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Health Impacts of Fluorosis

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Abstract: Fluorosis is a widespread disease related to ingestion of high levels of fluorine through water and food. Although sometimes of anthropogenic origin, high levels of fluorine are generally related to natural sources. One of the main sources is represented by volcanic activity, which releases magmatic fluorine generally as hydrogen fluorine through volcanic degassing. But the impact of fluorine on human health is highly dependent on its chemical state, which means that high rates of release not necessary point to high impacts. Contamination can happen either through direct uptake of gaseous HF or through rain waters and volcanic ashes. This paper mainly includes health effects and remedies to minimize the fluoride content in the environment.

Keywords: Fluorosis, magmatic fluorine, volcanic activity, groundwater

Introduction:

The influence of the geological environment on human health has long been known with the first links being recognized probably by Chinese physicians in the 4th century [1]. Such influence is related not only to excessive intake of particular elements but also to their deficiency. For fluorine, like for a few other elements (e.g. I, Se), human health status depends upon a delicate balance between excess and deficiency. Low intake of this element is related to dental carries while exposure to high chronic levels can lead to dental or skeletal fluorosis [2]. Many natural geological processes, sometimes exacerbated from anthropogenic influences (mining activities, fuel combustion, etc.), can be responsible of the impact of harmful compounds. One of the most important is volcanic activity. Fluorine is a chemical element (symbol F) and atomic number 9. Fluoride is the negative ion of the element fluorine. Any compound, whether it is organic or inorganic, that contains the fluoride ion is also known as a fluoride. Examples include CaF_2 (calcium fluoride) and NaF (sodium fluoride). Ions containing the fluoride ion are similarly called fluorides (e.g., bifluoride, HF_2). Water fluoridation is usually accomplished by adding sodium fluoride (NaF), fluorosilicic acid (H_2SiF_6), or sodium fluorosilicate (Na_2SiF_6) to drinking water. There is considerable variation in the level of naturally occurring fluoride in drinking water around the world and this variation is largely dependent on geological factors. These areas with naturally occurring fluoride in the water can be split into two groups, 1) where the naturally occurring fluoride is >1.5 ppm known as endemic areas and 2) where the naturally occurring fluoride is ≤1.5 ppm which is in line with the WHO permissible limit. High levels of naturally occurring fluoride in water occur in approximately 25 countries worldwide. In Asia, countries with the highest levels are India and China. In Latin America, Mexico and Argentina have the highest levels. Parts of east and North Africa also have high endemic levels of fluoride.

Environmental sources of fluoride:

Fluorides are released into the environment through a combination of natural and anthropogenic processes. Natural processes include the weathering of fluoride containing minerals and emissions from volcanoes. Additionally, a number of industrial processes such as coal combustion, steel production, and other manufacturing processes (aluminium, copper and nickel production, phosphate ore processing, phosphate fertilizer production, glass, brick and ceramic manufacturing) further contribute to fluoride levels. These processes result in the dispersion, accumulation, and ubiquitous prevalence of fluoride at various concentrations in all surface and groundwater reserves, mostly as fluoride ions or combined with aluminum; in the air, as gases or particulates; in soils, mainly combined with calcium or aluminum; and in living organisms.

Fluoride levels in naturally-occurring water:

