by the prevalence of dental fluorosis on São Miguel Island [28,29]. Nowadays, with the strict control measures of tap water quality, fluoride concentration tends to be within the recommended values [30,31]. Nevertheless, other features must be considered when studying the exposure to fluoride on São Miguel Island, such as the frequent habit of drinking tea, which results from the island having the only tea plantation in Europe and which also contributes to fluoride intake [31]. As bottled water also contains fluoride, it is important to understand if the change in the population's drinking habits represents health benefits or not. By this, the present study aimed to: (1) assess fluoride concentration in tap water and bottled water consumed on São Miguel Island, (2) confirm the accuracy of the labeling of fluoride levels on bottled water, and (3) assess the fluoride daily intake and risk exposure and possible health effects in adults and children.

2. Material and Methods

2.1. Tap Water Sampling

The selected study area was São Miguel Island, the largest (744 km^2) and the most populated (over 137,000 inhabitants) of the Azores archipelago, located in the triple junction of the North American, African, and Eurasian plates (in the North Atlantic Ocean) [32–34]. São Miguel is formed by three active central volcanoes (Sete Cidades, Fogo, and Furnas), two active fissure systems (Picos and Congro), and two extinct volcanic systems on the eastern part of the island (Povoação and Nordeste) [35,36].

Forty-nine samples of tap water were collected from several households in three counties of São Miguel Island: ten water samples were collected in Porto Formoso, a village in Ribeira Grande county, where the Azorean tea plantation is located; thirteen water samples were collected in Ponta Delgada county, with a predominance in Sete Cidades village (ten samples); and twenty-six water samples were collected in all the villages of Povoação county, with a predominance in the villages of Ribeira Quente and Furnas with eleven samples each. The villages of Sete Cidades, Furnas, and Ribeira Quente are near two active volcanoes (Sete Cidades and Furnas, respectively) and several reports describe the existence of endemic fluorosis in these areas.

Sampling collection occurred from March to April 2021. All samples were collected into pre-cleaned plastic containers with a 50 mL capacity and stored at 4 °C before being analyzed. The samples were analyzed within 6–12 h after collection.

2.2. Bottled Water Sampling

Twenty-three different bottled water brands, which were purchased from local supermarkets, were analyzed in this research for fluoride. Three samples were analyzed for each brand, performing sixty-nine tests. All the studied bottled waters were produced in Portugal (mainland) or on the Island of São Miguel, and the volume varied between 330 mL and 1500 mL. The bottled waters were divided into 4 categories: (A) mineral water (n = 10) (B) mineral flavored water (n = 2), (C) mineral gasified water (n = 7), and (D) mineral gasified water with flavor (n = 4). In each category, the water brands considered were consecutively numbered to maintain anonymity.

Only waters of Portuguese origin and available in the most frequented supermarket chains were considered. For the flavored waters, the selected flavor was lemon, due to it being the dominant flavor in the bottled waters available in local supermarkets.

2.3. Fluoride Quantification in Tap and Bottled Waters

The fluoride quantifications were made by the potentiometric method with a fluoride ion-selective electrode (Orion, Model 9409), according to the US National Institute for Occupational Safety and Health (1984) (NIOSH) [37].

A calibration curve was constructed from 0.125 to 4.0 mg/L. All samples were mixed with a total ion strength adjustment buffer (TISAB II) in a 1:1 ratio (v/v) for quantification. The fluoride concentration of the sample was determined by the interpolation of the potential in the calibration curve and triplicate. For the tap water samples, the mean slope was −56.6 with r^2 = 0.999; for the bottled water samples from categories A and B, the mean slope was −57.5 with r^2 = 0.999; and for bottled water samples from categories C and D, the mean slope was −57.9 with r^2 = 0.999. The analysis was validated using internal standards, and a coefficient of variation lower than 3% was considered acceptable.

2.4. Fluoride Daily Intake

The fluoride exposure doses were calculated by the following equation:

$$\text{Daily intake (DI)} = \text{C} \times \text{V} \tag{1}$$

where C is the fluoride concentration in water (tap or bottled) (mg/L) and V is the amount of ingested liquid (L) [38] represented in mg F/day/kg body weight. A volume of 0.250 L was considered one dose. The adequate intake for fluoride from all sources was set at 0.06 mg/day/kg body weight [39]. The DI was calculated for a child (BW of 10 kg) and an adult (BW of 70 kg) [40].

