Science of the Total Environment 982 (2025) 179635

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Research Paper

Fluoride levels in water sources inside the crater of Furnas volcano: Potential health implications for local communities and tourists

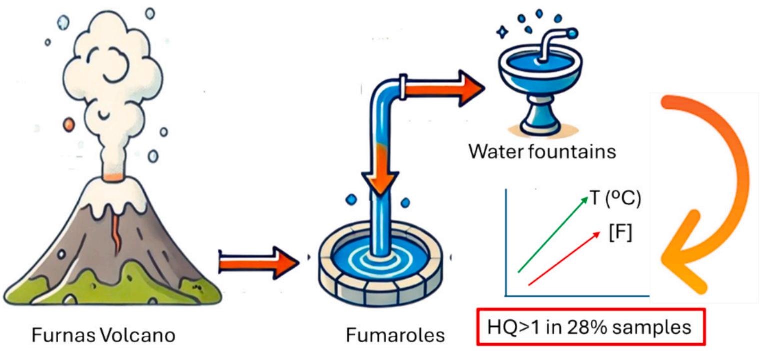
Diana Linhares[a,*], Diogo Gaspar[b], Filipe Bernardo[a], Isabelle Beney[d], Patricia Garcia[b,c], Armindo Rodrigues[a,b]

[a] IVAR, Research Institute for Volcanology and Risk Assessment, University of the Azores, 9501-801 Ponta Delgada, Portugal
[b] Faculty of Sciences and Technology, University of the Azores, 9501-801 Ponta Delgada, Portugal
[c] cE3c, Centre for Ecology, Evolution and Environmental Changes, and Azorean Biodiversity Group, University of the Azores, 9501-801 Ponta Delgada, Portugal
[d] Faculty of Science, University of Geneva (UNIGE), Quai Ernest-Ansermet 30, 1211, Genève 4, Switzerland

HIGHLIGHTS

- Fluoride in volcanic waters can pose health risks if consumed without monitoring.
- Hypothermal waters show distinct physicochemical properties from other categories.
- Hazard Quotient >1 was found in 28 % of samples for children, but none for adults.
- Untreated volcanic waters are marketed as "medicinal" warrant safety assessments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Anastasia Paschalidou

Keywords:
Volcanism
Geomedicine
Environment
Hot springs
Thermal

ABSTRACT

Fluoride, a naturally occurring mineral, is widely recognized for its dual role in human health. At optimal concentrations, it provides dental benefits; however, excessive fluoride can lead to dental and skeletal fluorosis. Volcanic regions are known for their geothermal water sources that contain elevated levels of fluoride, raising concerns about potential health impacts on local populations. This study focuses on the Furnas volcano region at the Island of São Miguel, Azores, where natural springs are promoted for their therapeutic and medicinal properties. However, these springs also raise concerns about health risks due to fluoride exposure, as they are freely consumed by locals and tourists without any formal treatment or monitoring. Eighteen water samples were collected from natural springs in the village of Furnas. *In situ* measurements were taken forphysicochemical parameters such as pH, temperature, and conductivity. Fluoride concentrations were quantified using a potentiometric method with a fluoride ion-selective electrode. To assess risks, we estimated daily fluoride intake (DFI) and calculated the Hazard Quotient (HQ) for both children and adults.

The fluoride concentrations in the samples ranged from 0.47 mg/L to 5.48 mg/L, with 72 % exceeding the recommended limit of 1.5 mg/L for drinking water. Significant correlations were found between temperature,

---

[*] Corresponding author at: IVAR, Research Institute for Volcanology and Risk Assessment, University of the Azores, Rua da Mãe de Deus, Apartado 1422, 9501-801 Ponta Delgada, Açores, Portugal.

E-mail address: diana.ps.linhares@uac.pt (D. Linhares).

https://doi.org/10.1016/j.scitotenv.2025.179635
Received 21 January 2025; Received in revised form 28 April 2025; Accepted 7 May 2025

conductivity, and fluoride concentration. Hazard Quotient values indicated potential health risks for children consuming untreated spring water. Waters categorized as hypothermal exhibited significantly lower fluoride concentrations compared to mesothermal, thermal, and hyperthermal samples.

These findings highlight the impact of volcanic activity on fluoride levels in the natural springs of Furnas, emphasizing the need for regular monitoring and public awareness. While these waters are frequently consumed for their perceived health benefits, elevated fluoride levels may pose health risks to residents and tourists, demanding informed decision-making and enhanced water safety measures.

1. Introduction

Fluoride is a non-essential mineral that plays a dual role in human health. It provides dental benefits when consumed at optimal levels but can lead to dental and skeletal fluorosis when ingested in excess (WHO, 2019). Excessive fluoride intake, primarily through drinking water, is linked to adverse health outcomes, such as dental and skeletal fluorosis. Dental fluorosis is characterized by enamel hypomineralization and discoloration of teeth, while skeletal fluorosis manifests as bone deformities, joint stiffness, and increased susceptibility to fractures (Mishra et al., 2010; WHO, 2019; Solanki et al., 2022; Umer, 2023). Due to these risks, regulating and monitoring fluoride levels in drinking water is crucial for public health authorities worldwide. According to WHO guidelines, the concentration of fluoride in drinking water should range from 0.5 to 1.5 mg/ L (WHO, 2011). However, research by Mohammad and C. B Majumder (2014) and Mehari et al. (2014) indicates that this level can vary between 0.5 and 1.0 mg/ L depending on climatic variables such as temperature.