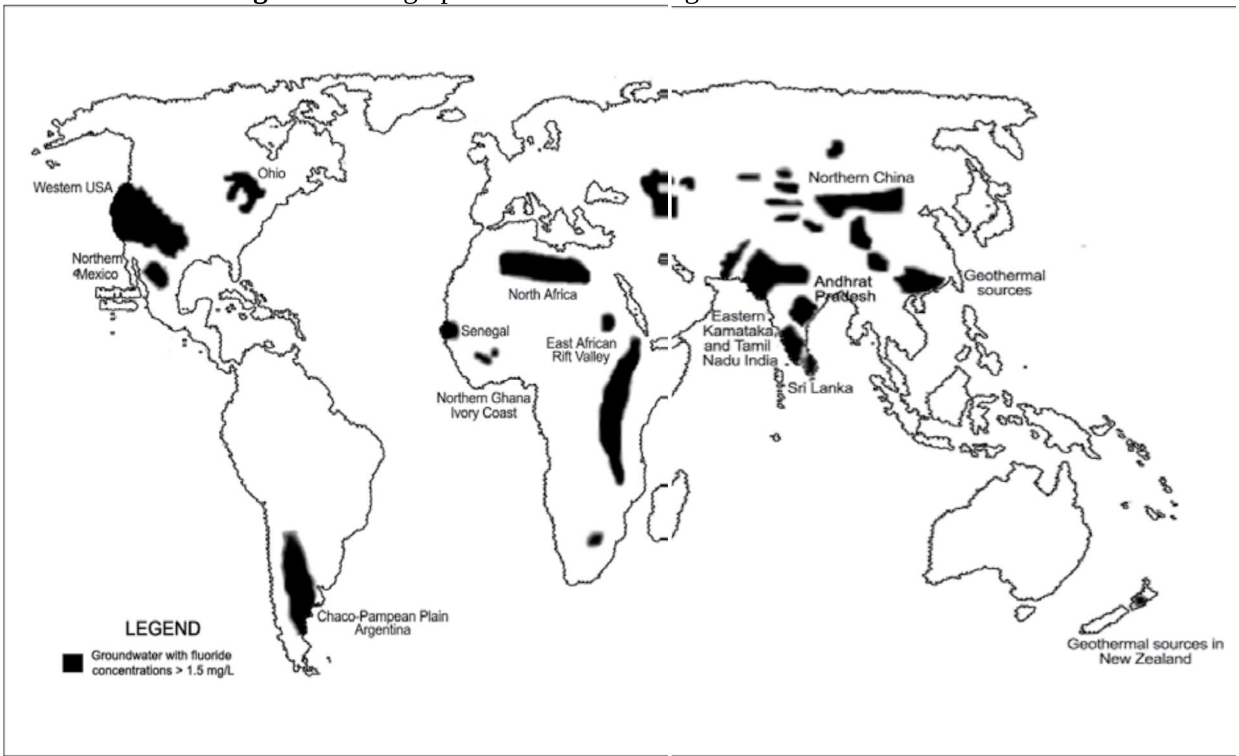
Fluoride levels in surface waters vary widely according to geographical location and proximity to emission sources but are 1.2 to 1.5 mg/L. Freshwater concentrations are usually lower than seawater ranging from 0.01 to 0.3 mg/L. Factors known to influence water fluoride levels include the presence of natural rock rich in fluoride (such as granites and gneisses and sediment of marine origin). Additionally, elevated inorganic fluoride levels are often seen in regions where there is geothermal or volcanic activity.

Low levels of calcium in water supplies may also lead to higher levels of fluoride solubility. Geographical areas associated with high groundwater fluoride concentrations include the East African Rift system (running from Jordan in northern Africa to Kenya and Tanzania in east Africa), large tracts of the Middle East (Iran, Iraq, and Syria) and Indian sub-continent (India, Pakistan, SriLanka), parts of Asia (China), and parts of the USA (Figure 1). Fluoride concentrations greater than 8 mg/L are not uncommon in many of these areas and have been measured as high as 2800 mg/L at Lake Nakuru in Kenya In Australia, naturally-occurring fluoride levels are generally very low (<0.1 mg/L), with the exception of some remote well water supplies in South Australia.

Fluoride levels in air:

Airborne fluoride enters the atmosphere in gaseous and particulate forms from a variety of natural and anthropogenic sources including volcanic eruptions and combustion of fluoride containing coal. Airborne concentrations are highest in areas close to emission sources and range from 2–3μg/m^3 in urban and industrialized zones to 0.05-1.90 μg/m^3 in non-industrial areas. Prevailing weather conditions, the type and strength of emission sources and chemical reactivity of the particulate matter may influence the distribution and deposition of airborne fluoride. High concentrations of airborne fluoride (16-46 μg/m^3) are noted in some communities that burn high-fluoride coal for cooking and curing food.

Figure 1 . Geographical Areas with High Natural Fluoride Levels



Fluoride levels in soil:

Fluoride is a component of most types of soil, with total fluoride concentrations ranging from 20 to 1000 μg/g in areas without natural phosphate or fluoride deposits and up to several thousand micrograms per gram in mineral soils with deposits of fluoride. The clay and organic carbon content as well as the pH of soil are primarily responsible for the retention of fluoride in soils. In general, fluoride bound to soil is relatively resistant to leaching and it is the soluble content that is most important to terrestrial animals and plants. According to the IPCS (2002) report the relative contribution of various anthropogenic sources to total emissions of fluoride to air, water and soil in industrialized countries such as Canada are estimated at 48% for phosphate fertilizer production, 20% for chemical production, 19% for aluminium production, 8% for steel and oil production and 5% for coal burning.