2.5. Risk Assessment

The risk assessment was evaluated by calculating the *exposure assessment* and *risk characterization*. The exposure assessment was evaluated using the following intake (IT) equation:

$$\text{IT} = (\text{CW} \times \text{IR} \times \text{EF} \times \text{ED})/(\text{BW} \times \text{AT}) \quad (2)$$

According to the U.S. EPA (1989) [40], the IT (mg/kg/day) represents the individual exposure or ingestion of chemicals in drinking water, and it depends on: chemical concentration in water (CW) in mg/L, ingestion rate (IR) in liters/day, exposure frequency (EF) in days/year, exposure duration (ED) in years, body weight (BW) in kg, and averaging time (AT) in days. The IT was calculated for a child (IR is 1 L/day and BW of 10 kg) and an adult (IR is 2 L/day and BW of 70 kg) [40].

Water is ingested daily, whether in the natural form or in the composition of several foodstuffs (e.g., soup, formulas, juices). By this, the EF has a value of 365 days/year. According to the Agency for Toxic Substances and Disease Registry, fluoride has not been associated with cancer [41], therefore, AT was considered equal to ED multiplied 365 days/year, which is a "pathway-specific period of exposure for non-carcinogenic effects". By this, the equation was simplified to:

$$\text{IT} = (\text{CW} \times \text{IR})/(\text{BW}) \quad (3)$$

The risk characterization was expressed using the non-cancer hazard quotient (*NHQ*) equation, which compares the *IT* to the reference dose value (RfD) for fluoride [40], as described by the following equation:

$$NHQ = \text{IT}/\text{RfD} \quad (4)$$

The RfD value for fluoride, 0.06 mg/kg/day, was obtained from the *Drinking Water Standards and Health Advisories* [40]. The *NHQ* value above 1 (unity), was considered a concern for the possible occurrence of non-cancer effects [41].

2.6. Statistical Analysis

The Kruskal–Wallis test was carried out to evaluate the significant differences in fluoride contents between the water samples from tap water and each group of bottled water. When significant, the Mann–Whitney *U* test was used for pairwise comparisons.

All statistical analyses were performed using IBM SPSS Statistics 27.0 for Windows (IBM SPSS 27.0 2020), and the level of statistical significance was set at $p \leq 0.05$.

3. Results

3.1. Tap Water Fluoride Concentrations

The tap water fluoride concentration was within the normal legislated values for the three selected counties of the Island (Table 1; Supplementary material Table S1). However, when considering the villages of the selected counties where endemic fluorosis has been described, results demonstrate that fluoride concentration in the tap water from Sete Cidades village is slightly above the WHO recommended maximum level (1.71 mg/L; Table 1).

Table 1. Tap water fluoride content from the three studied counties and villages with endemic fluorosis. Fluoride concentration is presented in mg/L.

	Fluoride (mg/L)				
	Min.	**Max.**	**Median**	**Mean ± SE**	***p*-Value [1]**
Counties					**<0.001**
Povoação	0.08	0.87	0.42	0.56 ± 0.05 [a]	
Ribeira Grande	0.28	0.29	0.29	0.29 ± 0.001 [b]	
Ponta Delgada	0.69	1.77	1.69	1.49 ± 0.12 [c]	

Table 1. *Cont.*

	Fluoride (mg/L)				
	Min.	**Max.**	**Median**	**Mean ± SE**	***p*-Value [1]**
Villages					**<0.001**
Furnas	0.39	0.55	0.42	0.43 ± 0.01 [a]	
Ribeira Quente	0.77	0.87	0.85	0.84 ± 0.01 [b]	
Porto Formoso	0.28	0.29	0.29	0.29 ± 0.001 [c]	
Sete Cidades	1.66	1.77	1.71	1.71 ± 0.008 [d]	

[1] *p*-value for group comparisons: Kruskal–Wallis tests were used to compare fluoride concentrations in tap water between the three counties and between the four villages, followed by the Mann–Whitney *U* test. Different letters represent significant differences between sites within counties and within villages ($p < 0.05$).