Geological formation and human activities influence fluoride levels in water, but volcanic activity is also a significant contributor. Volcanic emissions release fluorine-bearing compounds that enrich hydrothermal fluids with fluoride (Malago et al., 2017; Chowdhury et al., 2019; Schlesinger et al., 2020). The release of gases and minerals from magma chambers and volcanic vents, such as hydrogen fluoride (HF), is common in volcanic regions (Linhares et al., 2020; Regenspurg et al., 2022; Nordstrom, 2022). These substances dissolve in water, increasing the fluoride content of hydrothermal fluids and nearby water bodies (Edmunds and Smedley, 2005; Wang et al., 2020). Fluoride contamination in groundwater is a global environmental concern (Shaji et al., 2024), with elevated levels in drinking water linked to volcanic activity worldwide. For example, studies in volcanic areas of Macaronesia have reported high fluoride levels in groundwater, with some tap water sources reaching up to 9.9 mg/L due to the composition of volcanic rocks (Rubio et al., 2020). In Cauca, Colombia, fluoride concentrations in water are considered a risk for dental fluorosis (Revelo-Mejía et al., 2022). A study published in *Nature Communications* emphasized that aquifers in volcanic and geothermal regions often contain high levels of fluoride, highlighting the need for regular monitoring to mitigate health risks (Podgorski and Berg, 2022). In the Azores archipelago, particularly on São Miguel Island, several studies have shown that villages in the vicinity of Furnas volcano were, in the recent past, supplied with water containing very high concentrations of fluoride (Lobo, 1993; Baxter et al., 1999). However, a recent analysis report indicates that the fluoride concentrations in drinking water in these villages are now within legal limits. This improvement is attributed to the significant progress made in the last 20 years in the development of technologies and infrastructures to improve fluoride treatment in water (Linhares et al., 2016, 2017).

Volcanic activity remains a continual feature of Furnas volcano, rendering the settlement of Furnas village a premier tourist attraction due to its remarkable geothermal activity and abundant biodiversity (Guest et al., 2015). This touristic village is nestled inside a volcanic crater, characterized by many geothermal phenomena like hot springs, fumaroles, and mud pools. The therapeutic properties of the mineral-rich hot springs have also spurred health tourism, with visitors seeking the benefits of the local spa treatments. There are available several natural springs, characterized by the region's geothermal activity and volcanic geology. However, many natural springs are freely accessible for locals and tourists without any treatment or monitoring to ensure that the water quality meets the safety standards for consumption. The Regional Government homepage (Governo dos Açores, 2024) highlights the 'medicinal properties' of these waters, a claim echoed across various tourism sites about Furnas. According to local folk medicine, certain springs are believed to offer specific health benefits: "Azeda do Arrebentão" water is said to eliminate dandruff and aid digestion; "Água da Prata" is used for treating eye allergies, earning it the name "Água dos Olhos Belos"; and "Água Santa" when mixed with honey, cinnamon, and cachaça, is used as a remedy for flu.

Fluoride contamination due to volcanic activity is well-documented; however, there has been limited research on the health risks associated with consuming untreated geothermal waters in volcanic tourist areas like Furnas. Most existing studies focus on treated water, overlooking fluoride levels in freely available geothermal springs that are often consumed by locals and tourists.

In this study we aim to examine the potential health risks associated with consuming untreated water from various spring sources within the Furnas volcano crater, often presented to locals and tourists as a safe drinking water option. Our investigation focuses on raising awareness about the fluoride concentration in these spring waters, which are freely available for human consumption. This knowledge will support informed decision-making processes to mitigate health risks and enhance the well-being of both residents and tourists.

2. Material and methods

2.1. Study area

The Azores archipelago, located at the junction of the North American, African, and Eurasian plates (in the North Atlantic Ocean) (Searle, 1980; Madeira and Ribeiro, 1990; Vogt and Jung, 2004), consists of nine inhabited islands. São Miguel Island, the largest (744 km^2) and most populated (>137,000 inhabitants), features three active central volcanoes (Sete Cidades, Fogo, and Furnas), two active fissural systems (Picos and Congro) and two extinct volcanic systems (Povoação and Nordeste) (Pacheco et al., 2013; Gaspar et al., 2015).

Furnas Volcano, in eastern São Miguel, is a complex system comprising Furnas Lake, geothermal springs, and fumaroles (Fig. 1A). These geothermal manifestations not only enhance the village's unique charm but also play a crucial role in its socio-economic landscape by attracting tourists who seek therapeutic baths and gastronomic experiences. Hese geothermal features not only enhance the village's unique charm but also play a crucial role in its socio-economic landscape by attracting tourists who seek therapeutic baths, and culinary experiences. A detailed location map is provided in Supplementary Material (Fig. S1).

2.2. Water sampling

Eighteen natural springs in Furnas were sampled from July 18–20, 2022 (Fig. 1B). Three springs are in the village center (Fig. 1C), while fifteen are situated near fumarolic fields and calderas (Figs. 1D, E). Each spring was sampled in triplicate. A detailed and enlarged version of the location map is provided in Supplementary Material (Fig. S1).

Parameters such as pH, electric conductivity and temperature were measured *in situ*. According to the temperature of the water, springs were categorized into four distinct groups: hypothermal (< 25 °C); mesothermal (> 25 °C and < 35 °C), thermal (> 35 °C and < 40 °C) and hyperthermal (> 40 °C) (Herculano de Carvalho et al., 1961).

All samples were collected into pre-cleaned plastic containers with 50 mL of capacity and stored at 4 °C prior to analysis. The samples were analyzed within 6–12 h after collection.

2.3. Fluoride quantification

Fluoride concentration was determined potentiometrically using a fluoride ion-selective electrode (Orion, Model 9409) following NIOSH (1984) guidelines. Calibration curves were constructed using fluoride standards (0.125–8.0 mg/L), mixed with TISAB II (1:1, *v*/v). The fluoride concentration was determined by interpolation, with triplicate analyses. Internal standards were used to validate the results, and a coefficient of variation < 3 % was considered acceptable.

2.4. Estimation of daily fluoride consumption and risk assessment of fluoride intake

Estimated daily fluoride intake (DFI) and fluoride intake risk from consuming natural volcanic water was calculated as follows:

$$\text{Daily intake (DI)} = C \text{ x } V$$

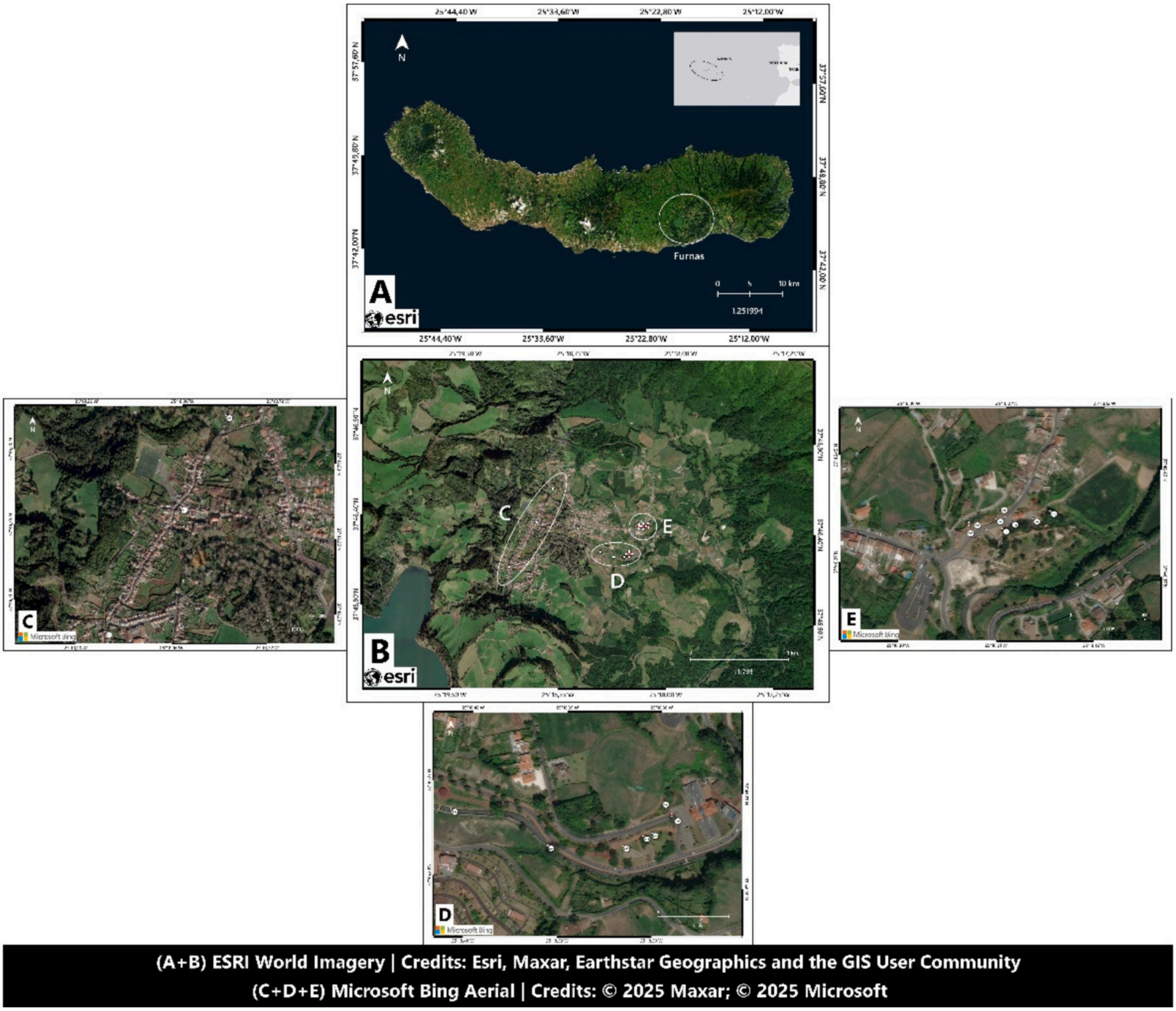
$$\text{Chronic Daily Intake (CDI)} = C \times V/BW$$

Where C is the fluoride concentration in water (mg/L), V is the average daily intake rate (L/day), and BW represents the Body weight (kg). A volume of 0.250 L was considered one daily dose. The CDI was calculated for a child (BW of 20 kg) and an adult (BW of 70 kg).