Magmatic fluorine:

Fluorine is the 13th most abundant element in the earth's crust [3]. Several natural and anthropogenic sources contribute to the geochemical cycling of fluorine. The most important industrial processes that release fluorine compounds are: aluminum smelting, coal burning, phosphate fertilizer and cement production, and brick and ceramic firing [4]. Volcanoes represent the main natural persistent source of fluorine [5,6]. Fluorine is emitted by volcanoes mostly in the form of HF(g) [5], but emissions also contain much lower amounts of gaseous NH_4F, SiF_4, $(NH_4)_2SiF_6$, $NaSiF_6$, K_2SiF_6 ,KBF_4 and Organo-fluorides [3,7,8]. Volcanic emissions of fluorine take the form of either sluggish permanent release from quiescent volcanoes (passive degassing) or rarer but more impacting discharges during short-lived volcanic eruptions. Estimates of the global volcanogenic fluorine flux range 50 to 8600 Gg/a [5,6,9], with the former figure being probably an under estimate. Total anthropogenic emissions are in the same order of magnitude with the highest emissions are due to chlorofluorocarbon production (300 Gg/a) and coal burning (200 Gg/a) [4].

It has been estimated that passive degassing, like that existing at Mt. Etna (Italy) and Masaya (Nicaragua) volcanoes, accounts for about 90% of the volcanic fluorine release. In particular Mt. Etna is the largest known point source of atmospheric fluorine, contributing for about 70 Gg/a [10], even stronger than today's total estimated anthropogenic release over Western Europe [11]. The influence of these emissions on the surrounding environment and in particular on vegetation has been investigated by several authors [11, 12, 13]. Although responsible on average for the emission of lower amounts, the impact of fluorine emitted during explosive volcanic eruptions has been better studied [14-16]. Fluoride was certainly the agent responsible for the death of sheep after the volcanic eruption described in the Icelandic sagas. Ashes emitted during explosive activity scavenge very effectively the erupted volcanic gases including HF thus enhancing their deposition around the erupting volcano up to distances of hundreds of km [14]. Acute and chronic fluorosis on grazing animals has been described for many explosive eruptions all around the world (Mt. Hekla – Iceland [17], Lonquimay – Chile [18], Nyamuragira – Democratic Republic of Congo [19], Mt. Ruapehu – New Zealand [16]. Consequences on livestock are due either to direct ingestion of F-rich ashes deposited on the grass or to grazing of grass or drinking water that are F-contaminated. The problem is widespread in Iceland were the magmas are particularly F-rich. Since its settling in 9th century many eruptions on Iceland were responsible of F-poisoning of livestock. The first account of this problem was made after the 1693 eruption of Mt. Hekla by the farmer Eiriksson and the clergyman Petursson, which described the deformed teeth in sheep, cattle and horse calling them "ash-teeth" . Death due to F-poisoning of livestock caused serious famines among Icelanders who were totally dependent on them. The worst episode followed the Laki eruption in 1783 causing the death of half of the population of Iceland.

Review of human fluorosis related to volcanic activity:

The problem of fluorosis related to volcanic activity was first recognised in Japan were this pathology was called "Aso volcano disease" due to the fact that fluorosis was widespread in the population living at the foot of this volcano. Water intake being the main route of fluorine into the human body, fluorosis in volcanic areas is generally associated to elevated fluoride content in surface- and ground-waters. Contamination of vegetation, which is the main agent of volcanic-related fluorosis in herbivorous animal, is only of secondary importance for human health. High fluorine content in waters derive either from water-rock interaction (WRI) processes in volcanic aquifers (ground waters) or to contamination due to wet or dry deposition of magmatic fluorine (surface waters - reservoirs). Furthermore, paleopathologic studies on human skeletons found in Herculaneum, referable to victims of 79 AD eruption of Mt. Vesuvius, evidenced that fluorosis in this area had the same incidence as in modern times, pointing to the constancy of the geochemical processes responsible for fluorine enrichment of the drinking water in the area over at least the last 2000 years.