3.2. Bottled Water

The measurements of the fluoride concentration on still waters from categories A (mineral water) and B (mineral flavored water) evidence that all the brands tested comply with the WHO and Portuguese law recommendations. The highest value was observed in water nº 7 with 1.28 ± 0.01 mg/L of fluoride and the lowest value was observed in water nº 5 with 0.06 ± 0.01 mg/L of fluoride, both from category A (Table 2). The results for the mineral water nº 7 stand in line with the information the brand presents on its label regarding fluoride concentration. Considering water from categories C and D (gasified waters) results in two brands, evidence shows that the fluoride concentrations are above 1.5 mg/L. In category C, two water brands (nº 5 and nº 7) present fluoride concentrations of 2.05 ± 0.04 mg/L and 2.36 ± 0.14 mg/L, respectively (Table 2). Our results comply with the information shown on both brand labels: water nº 5 = 1.9 ± 0.5 mg/L and water nº 7 = 2 mg/L. In category D, only one brand (nº 5) had fluoride concentrations above the recommended level (1.92 ± 0.03 mg/L).

Table 2. Characterization of fluoride content (mean ± SE) in bottled water from the four categories. A: mineral water; B: mineral flavored water; C: mineral gasified water; and D: mineral gasified water with flavor.

	Mineral Water A	**Mineral Water B**		**Mineral Water C**	**Mineral Water D**
	Fluoride (mg/L)	**Fluoride (mg/L)**		**Fluoride (mg/L)**	**Fluoride (mg/L)**
1	0.47 ± 0.07 [a]		**1**	0.71 ± 0.09 [a]	
2	0.45 ± 0.03 [a]		**2**	0.58 ± 0.05 [a]	
3	0.38 ± 0.03 [a]		**3**	0.16 ± 0.01 [b]	0.13 ± 0.01 [a]
4	0.1 ± 0.003 [b,e]	0.08 ± 0.005	**4**	1.25 ± 0.02 [c]	1.02 ± 0.01 [b]
5	0.06 ± 0.01 [c]	0.21 ± 0.03	**5**	2.05 ± 0.04 [d]	1.92 ± 0.03 [c]
6	0.14 ± 0.05 [a,b,c,e]		**6**	0.31 ± 0.01 [e]	
7	1.28 ± 0.01 [d]		**7**	2.36 ± 0.14 [f]	0.11 ± 0.01 [a]
8	0.11 ± 0.007 [e]				
9	0.07 ± 0.008 [b,c]				
10	0.07 ± 0.008 [c]				
***p*-value [1]**	**0.002**	0.1	***p*-value [1]**	**0.002**	**0.024**

[1] *p*-value for group comparisons by Kruskal–Wallis tests were used for fluoride concentration in bottled waters followed by the Mann–Whitney *U* test. Different letters within each line represent significant differences between sites ($p < 0.05$).

3.3. Daily Intake (DI) Assessment

An adequate intake of fluoride from all sources of 0.06 mgF/kg BW/day has been defined as the estimated intake that maximally reduces the occurrence of dental caries in a population without causing unwanted side effects. The DI assessment only considered waters that had a fluoride concentration ≥1.2 mg/L. Results demonstrate that, for children and adults, the consumption of 0.250 L of the selected waters presents no risk of exceeding the adequate intake. In children, the DI ranged from 0.03 mg F/day/kg (mineral water nº 7 from category A) to 0.059 mg F/day/kg (gasified water nº 7 from category C) (Figure 1). Regarding adults, the results ranged from 0.004 mg F/day/kg body (mineral water nº 7 from category A) to 0.008 mg F/day/kg body weight (gasified water nº 7 from category C) (Figure 1).