The Hazard Quotient (HQ) was calculated using the following formula (U.S. EPA, 1999):

$$HQ = CDI/RfD$$

The reference dose (RfD) is an estimate of daily exposure that is not expected to pose a significant risk of adverse effects throughout life. The RfD value for fluoride is set at 0.06 mg/kg/day, as established by the



(A+B) ESRI World Imagery | Credits: Esri, Maxar, Earthstar Geographics and the GIS User Community
(C+D+E) Microsoft Bing Aerial | Credits: © 2025 Maxar; © 2025 Microsoft

Fig. 1. Locations of the water sampling sites at Furnas village, São Miguel Island. Basemap aerial imagery by ESRI ArcGIS® online "World imagery" basemap (A + B) and Microsoft Bing maps (C + D + E). Attribution credits to the imagery providers are given below the figure.

Drinking Water Standards and Health Advisories (U.S. EPA, 2012). This value includes 0.05 mg/kg/day from fluoride intake through beverage and 0.01 mg/kg/day from fluoride intake *via* meals. When the HQ exceeds 1 (unity), it is considered as a concern for possible occurrence of non-cancer effects (U.S. EPA, 1989).

2.5. Statistical analysis

The normality of the data was assessed using the Shapiro-Wilk test, conducted in SPSS (version 29.0). The results indicated that the data did not follow a normal distribution ($p < 0.05$). To test differences between data sets, Kruskal-Wallis was employed. When significant differences were found, the Mann-Whitney *U* test was used for pairwise comparisons. Spearman's rank correlation was used to evaluate the relationships between these continuous variables as the data did not meet the assumptions for parametric tests. A multiple linear regression model was applied to examine the relationship between fluoride (the dependent variable) and the predictors: pH, conductivity, and temperature.

3. Results

3.1. General characterization

Water samples were categorized by temperature (hypothermal, mesothermal, thermal, hyperthermal), and Mann-Whitney *U* test was conducted to assess differences among numeric variables (Table 1). Significant differences were found in all variables except pH ($p = 0.775$). Hypothermal waters (< 25 °C) had distinctly lower conductivity and fluoride levels (1.25 ± 0.72 mg/L) compared to the other categories (> 4 mg/L) (Table 1).

Spearman correlation analysis was conducted to evaluate the association between pH, temperature, conductivity (μS/cm), fluoride concentration (mg/L) and daily intake (Table 2). The pH was not associated with any other variables. However, temperature (°C) demonstrated a strong positive correlation with conductivity ($r = 0.771$, $p < 0.01$), fluoride concentration ($r = 0.805$, $p < 0.01$), and daily intake ($r = 0.808$, $p < 0.01$). Conductivity also showed a very strong positive correlation with fluoride concentration ($r = 0.918$, $p < 0.01$) and with daily intake ($r = 0.918$, $p < 0.01$).

A linear regression analysis was conducted to predict fluoride concentration based on pH, conductivity, and temperature (Table 3). The model was significant, $F(3, N-1) = 129.58$, $p < 0.05$, with an R^2 of 0.965, indicating that 96.5 % of the variance in fluoride concentration was explained by the predictors. All the predictors were significant [pH] ($B = -0.73$, $p < 0.05$) and [Conductivity] ($B = 2.97$, $p < 0.05$) and temperature [Temperature] ($B = 0.03$, $p < 0.05$) (Table 3).

3.2. Risk assessment

Daily Intake (DI), Chronic Daily Intake (CDI), and Hazard Quotient (HQ) were evaluated to assess fluoride exposure in both children and adults. Fluoride levels varied widely between samples, ranging from 0.47 mg/L to 5.48 mg/L (samples 14 and 17, respectively). Generally, samples taken from higher-temperature sources (>30 °C) exhibited higher fluoride concentrations, consistent with the solubility of fluoride with increasing temperature (Supplementary material S2). A Hazard Quotient (HQ) exceeding 1 indicates a potential risk for adverse health effects due to fluoride exposure. The HQ values revealed potential health risks from fluoride exposure in children, with 28 % of the spring samples (5 out of 18) yielding HQ values greater than.

In contrast, none of the tested water samples indicated a risk for adults consuming an amount of 250 mL (Supplementary material S2).

4. Discussion

This study highlights the potential risks associated with fluoride exposure from untreated volcanic waters in Furnas village, São Miguel Island. These waters, marketed as "medicinal" and freely available to both locals and tourists, showed fluoride concentrations ranging from 0.47 mg/L to 5.48 mg/L. Notably, 72 % of the samples exceeded the recommended safe limit of 1.5 mg/L (WHO, 2011). However, it is important to note that the statistical analysis conducted in this study encountered certain limitations, mainly due to the small sample size and the non-normal distribution of the data. Future research with larger sample sizes will be needed to validate these findings and gain a deeper understanding of the complex dynamics of fluoride exposure in geothermal waters.

Conductivity and fluoride levels increased with temperature, which is expected since the solubility of minerals in water generally increases with temperature. As water warms, more minerals and ions dissolve, leading to higher conductivity and an increase in fluoride concentration. This fluoride often originates from the dissolution of fluoride-bearing minerals, such as fluorite (CaF_2), mica, or apatite. Additionally, warmer geothermal waters typically have a longer residence time underground, allowing them to interact more extensively with fluoride-rich rocks, which enhances the dissolution of salts and minerals. Even though fluoride is needed to inhibit dental caries (Fan et al., 2016; Sebastian et al., 2016), some studies indicate that patients with severe dental fluorosis also exhibit higher levels of caries. This may be explained by the loss of protective enamel associated with pitting in severe fluorosis (Hung et al., 2023; Ravuru et al., 2023). This has also been observed in the past in surveys conducted in the Azores, particularly near the Furnas volcano, where the presence of dental fluorosis was reported (Baxter et al., 1999; Linhares et al., 2017). Fluoride concentrations in drinking water above 4–8 mg/L can lead to skeletal fluorosis,

Table 1

Characterization of physicochemical parameters and fluoride risk assessment (mean ± SE) in water from the four temperature categories: hypothermal (< 25 °C); mesothermal (> 25 °C and < 35 °C), thermal (> 35 °C and < 40 °C) and hyperthermal (> 40 °C).

	Hypothermal	Mesothermal	Thermal	Hyperthermal	*p*-value[1]
Physicochemical parameters					
pH	5.91 ± 0.60	6.30 ± 0.00	6.33 ± 0.11	6.41 ± 0.17	0.775
Conductivity (μS/cm)	0.29 ± 0.07^{a}	1.53 ± 0.08^{b}	1.48 ± 0.11^{b}	1.08 ± 0.48^{b}	0.005
Fluoride (mg/L)	1.25 ± 0.72^{a}	4.82 ± 0.93^{b}	5.28 ± 0.13^{b}	4.34 ± 1.23^{b}	0.006
Fluoride Risk Assessment					
Daily intake	0.31 ± 0.18^{a}	1.20 ± 0.23^{b}	1.32 ± 0.03^{b}	1.08 ± 0.31^{b}	0.006
CDI child	0.016 ± 0.009^{a}	0.060 ± 0.011^{b}	0.066 ± 0.002^{b}	0.054 ± 0.015^{b}	0.006
HQ child	0.26 ± 0.15^{a}	1.00 ± 0.20^{b}	1.10 ± 0.03^{b}	0.90 ± 0.01^{b}	0.006
CDI adult	0.004 ± 0.002^{a}	0.017 ± 0.003^{b}	0.019 ± 0.0004^{b}	0.015 ± 0.004^{b}	0.006
HQ adult	0.075 ± 0.04^{a}	0.29 ± 0.06^{b}	0.31 ± 0.008^{b}	0.26 ± 0.07^{b}	0.006

[1] *p* value for group comparisons by: Kruskal–Wallis for all continuous variables followed by Mann–Whitney *U* test. Different letters within each study group represent significant differences between sites.

Table 2
Spearman correlation coefficients between variables.

	pH	Temperature (°C)	Conductivity (μS/cm)	Fluoride (mg/L)	Daily Intake
pH	1.000	0.166	−0.102	−0.059	−0.062
Temperature (°C)	0.166	1.000	0.771**	0.805**	0.808**
Conductivity (μS/cm)	−0.102	0.771**	1.000	0.918**	0.918**
Fluoride (mg/L)	−0.059	0.805**	0.918**	1.000	0.999**
Daily Intake	−0.062	0.808**	0.918**	0.999**	1.000

** Spearman's correlation is significant at $p < 0.01$.

Table 3
Results of multiple linear regression analysis predicting fluoride concentration.

Predictor Variable	Coefficient (B)[1]	Standard Error	t-Statistic	*p*-value	95 % CI (Lower, Upper)
pH	−0.73	0.200	- 3.678	0.02	−1.163; −0.306
Conductivity	2.97	0.006	3.974	0.01	0.012, 0.040
Temperature	0.03	0.214	13.929	<0.001	2.516, 3.432
Model Metrics					
R^2	0.965				
Adjusted R^2	0.958				
F-Statistic (df1, df2)	129.58 (3, N-1)			<0.001	

[1] Coefficients represent unstandardized regression weigh.

which presents symptoms such as increased bone density, joint pain, stiffness, and excessive bone formation (Ayoob and Gupta, 2006; Simon et al., 2014; Dar and Kurella, 2024). In Furnas, groundwater fluoride levels have been recorded at 5.09 mg/L, likely due to fluoride-rich gases emitted by the volcano (Aiuppa et al., 2003; Cronin et al., 2003) and the weathering of silicate in aquifers and volcanic rocks (Vivona et al., 2007; Rango et al., 2009).

The results of this study align with previous findings highlight the health risks associated with consuming volcanic waters. The strong positive correlation between water temperature, conductivity, and fluoride concentration suggests geothermal processes contribute to fluoride enrichment. As the temperature increased, fluoride levels also increased, indicating that geothermal activity plays a role in the dissolution of fluoride from volcanic rocks (Nordstrom, 2022; Huang et al., 2025). Similar trends have been observed in other volcanic regions, such as Rotorua, Mount Etna, and Popocatépetl. Notably, significant differences in fluoride levels between hypothermal and hotter waters suggest temperature can serve as a proxy for fluoride risk, especially in resource-limited settings. Regression analysis further corroborates the strong influence of conductivity and temperature on fluoride concentrations, explaining 96.5 % of the variance. This underscores the importance of these parameters in understanding and managing fluoride risk in volcanic regions. Future studies should explore the temporal variability of fluoride concentrations, considering factors such as seasonal changes, rainfall, and the intensity of volcanic activity, to develop a comprehensive risk management strategy. Regarding risk assessment, data revealed significant differences in fluoride intake risk between children and adults. The Hazard Quotient (HQ) values for children exceeded 1 for 28 % of the water samples, indicating a potential risk for dental or skeletal fluorosis in this group. In contrast, none of the samples posed a risk for the adults based on the standard 250 mL daily intake. This finding underscore children's increased vulnerability to fluoride due to their lower body weight and higher water consumption per kilogram, supporting previous studies on the susceptibility of children to fluoride toxicity (Erdal and Buchanan, 2005; Buzalaf and Levy, 2011; Nakamoto and Rawls, 2018). These results emphasize the need for targeted interventions to manage fluoride levels in water sources consumed by children.

Although these waters have therapeutic and cultural significance, the lack of treatment or quality control raises concerns about long-term health risks. While most people use thermal spring water for short-term therapeutic purposes, some residents incorporate it into their daily routines, resulting in longer-term, intermittent exposure. None of the tested samples posed a risk for adults consuming 250 mL daily; however, prolonged daily intake could increase cumulative exposure and risk. These findings highlight the need for targeted interventions to monitor and manage fluoride concentrations in water used by regular consumers.

While the local government promotes these waters for their medicinal properties, the findings emphasize the need for a balanced perspective on both their benefits and risks. Key limitations of this study include the lack of detailed physicochemical and mineralogical characterization, the absence of seasonal variation analysis, and the exclusion of other pathways of fluoride exposure, such as diet. Additionally, there is no epidemiological data linking fluoride exposure to health outcomes in the local population. Future research should focus on long-term monitoring of water quality, evaluating fluoride exposure through multiple pathways, and assessing seasonal and temporal variability. Surveys on water intake behaviors and tourists' perceptions of the therapeutic benefits could also provide valuable insights. Strategies to mitigate fluoride exposure, such as public awareness campaigns and updated regulations, should be considered to ensure the safe use of these waters. Addressing these gaps will help develop a comprehensive risk assessment framework for the sustainable use of geothermal waters.

5. Conclusion

This study highlights the dual role of volcanic waters in Furnas village as both a cultural and therapeutic resource, while posing potential health risks due to elevated fluoride concentrations. Geothermal processes clearly influence water quality, with temperature and conductivity being significant predictors of fluoride levels. Notably, 72 % of water samples exceeded the recommended fluoride limit, raising concerns about long-term health impacts. The risk assessment indicates children are particularly vulnerable to fluoride exposure, while adults face no immediate risk, though monitoring is crucial as environmental fluctuations may increase fluoride levels. Further analysis of physicochemical and mineralogical properties of the water is needed to better assess the health risks and benefits associated with it. To ensure public safety, proactive public health measures are recommended, including regular water quality monitoring, public education campaigns, clear signage, and possible water treatment systems. Additionally, identifying and mapping safe water sources should be prioritized.

Future research should focus on the long-term effects of fluoride exposure, seasonal variations, and fluoride mitigation strategies. Balancing the therapeutic benefits of geothermal waters with safety standards will ensure their sustainable use for both tourism and public health.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.179635.

CRediT authorship contribution statement

Diana Linhares: Writing – original draft, Supervision, Project administration, Investigation, Formal analysis. **Diogo Gaspar:** Validation, Investigation, Data curation. **Filipe Bernardo:** Software, Resources. **Isabelle Beney:** Investigation, Data curation. **Patricia Garcia:** Writing – review & editing, Formal analysis. **Armindo Rodrigues:** Writing – review & editing, Supervision, Conceptualization.

Funding

This research was funded by cE3c (DOI:10.54499/UIDB/00329/2020) and IVAR (DOI:10.54499/UIDP/00643/2020).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Isabelle Beney, while attending the ELSTE master's program at the University of Geneva (Switzerland), participated in the thematic internship ET.7 Effects of volcanism on health: identification and action strategies, from IVAR Academy.

Data availability

Data will be made available on request.

References

Aiuppa, A., Bellomo, S., Brusca, L., d'Alessandro, W., Federico, C., 2003. Natural and anthropogenic factors affecting groundwater quality of an active volcano (Mt. Etna, Italy). Appl. Geochem. 18 (6), 863–882.

Ayoob, S., Gupta, A.K., 2006. Fluoride in drinking water: a review on the status and stress effects. Crit. Rev. Environ. Sci. Technol. 36 (6), 433–487.

Baxter, P., Baubron, J., Coutinho, R., 1999. Health hazards and disaster potential of ground gas emissions at Furnas volcano, São Miguel, Azores. J. Volcanol. Geotherm. Res. 92, 95–106.

Buzalaf, M.A.R., Levy, S.M., 2011. Fluoride intake of children: considerations for dental caries and dental fluorosis. Fluoride and the Oral Environment 22, 1–19.

Chowdhury, A., Adak, M.K., Mukherjee, A., Dhak, P., Khatun, J., Dhak, D., 2019. A critical review on geochemical and geological aspects of fluoride belts, fluorosis and natural materials and other sources for alternatives to fluoride exposure. J. Hydrol. 574, 333–359.

Cronin, S.J., Neall, V.E., Lecointre, J.A., Hedley, M.J., Loganathan, P., 2003. Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano, New Zealand. J. Volcanol. Geotherm. Res. 121 (3–4), 271–291.

Dar, F.A., Kurella, S., 2024. Fluoride in drinking water: an in-depth analysis of its prevalence, health effects, advances in detection and treatment. Mater. Today Proc. 102, 349–360. https://doi.org/10.1016/j.matpr.2023.05.645.

Edmunds, M., Smedley, P.L., 2005. Fluoride in natural waters. Essentials of medical geology: impacts of natural environment on public health 301–329.

Erdal, S., Buchanan, S.N., 2005. A quantitative look at fluorosis, fluoride exposure, and intake in children using a health risk assessment approach. Environ. Health Perspect. 113 (1), 111–117.

Fan, C., Wang, W., Xu, T., et al., 2016. Risk factors of early childhood caries among children in Beijing: a case-control study. BMC Oral Health 16, 98. https://doi.org/10.1186/s12903-016-0289-6.

Gaspar, J. L., Guest, J. E., Queiroz, G., Pacheco, J., Pimentel, A., & Gomes, A. (2015). Eruptive frequency and volcanic hazards zonation in São Miguel Island, Azores. Volcanic geology of São Miguel Island (Azores Archipelago): Memoirs 44 (pp. 155–166). Geological Society: London, UK.

Governo dos Açores. 2024. https://www.azores.gov.pt/NR/exeres/6C09D463-E09A-40EC-A886-7357C032346F.htm. Webpage accessed in 25-06-2024.

Guest, J., Pacheco, J., Cole, P., Duncan, A., Wallenstein, N., Queiroz, G., et al., 2015. Chapter 9 the Volcanic History of Furnas Volcano. Sao Miguel, Azores. https://doi.org/10.1144/M44.9.

Herculano de Carvalho, A., Almeida, J.D., Reis, E.M., 1961. Guia de Análise Química das águas (potáveis, minerais e para a indústria). Associação dos Estudantes do IST, Lisboa, p. 162.

Huang, X., Wang, S., Xiao, Z., Zhang, M., Zhang, H., Qi, S., 2025. Fluoride in geothermal water: occurrence, origin, migration and environmental impact. J. Geochem. Explor. 270, 107640. https://doi.org/10.1016/j.gexplo.2024.107640.

Hung, M., Hon, E.S., Mohajeri, A., Moparthi, H., Vu, T., Jeon, J., Lipsky, M.S., 2023. A national study exploring the association between fluoride levels and dental fluorosis. JAMA Netw. Open 6 (6), e2318406-e2318406.

Linhares, D., Garcia, P., Amaral, L., Ferreira, T., Cury, J., Vieira, W., Rodrigues, A., 2016. Sensitivity of two biomarkers for biomonitoring exposure to fluoride in children and women: a study in a volcanic area. Chemosphere 155, 614–620.

Linhares, D., Garcia, P., Ferreira, T., Rodrigues, A., 2017. Safety evaluation of fluoride content in tea infusions consumed in the Azores—a volcanic region with water springs naturally enriched in fluoride. Biological and Trace Element Research 179, 158–164.

Linhares, D., Garcia, P.V., Rodrigues, R., 2020. Fluoride in volcanic areas: A case study in medical geology. In: Makan, Abdelhadi (Ed.), Environmental Health. IntechOpen, pp. 51–63. https://doi.org/10.5772/intechopen.86058.

Lobo, M., 1993. Contribuição para o estudo Físico-Químico e Microbiológico da água para Consumo Humano do Arquipélago dos Açores; Universidade dos Açores, Departamento de Ciências Agrárias: Açores, Portugal.

Madeira, J., Ribeiro, A., 1990. Geodynamic models for the Azores triple junction: a contribution from tectonics. Tectonophysics 184, 405–415.

Malago, J., Makoba, E., Muzuka, Alfred N.N., 2017. Fluoride levels in surface and groundwater in Africa: a review. Am. J. Water Sci. Eng. 3 (1), 1–17. https://doi.org/10.11648/j.ajwse.20170301.11.

Mehari, B.B., Mayabi, A.O., Kakoi, K.B., 2014. Development of a household defluoridation unit based on crushed burnt clay pot as sorbent medium: a case of Keren Community, Eritrea. Environ. Nat. Resour. Res. 4, 67–82.

Mishra, S.P., Das, M., Dash, U.N., 2010. Review on adverse effects of water contaminants like arsenic, fluoride and phosphate and their remediation. J. Sci. Ind. Res. 69, 249–253.

Mohammad, A., C. B Majumder, C.B., 2014. Removal of fluoride from synthetic wastewater by using "bio-adsorbents". International Journal of Renew. Energy Technology 3, 776–785. Search PubMed.

Nakamoto, T., Rawls, H.R., 2018. Fluoride exposure in early life as the possible root cause of disease in later life. J. Clin. Pediatr. Dent. 42 (5), 325–330.

Nordstrom, D., 2022. Fluoride in thermal and non-thermal groundwater: insights from geochemical modeling. Sci. Total Environ. 824, 153606.

Pacheco, J.M., Ferreira, T., Queiroz, G., Wallenstein, N., Coutinho, R., Cruz, J.V., 2013. Notas sobre a geologia do arquipélago dos Açores. In: Geologia de Portugal*; Volume 2*. Escolar Editora, Lisboa, Portugal, pp. 595–690.