Water - rock interaction:

Volcanic rocks are often enriched in fluorine. Hydrogen fluorine is, in fact, one of the most soluble gases in magmas and exsolves only partially during eruptive activity. Burton et al. [estimated for example that Etnean magmas exsolve only about 20% of their initial HF content during effusive activity. Furthermore fluorine behaves as incompatible element being highly enriched in differentiated volcanic products. In volcanic aquifers elevated temperatures and/or strong acidic conditions enhance WRI processes. Such conditions often lead to high concentrations of harmful elements. Therefore fluorine concentrations in volcanic aquifers above safe drinking limits are rather the rule than the exception. Values as high as tens of mg/ l of fluorine are often achieved in groundwaters, which if used for human consumption can easily lead to skeletal fluorosis. Dental fluorosis due to groundwaters enriched by WRI in recent or active volcanic areas has been assessed in many parts of the world. Many articles illustrates such cases. Some of them refer to limited areas like Gölcük – SW Turkey , Mt. Aso volcano, Japan , Island of Tenerife – Spain, Furnas volcano, São Miguel – Azores, Portugal , Albano Lake – Italy, while other evidence a widespread problem throughout entire countries like Mexico , Ethiopia , Kenya , Tanzania. In these areas, populations as high as 200,000 people could be at risk to develop fluorosis like for example the inhabitants of the Los Altos the Jalisco region in Mexico. Particularly high fluorine concentrations (thousands of mg/l) can only be achieved under extreme conditions, partially or totally ascribable to volcanic activity. Lakes along the East Africa Rift Valley display values as high as 1980 mg/l (Lake Magadi – Kenia). Such high contents originate from geothermal weathering of the F-rich volcanic rocks further concentrated by evaporative processes in arid climate. Calcium concentrations in these lakes, which could limit fluorine concentrations through fluorite precipitation, are very low due to precipitation of carbonate phases in a highly alkaline environment. Very acidic lakes in active volcanic systems (pH values ≈ 0) can also achieve extreme fluorine concentrations not only due to intense WRI processes but also to direct input of F-rich volcanic gases. Lakes like Poas – Costa Rica and Ijen Crater Lake – Indonesia reach concentrations far above 1000 mg/l. Seepage or effluent rivers from these extremely F-rich lakes can easily contaminate ground- or surface waters. It has been estimated that the Ijen Crater Lake discharges daily in the surface and ground waters of the highly populated area of Asembagus about 2800 kg of fluorine [25,22], which is responsible of the widespread occurrence of fluorosis in the area. Furthermore the fluorine contained in the salts extracted from the shores of the East African Rift Valley lakes and used for cooking purposes represent an additional fluorine source for the local population .

Health effects of fluorosis:

Many of the studies have focused on ingestion of higher, naturally occurring levels of fluoride rather than on artificial fluoridation levels. The studies generally have shown that fluoride ingestion at elevated levels primarily produces effects on skeletal tissues (skeletal fluorosis) and that these effects are more severe as exposure to fluoride increases above a threshold. Very mild, skeletal fluorosis is characterized by slight increases in bone mass. The most severe form of this condition, "crippling skeletal fluorosis," involves bone deformities, calcification of ligaments, pain, and immobility. In 1993, NRC reported that few cases of this condition had been reported in the United States and that it was not considered a public health concern

Bone fracture incidence:

A related question that has been the subject of scientific research concerns whether artificial water fluoridation increases the risk of bone fracture in older women. A number of community-level studies conducted in the 1980s and 1990s compared rates of fracture, specific for age and gender, between fluoridated and non-fluoridated communities. Several of these studies indicated that exposure to fluoridated water increased the risk of fracture; a few studies indicated that water fluoridation reduced the risk of fracture; and several studies found no effect. However, a weakness of these studies was that they were based on community-level data and lacked data on individuals. To improve understanding of this issue, a 2000 study looked at the consumption of fluoridated water and fractures in individual women. The results of this study suggested that water fluoridation may reduce the risk of fractures of the hip and vertebrae in older white women (the subjects of the study).

Cancer studies:

A possible link asserted in the 1970s between water fluoridation and increased cancer mortality raised health concerns and heightened controversy over the practice of fluoridation. Some researchers had reported that cancer mortality was higher in areas with fluoridated drinking water than in non-fluoridated areas. These findings were refuted subsequently by other investigators who identified problems with the study's research methodology. However, because of the importance of this question, researchers have continued to examine the possibility of an association between artificially fluoridated water and cancer in humans. Independent expert panels conducted reviews of the available scientific studies in 1982 and 1985. The panels concluded that the studies provided "no credible evidence for an association between fluoride in drinking water and risk of cancer." However, according to the 1993 NRC fluoride review, all but one of these studies were ecological studies; that is, they were either geographic correlation or time-line studies that looked at exposures at the community level rather than individual exposures. