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Excess of Naturally Occurring Fluoride in Groundwater Discharge in Macaronesia: Brava Island, Cape Verde

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Abstract: A high concentration of fluoride in groundwater poses a risk to human health. One of the best-known problems related to excess fluoride in drinking water is dental fluorosis. The characteristic composition of volcanic rocks in oceanic islands tends to present high concentrations of fluoride in groundwater discharge in springs. This study investigates fluoride content in two springs (Encontro and Ferreiros) on the island of Brava (Cape Verde), with the objective of monitoring the operational control production and distribution of drinking water. Using a spectrophotometric method, the level of fluoride found in the water discharged from the Encontro spring was found to be in the range of 4.8 to 6.5 mg/L, whereas at the Ferreiros spring, it was 5.8 to 6.2 mg/L. These results are far above the threshold limit established in the decree No. 5 of 2017 of the Cape Verdean legislation, whose legal threshold value for fluoride is 1.5 mg/L, the same value established by the World Health Organization (WHO). Due to geological conditions and consequences for the health of the population, the water is not adequate for consumption without proper treatment.

Keywords: drinking water; excess fluoride; dental fluorosis; water quality; volcanic island; aquifer

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1. Introduction

Ensuring that water for human consumption is free of pathogenic microorganisms, substances, and chemical elements that are harmful to health is an effective action to prevent water-related diseases [1].

One of the compounds that, in excess in water, is harmful to health is fluoride, which is usually found in soil, air, and food, and its proper use benefits bone and dental integrity [2]. Several studies around the world show direct proportional correlation between the prevalence of dental fluorosis and the concentration of fluoride in water intended for consumption [3–5]. In some islands of the Cape Verde archipelago, high levels of fluoride have been found in the water [6], but this is regulated by Cape Verdean Legislation and by the World Health Organization to 1.5 mg/L [7].

Water supply can originate from several sources such as groundwater captured through wells, catchment basins or infiltration galleries [8] or from surface water that comes mainly from rainfall, with collection through reservoirs and dams, in addition to rivers, lakes, and the sea. In the Cape Verdean scenario, low rainfall, combined with great variability and concentration over a few days, sandy soils with low retention capacity, and a mountainous topography make it difficult to capture and use rainwater [9]. Thus, the sequential use of small deep wells, dikes to capture and store water for agriculture, boreholes to supply the population, desalination, and now small- and medium-sized dams for agriculture have been used [10].

The contamination of water used for human consumption by elements that can be harmful to the environment and human health may come from anthropogenic activities or by the natural leaching effect of harmful elements through prolonged contact with rocks rich in these components [11].

In the earth's crust, fluoride is widely distributed, mainly as the fluorite minerals, composed of calcium fluoride (CaF_2), cryolite, sodium aluminofluoride ($Na_3(AlF_6)$), and fluorapatite ($Ca_5(PO_4)_3F$). Fluorine, being the most electronegative element, has a strong tendency to acquire a negative charge and, in solution, forms fluoride (F^-) ions [2].

The fluoride ion is a Lewis base, and its conjugate acid hydrogen fluoride is a weak acid in water; however, its acidity is higher than anhydrous acetic acid due to the basicity of fluoride ions, which show basic characters in aqueous media. Based on the pH of the medium, fluoride forms water-soluble complexes with polyvalent metal ions such as Mg^{2+}, Ca^{2+}, Al^{3+}, and Fe^{3+} [12].

The positive effect of fluoride on teeth lies in its contribution to the prevention of caries, caused by the action of bacteria called cryogenic bacteria, such as streptococcus mutans and lactobacilli in the mouth [13]. Associated with poor diet and oral hygiene, they cause partial or total destruction of the teeth through the decomposition of ingested carbohydrates originating in the acids, including lactic, acetic, and formic acids that cause the dissolution of the mineral content of teeth [14].

This study presents the analysis and conclusions from the results obtained after measuring the fluoride concentration in the drinking water of the island of Brava, Cape Verde. To this end, this study had the following objectives: (i) to determine the level of fluoride concentration in the water of the island of Brava and compare the results with the regulatory Decree of Cape Verde; (ii) to exemplify the health effects caused by excess fluoride in water intended for human consumption, whose highlight is dental fluorosis, and (iii) to address the treatment solutions for water with excess fluoride, focusing on defluoridation by active alumina.

Study Area

The research area is located in the Republic of Cape Verde, an archipelago in the Atlantic Ocean, west of Senegal, composed of ten volcanic islands (Figure 1). It is characterized by an arid to semi-arid climate, with an average temperature of 26 °C, and a scarcity of water resources on the surface, due to an average annual rainfall of 154 mm and adverse geology. On one of the islands, Brava, groundwater is a resource for the population. Here, samples from two springs—Encontro and Ferreiros—were collected and sent for analysis to another island, Fogo.

