Chapter

Fluoride in Volcanic Areas: A Case Study in Medical Geology

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Abstract

Volcanic regions have always attracted many people worldwide because of the high fertility of their soils. However, human proximity to volcanoes can lead to several health problems as consequence of the chronic exposure to the materials released from the volcanic activity. An element often found in elevated concentrations in volcanic regions is fluorine. Although fluoride is recognized to have a beneficial effect on the rate of occurrence of dental caries when ingested in small amounts, its excessive intake results in a widespread but preventable pathological disease called fluorosis. While skeletal fluorosis, the most severe form of fluorosis, requires a chronic exposure to high concentrations of fluoride in water (4–8 mg/L), dental fluorosis occurs after shorter periods of exposure to fluoride in lower concentrations (1.5–2.0 mg/L). In some volcanic regions, where exposure to elevated amounts of fluoride is persistent, biomonitoring programs are fundamental to assess the main sources of exposure and to evaluate the effects of the exposure in resident populations. This chapter aims to cover the main effects of fluoride exposure in humans and discuss the use of a multidisciplinary approach that brings together the geoscience, biomedical, and public health communities to address environmental health problems.

Keywords: fluoride, volcanism, geomedicine, geology, geochemistry, health

1. Introduction

1.1 Definition and physical and chemical properties

Fluorine was discovered by Georgius Agricola in 1529. It is a univalent poisonous gaseous halogen with pale yellow-green color and the most chemically reactive and electronegative of all the elements. It is the 13th most abundant element in the earth's crust and is widely dispersed in nature, almost entirely in the form of fluoride.

Fluoride is an inorganic, monoatomic anion being considered the simplest fluorine anion. It is classified as a weak base, since it only partially associates in solution, but concentrated fluoride is corrosive, and it can attack the skin.

1.2 Geochemistry of fluoride

Fluorine is a naturally occurring chemical substance in the earth's crust where it can be found in rocks, coal, and clay; it is also present in minor quantities in air, water, soil, plants, animals, and humans [1].

The distribution of fluorine in the environment is uneven because of geogenic causes. The most common natural sources of fluorine are fluorite, fluorapatite, and cryolite; as for the anthropogenic sources, these include coal burning, oil refining, steel production, brick-making industries, and phosphatic plant fertilizers, among others [2].

Humans can be exposed to fluoride through food and breathing air, but, considering that the most common sources of fluoride in surface and groundwaters are usually natural, such as the leaching of rocks and dissolution of fluorides from volcanic gases [3], the main source of human exposure, especially in volcanic regions, is drinking water.

1.3 Volcanic environments

Volcanoes emit a variety of gases, both between and during eruptions, including H_2O, CO_2, SO_2, HCl, NH_3, H_2S, and HF, and a few other minor constituents [4, 5]. The volcanic activity represents the main natural persistent source of fluorine that is emitted mostly in the form of HF. Its fraction in volcanic gas emissions is less than 1 ppm and presents an annual global emission of 0.06–6 Tg [4]. Although HF is not of importance in general, during specific events the HF emissions may be extreme and lead to severe environmental contamination with hazards to plants and livestock. According to Halmer et al. [6], the annual global HF volcanic gas input into the atmosphere from 1972 to 2000 was of 0.7–8.6 × 1012 g/yr. For volcanic areas, such as Mt. Etna in Italy or Masaya in Nicaragua, it has been estimated that the passive degassing from these volcanoes accounts for 90% of the volcanic fluorine release. The high amounts of fluorine release in volcanic regions and the natural occurrence of excessive amounts of fluoride in drinking water are associated with acute and chronic fluorosis on grazing animals, due either to direct ingestion of F-rich ashes deposited on the grazing grass or drinking water that are F-contaminated [7]. This problem was first recognized in Iceland, a region with F-rich magmas, by Eiriksson in 1693 after the eruption of Mt. Hekla where this farmer observed deformed teeth in sheep, cattle, and horse calling them "ash-teeth"; later on, also in Iceland, half of the livestock population died in 1783 after Laki eruption that released 42 billion tons of basalt lava and clouds of poisonous HF and SO2 compounds that contaminated the soil [8]. Several cases of chronic fluorosis have been associated to passive degassing in the island of Ambrym in Vanuatu, where it is located one of the most vigorous and persistently degassing volcanoes on Earth; throughout this island, the prevalence of dental fluorosis in children aged 6–18 years ranged between 61 and 96% [9]. In Kenya, situated in East Africa, where the Kenyan Rift is formed by numerous volcanoes, the prevalence of dental fluorosis ranges between 44 and 77% [10].

Considering that, in volcanic regions, fluoride is continuously released and that it can pose a health problem for animals and humans, it can be considered a health risk to the populations inhabiting nearby an active volcano, as it happens in the volcanic islands of the Azores archipelago.

The Azores archipelago (Portugal), located in the North Atlantic Ocean, comprises nine volcanic inhabited islands, located between 36°45′–39°45'N and 24°45′–31°17'W, where the Eurasian, African, and American lithospheric plates meet [11]. Due to its specific formation context, seismicity and volcanism are frequent in the archipelago, resulting in the existence of aquifers formed by the volcanic rocks that erupted during the principal building stage of each volcano. In São Miguel island, the largest of archipelago, formed by three major active central volcanoes (Sete Cidades, Fogo and Furnas), high values of fluoride in the groundwaters and endemic fluorosis in some areas of the island have been reported. In

1993, Lobo measured the fluoride concentration in São Miguel Island springs and observed values ranging from 0.1 to 9.9 mg/L [12], evidencing that in some areas fluoride in drinking water exceeded the WHO maximum level (1.5 mg/L) [13]. In some areas, such as the village of Ribeira Quente, located only 5 km from the caldera of Furnas volcano, most of the inhabitants have visible evidence of dental fluorosis in the permanent dentition, due to raised fluoride levels in the drinking water [14]. More recently, in 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, results revealed that the prevalence of dental fluorosis in the students of Ponta Delgada was fourfold higher (15.3 vs. 4.1%) [15]. This tendency is observed through the other islands of the archipelago. In Terceira Island, fluoride content in drinking water above the recommended legal values has been recorded, especially in Praia da Vitória municipality area, where the dental fluorosis prevalence in schoolchildren is of 25% [16]. According to Cordeiro et al. [17], about 98% of the Azores water supply originates in groundwater sources, which is a very important feature to consider, since fluoride content in volcanic aquifers may result from rock leaching processes and from the rising volcanic gases that are dissolved in the groundwaters [18–20]. Another feature important to consider when studying the exposure to fluoride in São Miguel Island is that the only tea plantation in Europe occurs in this island and thus the inhabitants have the frequent habit of drinking tea that also contributes to the exacerbation of the effects of fluoride exposure.

2. Human exposure to fluoride

The main sources of human exposure to fluoride are diet, dental hygiene products, dermal absorption from chemicals or pharmaceuticals, and exposure to industrial emissions. Regarding the exposure by diet, it is recognized that of all the common foodstuffs, tea has one of the highest potentials to increase the daily fluoride intake [21, 22], having a fluoride bioavailability close to 100% [23], similar to the drinking water [24]. Most of the fluoride (about 90%) is absorbed in the gastrointestinal tract after its consumption and distributed through the organism via the bloodstream.

Although fluoride has no recognized essential function in human growth and development, it has a fundamental role in the prevention of caries (tooth decay) [25, 26]. As a result, throughout the world many countries started programs of fluoridation of drinking water and the development of fluoride containing oral care products (toothpastes and mouth rinses) and supplements (fluoride tablets), as public health protective measures against tooth decay.

2.1 Human fluorosis

Fluorosis results of a high consumption of F that may cause chronic fluoride toxicity, being harmful and, sometimes, causing severe poisoning that in the absence of medical treatment, can be lethal. One of the main mechanisms involved in the pathogenesis of fluorosis is an increased oxygen radical generation and lipid peroxidation.

Chronic exposure to high levels of fluoride affects specially the skeleton and teeth which are the prime organs of F retention/accumulation in the human body, while relatively small amounts may be deposited in another calcifying organ, as the pineal gland [27, 28]. The most common pathology in fluoride endemic areas is dental fluorosis, which usually occurs in areas where fluoride exposure concentrations are above 1.5–2.0 mg/L. Dental fluorosis has a progressive outcome [29]: in its initial stages, the teeth develop chalky white patches and become rough, and as time goes by, yellow to dark brown lines may also become visible [28–30] in the teeth.

Skeletal fluorosis results from exposure to fluoride in minimum concentrations of 4–8 mg/L [13] and leads to an increase in bone density, calcification of ligaments, and rheumatic or arthritic pain in joints and muscles, along with stiffness and rigidity of the joints. The early symptoms are severe pain in the spine, joints, and hip area; on time, the muscles in the spine will become calcified, and crippling deformities of the spine and the major joints will occur [31].

Since the dental and skeletal fluorosis are irreversible pathologies, the only way to mitigate its effects is through prevention, by keeping fluoride intake within the safety limits defined by the WHO, such as a maximum that is below 1.5 mg/L of fluoride in drinking water [13].

2.2 Human fluorosis due to volcanic activity

Several cases of endemic fluorosis due to high F concentrations in groundwater have been reported in volcanic areas worldwide, particularly in East Africa, India, and China, where millions of people are affected [32]. The association between volcanic activity and human fluorosis was first established in Kyushu Island, Southwest Japan. Due to the activity of the Aso volcano, fluorosis was known as the "Aso volcano disease" and affected all the population living in the hill's foot [33]. After the recognition of this association between the active volcanism and fluorosis, dental fluorosis has been described in many volcanic areas such as Indonesia [34], Kenya [35], Turkey [36], Tenerife Island (Canary, Spain) [37], and São Miguel Island (Azores, Portugal) [14].

The prevalence of skeletal fluorosis is often underestimated due to the similarity of its symptoms with other skeletal diseases; for instance, in 2005 Weinstein [38] showed that Egil Skallagrimsson, an Icelandic poet and warrior, probably suffered from skeletal fluorosis for being chronically exposed to emissions of volcanic eruptions in Iceland, instead of Paget's disease. Weinstein's study highlights the importance of understanding if chronic exposure to fluoride in volcanic environments may lead to the development of fluorosis.

3. Human biomonitoring

In an attempt to prevent excessive exposure to fluoride, the drinking water concentration standards and guidelines are targeted so that total fluoride intake from all sources does not exceed exposure guidance values [39, 40]. Since fluoride occurs naturally in several sources, the exposure to this element is widespread, and therefore programs to quantify the exposure and its effects in human health are often necessary. In human biomonitoring, measurements of the internal dose are assessed in human biological fluids or tissues, thus integrating fluoride absorbed from all exposure routes [41].

3.1 Urine

The concentration of fluoride in urine is used as a biomarker of recent exposure [22, 42, 43], because urine is the main route of elimination of fluoride. In the adult population, about 50% of absorbed fluoride is deposited in calcified tissues, and the remaining is excreted in the urine [44]. Although urinary fluoride concentrations do not provide a direct measure of fluoride due to variations in urine flow and pH, the studies of urinary fluoride levels are ideal for assessing the intake of fluoride in populations [45]. The measurement of urinary fluoride can be performed by several techniques, such as fluoride ion-selective electrode (FISE), based on the methods described by the National Institute for Occupational Safety and Health (NIOSH) [46], high-performance liquid chromatography (HPLC), ion chromatography spectrometry (IC), and colorimetric methods.

3.2 Fingernails

Nails have been used as biomarkers of acute, sub-chronic, and chronic exposure to fluoride [47, 48] in humans, since in this matrix the fluoride concentration reflects the average level of intake and the plasma concentration over a protracted period, usually 1–2 weeks depending on how often the nails are clipped [49].

Fingernails' fluoride is generally measured with a fluoride ion-selective electrode, applying the method developed by Taves [50] and modified by Whitford [51] after overnight HMDS-facilitated diffusion.

Considering that the fluoride measured in nail clippings represents the fluoride obtained from the systemic circulation, either by secondary concentration or by continuous incorporation, this makes nails a useful biomarker for both sub-chronic (exposure to 1–2 mg/L F) and chronic fluoride exposures (exposure to >2 mg/L F).

4. Medical geology

There are several studies about the occurrence of fluoride in the environment and its relationship to human health spanning a wide variety of disciplines that include the fields of medicine, dentistry, environmental and occupational health, toxicology, environmental geology, petrology, geochemistry, economic geology, hydrogeology, and soil science [52].

For more robust evidence of the relationship between fluoride and human health, studies regarding interdisciplinary approaches and combined methods to establish environmental exposures, health outcomes, and the relationships between them [53] are required, instead of the usual unidirectional approaches. Medical geology is defined as "the science dealing with the relationship between geological factors and health problems in humans, animals and plants" [54, 55], and its interdisciplinary approach brings together geosciences, biomedical, and public health communities. This multidisciplinary association allows the identification of natural and anthropogenic sources of harmful materials in the environment, the understanding of how people are exposed to such materials, and what can be done to minimize or prevent such exposure [56].

Medical geology studies allow to establish the background concentrations in the environment of elements, such as fluoride, identifying the areas with high concentrations of this element from those with low and enabling the modeling of the elemental deposition/uptake in the environment.

4.1 Case studies with a medical geology approach

The effects in human health for excessive exposure to fluoride have been studied worldwide, and exposure guidance values have been established. However, nowadays in many regions of the world, fluorosis continues to be endemic. Considering that volcanic aquifers can promote the occurrence of high F contents in groundwater [57, 58], some studies have determined the health impacts of fluoride exposure in drinking water due to volcanic activity. In Vanuatu the constant low-level basaltic volcanic activity results in a continuous release of fluoride gas, which is reflected in cow rib bones and teeth fluoride content in grazing animals. According to Cronin and Sharp (2002), the possible long-term accumulation of F in the grazing animals results from the consumption of plants F-bearing volcanic ash and drinking F-rich waters (in some areas the fluoride concentration in water reached values up to 2.8 mg/L), which represent potential sources of F causing chronic dental and skeletal fluorosis [59]. Also, in New Zealand in the hydrothermal system of Ruapehu volcano, significant concentrations of soluble F in ashes are leached into the soils and water over longer periods, representing a long-term environmental hazard for the inhabitants of this area [19].

Despite the results evidencing the clear association between volcanic activity and fluoride availability, to act in the mitigation and prevention of fluoride exposure, it is necessary to better understand which are the main routes of exposure, since they can differ according to the region in study. In the specific case of São Miguel Island in the Azores archipelago, Portugal, the main routes of human fluoride exposure are the water and some dietary habits, such as the frequent consumption of tea. In this volcanic island, the groundwater geochemistry is influenced by the dissolution of primary minerals of the volcanic rocks [60] that are naturally enriched in fluoride. Also, the habit of tea consumption is well established in the local communities, because this is the only place in Europe where tea is produced, processed, and commercialized [61] since 1883.

Until 2016, there was no information regarding the health effects of chronic fluoride exposure in the inhabitants of this island; although in some studies the authors have identified anomalous values of fluoride in water [12] and clear signals of dental fluorosis in humans [14] and animals [62], none was focused on estimating the effects of the exposure to fluoride in humans. To identify the sources of fluoride in the environment and to assess the effects of the exposure in São Miguel Island inhabitants, studies in medical geology have been developed. In the study by Linhares et al. [63], it was observed that even with modern water treatment systems, there are areas in the island of São Miguel that have fluoride concentrations in water slightly above the recommended legal values. Therefore, these authors developed a study that investigated if urine and nail clippings had sensitivity and/or utility for biomonitoring human population from different age classes that are chronically exposed to fluoride; a positive correlation was found between the fluoride daily intake and fluoride content in children urine, and in adults and children nail clippings, revealing that nail clippings are a more reliable biomarker of chronic exposure to fluoride than urine for populations of different age classes (children vs. adults).

Considering that within the residents of this island, the tea consumption is a well-established habit in adults and children and that tea is a fluoride-bioconcentrating plant, another study was developed in 2017 by Linhares et al. to assess the exposure of humans to fluoride intake through tea infusion consumption [64]. The authors concluded that the Azorean tea brands had higher fluoride content than other international brands. The higher concentration of fluoride in the Azorean tea brands is related to the fact that the soils of the Azores archipelago originate from modern volcanic materials that have evolved under the humid and moderate Atlantic climate, classified as Andosols [65], being naturally enriched in fluoride. With mean results of 3.53 mg/L of fluoride in tea infusions, several concerns regarding the consumption of tea, especially in children, were raised by this study, since by consuming tea the daily intake of fluoride could easily overcome the recommended daily values [64]. This work evidenced that in areas where tea consumption is habitual in all ages and where fluoride content in drinking water exceeds the legislated values, the upper limit threshold for the average fluoride daily intake can be easily exceeded only by tea drinking, contributing to the development of fluorosis in these areas. In this paper, the authors also point out the importance of considering the concentration of fluoride in the water used to make tea.

More recently, Linhares et al. [66] carried a fieldwork using mice (*Mus musculus*) collected in Furnas village (a village located inside the caldera of Furnas volcano, an area where volcanic activity is marked by active fumarolic fields, hot and cold CO2-rich springs, and soil diffuse degassing phenomena [67, 68]) to assess the risk of skeletal fluorosis from the environmental exposure to fluoride in hydrothermal areas. Results showed that mice from Furnas village had higher concentrations of fluoride in bones than mice from an area without volcanic activity [66]. These results reinforce that chronic exposure to fluoride may lead to the development of not only dental fluorosis but also of skeletal fluorosis, which can be misdiagnosed as rheumatism and arthrosis [38], pinpointing the fact that elderly people living chronically exposed to volcanic environments can also suffer from undiagnosed skeletal fluorosis.

5. Risk management

The excessive intake of fluoride and its role on the development of human fluorosis is well known; despite this, fluorosis still occurs in several parts of the world. It continues to show up, not only in the Third World countries, due to the population's lack of choice in their sources of drinking water and food, but also in developed countries, because of fluoridation of the public drinking water, private water supplies, dietary choices, dental products, industrial emissions, and/or occupational exposure. Adding to all these sources of exposure, we must also consider the exposure to fluoride due to natural events, such as volcanic activity, which affects many persons in several regions worldwide.

Since fluorosis, dental and skeletal, can impact upon the biological and psychosocial dimensions of health, it is urgent to work on the prevention and mitigation of human exposure to fluoride. According to the main sources of exposure, the actions that can be taken to address this issue are defluoridation of existing water supplies and/or the establishment of an alternative low-fluoride water source [13]; the modification of rainwater harvesting practices; changes in dietary habits, specifically regarding tea consumption; and an adequate use of dental products.

Nonetheless, multidisciplinary epidemiological studies, gathering areas such geochemistry, epidemiology, and ecotoxicology, are still required since they provide adequate insights regarding dose-response relationship and detailed information about the areas that are naturally fluoride rich. This will assist and guide authorities implementing environmental remediation decisions and developing public health planning and response efforts to reduce fluoride-related health problems.

6. Conclusions

In the Azores, human exposure to fluoride can easily reach values above the recommended guidelines. The most common factors that contribute to an excessive concentration of this element are groundwater naturally enriched in fluoride and consumption of tea. Results from several studies evidence that the chronic exposure to elevated fluoride concentrations contributes not only to the development of dental fluorosis but also, in more severe cases, to the development of skeletal fluorosis.

Considering that water consumption is the most important, but not the only exposure pathway to fluoride, it is fundamental to implement multidisciplinary biomonitoring studies combined with a medical geology approach. This type of strategy identifies harmful geologic agents and determines the conditions of exposure that promote deteriorating health status, providing the necessary knowledge to track a wide range of environmentally and naturally induced health issues such as fluorosis.

Conflict of interest

All the authors state that they have no conflict of interest.

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