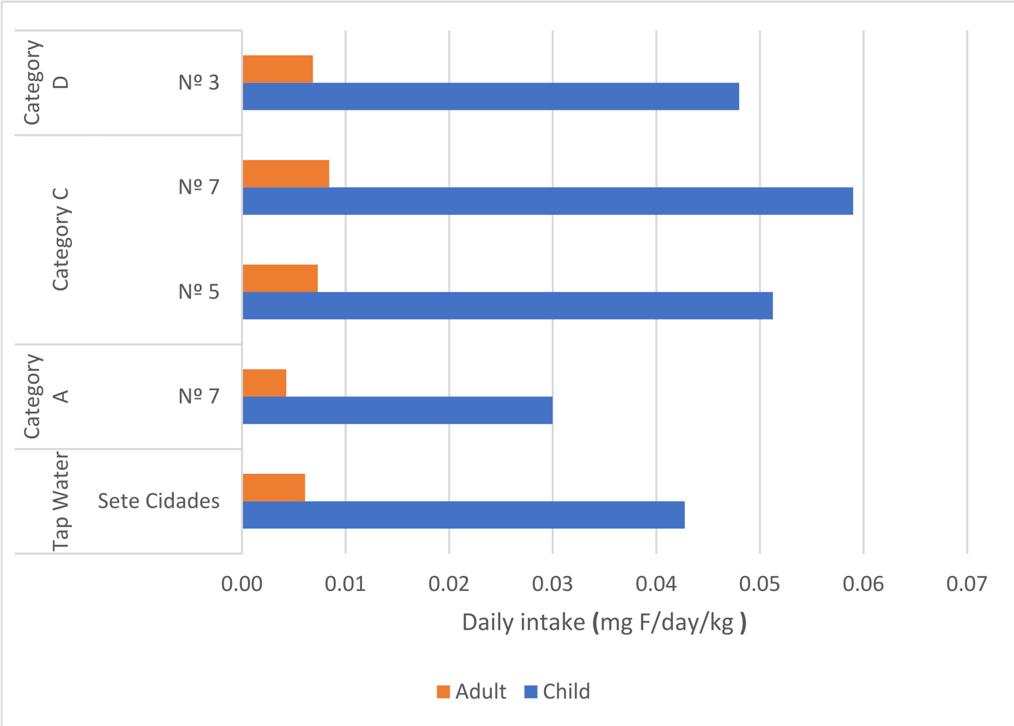

Figure 1. Daily intake assessment in a child and an adult considering the water sample's fluoride mean concentration was higher than 1.2 mg/L.

3.4. Risk Assessment

The risk assessment was investigated by calculating the exposure assessment and risk characterization by considering the same waters used for the assessment of daily intake. For a child and an adult, the highest exposure values to fluoride, IT, were observed in gasified water (0.24 mg/kg/day and 0.67 mg/kg/day, respectively) (Figure 2). For a child, all the considered waters (bottled waters and tap water from Sete Cidades) had *NHQ* values above 1, with *NHQ* ranging from 2.00 to 3.93 (Figure 2), suggesting that these waters may be of concern for potential non-cancer effects. For an adult, the same tendency was observed, with all the considered waters having *NHQ* values above 1, with values ranging from 5.71 to 11.24 (Figure 2).

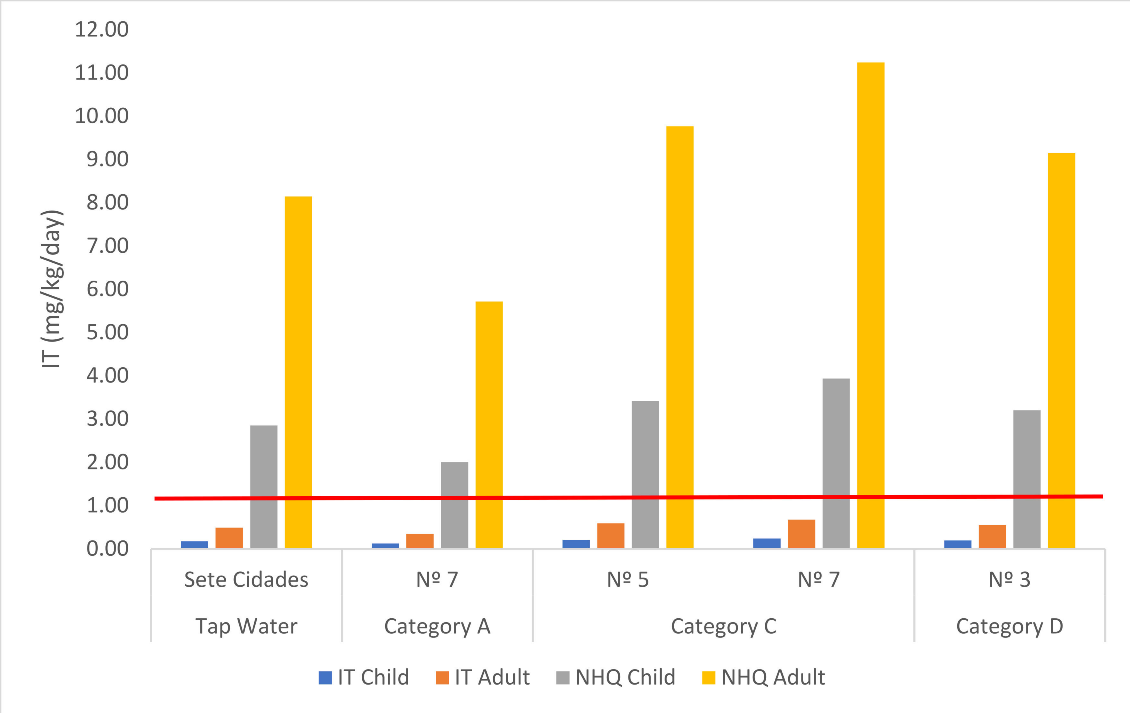

Figure 2. Representation of the exposure assessment (mg/kg/day) and the risk assessment, in lines, for both adults and children. The red line marks the *NHQ* value of 1 (unit); values above this baseline value denote the possible occurrence of non-cancer effects.

4. Discussion

According to consumers, the most important factor to consider when choosing to use tap water is the recognition that is safe and potable for human use [42]. In the Azores, a volcanic region that has about 98% of the water supply originating from groundwater sources [43], there have been some struggles in the past to provide water considered safe for the populations. The groundwater in the Azores occurs in two main aquifers, namely perched-water bodies, corresponding to confined or leaky altitude aquifers [44,45]. Besides salinization, other groundwater quality problems are of concern, such as nutrient and microorganism fecal pollution due to agricultural activity and untreated wastewater discharges [46–48] or high fluoride contents in the water of São Miguel Island due to the volcanic influences [43]. As groundwater is the main source of water supply on São Miguel, and since high fluoride content cannot be eliminated in the source, for the last twenty years, the regulatory entities have been working on the implementation of strict control measures to keep the fluoride concentration in tap water below the recommended value of 1.5 mg/L. Our most recent results evidence that the implementation of these measures resulted in fluoride concentrations in tap water within the recommended values for most of the water available to the population. The only area where fluoride values are slightly above the recommended values is Sete Cidades; this was also evidenced in previous studies by Linhares et al. [30,31], reinforcing the need for an adequate intervention of local authorities in this water supply and the continuous control of the water safety in this area.

Even though, as in many other countries, Portugal provides cheap and safe potable tap water, the demand for bottled water has consistently increased during the last decade [21,22]. In 2018, 1179.6 million liters of natural and spring mineral water (bottled) were consumed in Portugal, with still and flavorless waters accounting for 95% of this consumption [24]. This represents an average loss of 30% of the public water supply. The results of our study evidence that the waters from category A, the most consumed, have a wide range of fluoride concentrations but are all within the recommended values. The only brand that presents the fluoride concentration on its label is the mineral water A nº 7 with 1.2 mg/L ± 0.5.

The value given in the label is similar to our findings (1.28 mg/L $\pm$ 0.01), reinforcing the accuracy of the labeling and of the control that is required to place mineral bottled waters in the market. The scenario changes when we consider the gasified waters: categories C and D. In category C, two brands deliver bottled water with fluoride concentrations above 1.5 mg/L (gasified water nº 5 and 7). Both brands show, as required, that the products contain over 1.5 mg /L of fluoride, but only one indicates on the label that the product is not suitable for the regular consumption of infants and children under 7 years of age. Though the labeling of the brands complies with the regulations, it would be important to assess if parents consider this information in the water selection process. Regarding category D, only one brand had fluoride concentrations higher than 1.5 mg/L. For this type of water (gasified and flavored), there are no legal requirements to indicate the fluoride concentration on the label. Nevertheless, as these types of water tend to be preferred over soft drinks, especially in the summer, as they are less caloric, it is important to provide the consumers with information on the attributes of the water, avoiding the consumers being misled by not knowing all the characteristics of the product.