Podgorski, J., Berg, M., 2022. Global analysis and prediction of fluoride in groundwater. Nat. Commun. 13, 4232. https://doi.org/10.1038/s41467-022-31940-x.

Rango, T., Bianchini, G., Beccaluva, L., Ayenew, T., Colombani, N., 2009. Hydrogeochemical study in the Main Ethiopian rift: new insights to the source and enrichment mechanism of fluoride. Environ. Geol. 58, 109–118.

Ravuru, N., Reginald, B.A., Reddy, B.S., Samatha, M., 2023. Relationship between dental fluorosis, dental caries and salivary levels of *Streptococcus mutans*. J. Oral Maxillofac. Pathol. 27 (3), 603. https://doi.org/10.4103/jomfp.jomfp_59_23.

Regenspurg, S., Virchow, L., Wilke, F., Zimmer, M., Jolie, E., Hachenberger, A., et al., 2022. Origin and migration of fluoride in the area of the Aluto volcanic complex (Main Ethiopian rift). Appl. Geochem. 146, 105403.

Revelo-Mejía, I.A., Gutiérrez-Idrobo, R., López-Fernández, V.A., López-Rosales, A., Astaiza-Montenegro, F.C., 2022. Fluoride levels in river water from the volcanic regions of Cauca (Colombia). Environ. Monit. Assess. 194 (5), 327. https://doi.org/10.1007/s10661-022-09999-2.

Rubio, C., Rodríguez, I., Jaudenes, J.R., Gutiérrez, A.J., Paz, S., Burgos, A., Hardisson, A., Revert, C., 2020. Fluoride levels in supply water from a volcanic area in the Macaronesia region. Environ. Sci. Pollut. Res. 27, 11587–11595.

Schlesinger, W.H., Klein, E.M., Vengosh, A., 2020. Global biogeochemical cycle of fluorine. Glob. Biogeochem. Cycles 34 (12), e2020GB006722.

Searle, R., 1980. Tectonic pattern of the Azores spreading center and triple junction. Earth Planet. Sci. Lett. 51 (2), 415–434. https://doi.org/10.1016/0012-821X(80)90221-6.

Sebastian, S.T., Soman, R.R., Sunitha, S., 2016. Prevalence of dental fluorosis among primary school children in association with different water fluoride levels in Mysore district, Karnataka. Indian J. Dent. Res. 27 (2), 151–154. https://doi.org/10.4103/0970-9290.183126.

Shaji, E., Sarath, K.V., Santosh, M., Krishnaprasad, P.K., Arya, B.K., Babu, M.S., 2024. Fluoride contamination in groundwater: a global review of the status, processes, challenges, and remedial measures. Geosci. Front. 15 (2), 101734.

Simon, M.J.K., Beil, F.T., Rüther, W., Busse, B., Koehne, T., Steiner, M., et al., 2014. High fluoride and low calcium levels in drinking water is associated with low bone mass, reduced bone quality and fragility fractures in sheep. Osteoporos. Int. 25, 1891–1903.

Solanki YS., Agarwal M., Gupta AB., Gupta S., Shukla P. (2022). Fluoride occurrences, health problems, detection, and remediation methods for drinking water: a comprehensive review. Sci. Total Environ., 10;807(Pt 1):150601.

Umer, M.F., 2023. A systematic review on water fluoride levels causing dental fluorosis. Sustainability 15 (16), 12227.

United States Environmental Protection Agency (U.S. EPA) (1989). Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A), EPA/540/1–89/002. Available online: http://www.epa.gov/swerrims/riskassessment/ragsa/ pdf/rags_ch6.3.pdf (accessed on 14 May 2024).

United States Environmental Protection Agency (U.S. EPA), 1999. Guidelines for exposure assessment. Fed Reg. 57, 22887–22938.

United States Environmental Protection Agency (U.S. EPA). (2012). Edition of the Drinking Water Standards and Health Advisories; Office of Water U.S. EPA: Washington, DC, USA, EPA 822-S-12-001. Available online: http://water.epa.gov/a ction/ advisories/drinking/upload/dwstandards2012.pdf (accessed on 14 May 2024).

US National Institute for Occupational Safety and Health (NIOSH), 1984. Fluoride in urine. In: Manual of Analytical Methods, 3rd ed. 11. US Department of Health and Human Services, Washington, DC, USA. 8308–1–8308-3.

Vivona, R., Preziosi, E., Madé, B., Giuliano, G., 2007. Occurrence of minor toxic elements in volcanic-sedimentary aquifers: a case study in central Italy. Hydrogeol. J. 15 (2007), 1183–1196.

Vogt, P.R., Jung, W.Y., 2004. The Terceira rift as hyper-slow, hotspot-dominated oblique spreading axis: a comparison with other slow-spreading plate boundaries. Earth Planet. Sci. Lett. 218, 77–90.

Wang, Y., et al., 2020. Genesis of geogenic contaminated groundwater: As, F and I. Crit. Rev. Environ. Sci. Technol. 51, 1–39.

World Health Organization (WHO), 2011. Guidelines for drinking-water quality. In: WHO: Geneva, Switzerland, 4th ed.

World Health Organization (WHO), 2019. Preventing disease through healthy environments: inadequate or excess fluoride: a major public health concern. WHO/CED/PHE/EPE/19.4.5.