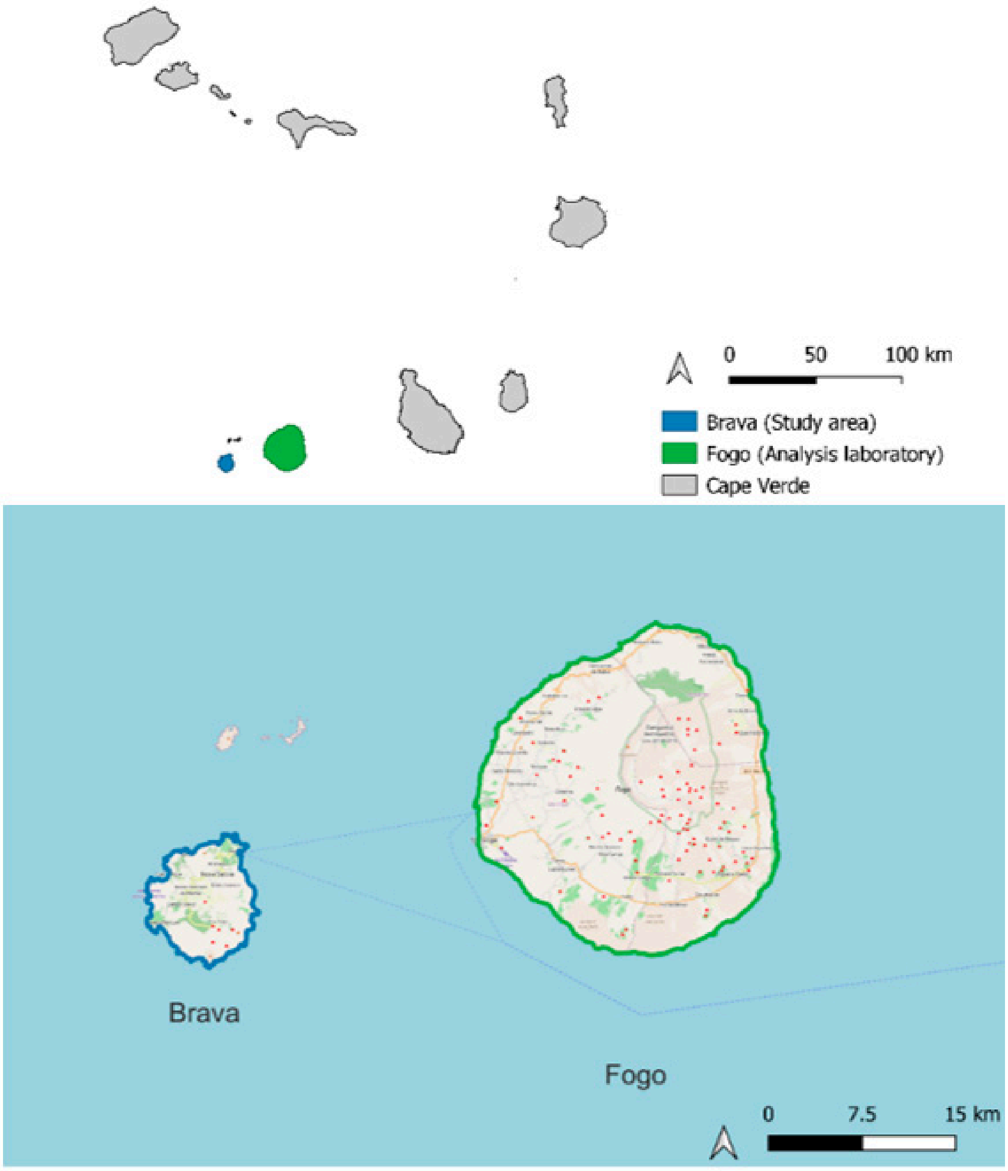

Figure 1. Location of Brava and Fogo Islands.

2. Materials and Methods

2.1. Sampling

Four water samples were collected in PET bottles at the Encontro and Ferreiros springs (Brava Island) on different dates: (i) 22 January 2021, (ii) 3 February 2021, (iii) 19 February 2021, and (iv) 26 March 2021. They were sent, along with the date and time of collection, to ÁguaBrava headquarters on the island of Fogo and stored at room temperature in the DQA laboratory, where the parameters of pH, conductivity, total dissolved solids, and temperature were determined.

Analyses for the determination of hardness and fluoride quantity were performed in triplicate and took place during the months of January to March in the water quality analysis laboratory at the company's headquarters in São Filipe (Fogo Island).

2.2. Procedure

Laboratory tests to determine hardness and the fluoride concentration in the samples collected on the island of Brava were completed using spectrophotometry. The multiparameter photometer used was the HANNA brand model HI83399 (Figure 2).