The cautions regarding the consumption of these waters are patent in the daily intake quantification, especially in children, since with a little more than 0.250 L, fluoride levels overcome the daily adequate intake. Moreover, the risk assessment characterization evidenced that the selection of the type of water and brand consumed is very important, even when the regulatory limits are fulfilled. It was expected that the waters that had fluoride concentrations above 1.5 mg/L would represent a higher risk, as was observed in our results, evidencing that the *NHQ* is higher for both children and adults, particularly in two brands of gasified water. The *NHQ* for children and adults was also above 1 in one brand of flavored *water* and tap water from Sete Cidades. The concerns about the consumption of water with higher concentrations of fluoride increase when results evidence that even the water brand that has an adequate concentration of fluoride has an *NHQ* value above 1, ranging from 2 to 5.71 in children and adults, respectively. These results show that adults, due to a higher consumption rate, are at higher risk than children and that even the consumption of water that has a fluoride concentration within the recommended value can pose risks to human health.

Given that the most recognized brands of gasified and gasified flavored waters represent a higher risk for exceeding fluoride DI, these should be consumed with caution to prevent or mitigate the development of dental fluorosis that has a progressive outcome [49], evolving from the development of chalky white patches to yellow to dark brown lines visible on the teeth [3,50]. Several cases of endemic fluorosis due to the consumption of water with high F concentrations have been reported in the volcanic region of the Azores [28]. More recently, a cross-sectional study conducted among a sample of students from Ponta Delgada, the largest city of the archipelago, and students from Viseu, a non-fluoridated region on the mainland, revealed that the prevalence of dental fluorosis in the students of Ponta Delgada was four-fold higher (15.3 vs. 4.1%) [26]. Considering our results and the knowledge that among the residents of this island, tea consumption with high concentrations of fluoride is a well-established habit in adults and children [29], it is safe to assume that the fluoride DI is easily exceeded, increasing the risk for the development of dental fluorosis.

Our results evidence that fluoride levels vary when considering different water sources and brands and that several types of water have fluoride concentrations above the recommended limits, including tap water in some areas of the island. This reinforces the need for a very detailed study on the ideal type of water for consumption since several factors must be considered (e.g., the amount consumed and other sources of fluoride supply). Moreover, considering the geogenic existence of fluoride in volcanic islands and the frequent habit of tea consumption by the Azorean population, it seems clear that the regular monitoring of fluoride is important to reduce the problematic health effects associated with fluoride exposure.

5. Conclusions

This study discloses the relevance of monitoring the water quality regarding fluoride amount and surveillance measures to protect and improve population health. Since fluoride levels vary from one brand to another, the monitoring of fluoride in bottled water, especially gasified water, should be continuous for the assessment and review of its safety and adequacy to the populations.

Results indicate that the consumption of mineral water may be more beneficial to human health, especially in areas such as Sete Cidades, where tap water has fluoride concentrations above the recommended level. Nevertheless, the regular consumption of gasified water does not pose a health benefit when compared to tap or mineral bottled water, since several tested brands had fluoride concentrations higher than 1.5 mg/L.

The analysis of risk assessment revealed that the ingestion of some types and water brands can potentiate non-cancer health effects, indicating the need for the regular monitoring of fluoride levels in water for consumption, particularly in volcanic regions, to reduce the problematic health effects associated with fluoride exposure.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14152424/s1, Table S1: Tap water fluoride concentration (mean) obtained by the potentiometric method with a fluoride ion-selective electrode; the remaining drinking water physicochemical properties (mean), were obtained from the city councils records (Povoação, Ribeira Grande and Ponta Delgada) for each village considered in the study.

Author Contributions: D.L. analyzed and interpreted the data regarding the fluoride concentrations in water and calculated the daily intake and risk exposure. D.G. executed the fluoride quantifications by the potentiometric method with a fluoride ion-selective electrode. P.G. and A.R. were major contributors to writing the manuscript. All authors have read and agreed to the published version of the manuscript.

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