Figure 2. Multiparameter photometer used in the study.

In order to determine the physical–chemical parameters, the portable multiparameter probe model HI9811-5 from HANNA instrument was used to measure pH, electrical conductivity, temperature, and total dissolved solids.

For hardness determination, the following steps were conducted:

- 0.5 mL of the untreated sample was added to the cell, as was 0.5 mL of the hardness indicator reagent HI93735IND-0; and a Pasteur pipette was used to make up to the 10 mL mark with the HI93735A-LR reagent;
- Two drops of HI93435B-0 buffer were added; after replacing the cap, the cell was inverted five times to mix it, and this was inserted into the photometer by closing the cap;
- The 'zero' key was selected, and, when 0.0 mg/L appeared on the screen, the cell was removed and the HI93735C-0 fixing reagent was added;
- The cell cap was closed and gently inverted for 20 s; then the solution was introduced into the photometer, the read key was selected, and the result was obtained.

Regarding the determination of fluoride concentration, with the photometer turned on, the "Fluoride HR (R. high) method" was selected, and the same steps described in Table 1 were performed.

Table 1. Description of the procedure for fluoride determination.

Steps	Photographs
(a) A total of 2 mL of the fluoride indicator reagent A was added to the cell, and this was made up to the 10 mL mark with fluoride indicator B using a Pasteur pipette.	
(b) The lid was put on and several inversions were made to obtain a homogeneous mixture. The cell was then introduced into the photometer, and the lid was closed.	

Table 1. *Cont.*

Steps	Photographs	
(c) The 'clock' key was selected to zero the blank. After one minute, it was removed, and a syringe with 1 mL of the water sample was added. With the lid closed, the cell was inverted several times to mix the solution completely.		
(d) The cell was inserted back into the photometer, and the 'clock' key was selected. After one minute of reading, the 'read' key was selected, and the value of fluoride concentration in the sample was obtained.		

3. Results and Discussion

The four samples collected were analyzed in triplicate for better reliability and accuracy of the results. Table 2 shows the results obtained for the physical–chemical parameters (pH, electrical conductivity, total dissolved solids, and temperature). Based on regulatory decree No. 5 of November 6, 2017, it can be observed that both the Encontro and Ferreiros waters have parameters within the limit established by Cape Verdean legislation.

Table 2. Average of Brava water parameters.

Spring	pH	CE (µs/cm)	TDS (mg/L)	T (°C)	Hardness (mg/L)
Encontro	7.8	1045	522.5	22	76 ± 3.1
Ferreiros	8	1332.5	657.5	22.8	60.2 ± 2.9
Reference average values (decree Nº5/2017)	6.5–9.5	2000	1000	25	500

Water hardness refers to the total concentration of ions in water, particularly (Ca^{2+}) and (Mg^{2+}). According to the level of hardness, characterized as: very sweet (0–60mg/L), sweet or soft (60–150mg/L), not very hard (150–300 mg/L), and hard (≥300 mg/L) [15], the waters from both the Encontro and Ferreiros springs re sweet/soft, with an average concentration of 76 mg/L and 60.2 mg/L respectively (see Table 2).

Regarding the analyses performed to determine fluoride concentration, represented in Figure 3, it can be observed that, for both Ferreiros and Encontro, the average values of the sample for each date are well above the established national limit for fluoride, which is 1.5 mg/L.

Even the minimum concentrations found—4.8 mg/L in Encontro and 5.8 mg/L in Ferreiros—are far above the value stipulated in the current legislation. Similar results were found by Shinzato and Ezaki [16] in the municipality of Pereiras (SP), in which the tests performed were based on raw water with an initial concentration of 6 mg/L of F.

According to the literature, geology is the main factor that influences the concentration of fluoride in a place, because of rocks that have biotite in their mineralogy [17]. This includes host rocks such as granite, basalt, and schist; due to various transport mechanisms, fluoride reaches the groundwater, where it remains dissolved [18]. Therefore, high fluoride waters are mostly calcium-deficient groundwater, geothermal waters, and water in some sedimentary basins, occurring in many areas of the world, including large parts of Africa, China, the Middle East, and South Asia [19,20].

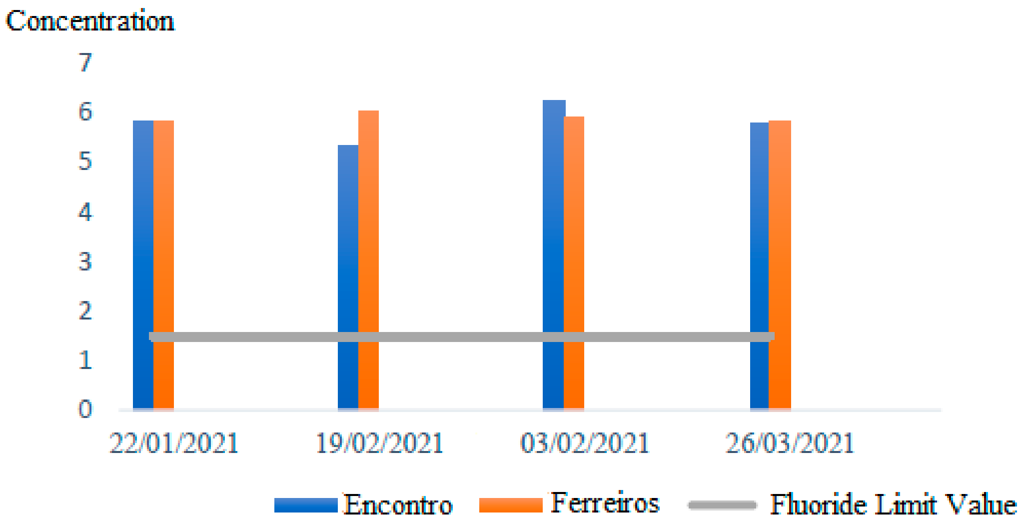

Figure 3. Comparison of the fluoride results obtained for both springs on the four selected dates with the established limit values.

Indeed, this rock–water–fluorine relationship has been detected on other islands that make up Macaronesia (Macaronesia is composed of the archipelagos of the Azores, the Canary Islands, and Cape Verde). In a 2015 study conducted in the Azores and Canary Islands [21], it was found that, in some municipalities of the islands studied, fluoride was a common problem in groundwater. In the Azores, values of up to 4.3 mg/L were observed, and in numerous samples, values higher than the 1.5 mg/L allowed by legislation were found. In the case of the Canary Islands, values of up to 8.13 mg/L were observed in groundwater from the north of the island of Tenerife [22].

In the studies of Netto et al. [23], in Brazil, the average fluoride value was 2.73 mg/L, reaching up to 12 mg/L in one of the wells. These studies explain that fluoride is commonly found as a constituent of magmatic rocks that, in some rocks, especially those in the late stages of magmatism evolution, fluoride-silicates can exceed the amount fixed in the apatite.

Anomalies in fluorine contents of 2.37 to 12 mg/L and up to 10 mg/L were also found in wells drilled in the sedimentary basin of São Paulo [16]. According to the explanation, the presence of fluorine in these aquifers is due to past geological events related to hydrothermal and tectonic processes, which propitiated the circulation of residual solutions from the magma and caused the mineralization and remobilization of the F contained in the rocks. It has been highlighted by Komati and Figueiredo [24] that the content of dissolved substances in groundwater increases as its path in the aquifer and its residence time increases. The highest value ever found is in lakes in East Africa, which showed up to 2800 mg/L.

On the island of Brava, most of the population suffers from dental fluorosis, which is a noticeable problem in the study by Dozal et al. [25], wherein the F concentration was found to be from 0.7 to 8.6 mg/L. The approach in the literature is that the disease is more frequent in teeth of late mineralization, i.e., permanent dentition in children of low weight or poor nutritional status or chronic renal failure. This disorder can become a public health problem. It not only affects the aesthetics of the individual but also causes functional changes that can interfere with issues of self-esteem, besides being a factor that can hinder the insertion of those affected into the labor market [26].

4. Conclusions

Through the results obtained, it was found that the water from the island of Brava is not suitable for consumption without first undergoing some treatment process. It was clear that the concentration of fluoride in both the Encontro and Ferreiros waters were well above the limit allowed by Cape Verdean legislation and the WHO, which is 1.5 mg/L.

What has been found through the literature is that the excess fluoride existing on Brava Island is related to the geology of the rocks and not to soil pollution from industries, since this does not exist on the island.

The use of water with high fluoride content constitutes a public health issue, because it can result in several health problems, including dental fluorosis which affects the Bravenses. This is a chronic intoxication which develops in early childhood.

It is concluded that more investment is needed in research on fluoride in water, as this is a typical problem in the Macaronesia region to which Cape Verde belongs. Investment is required in the materials, filters, and industrial processes needed to reduce this endemic problem that has economic, sanitary, and social impacts. Furthermore, a future line of work could be to analyze the variability of the data over the years and, based on the values obtained as annual averages, to select the best fluoride removal methods applied to this particular geographical area.

In addition to the health problems associated with high fluoride content in drinking water, other adverse effects on human health have been observed. A study by Kheradpisheh et al. [27] shows that fluoride affects the TSH and T3 hormones responsible for hypothyroidism. Furthermore, another Iranian study [28] has concluded that, in the study area of the article, children living in an area with high fluoride content have a lower IQ than those living in areas with lower fluoride content. Therefore, measuring fluoride content in water and, based on the results obtained, applying the best fluoride removal process is considered vital to improving the lives of future generations.

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

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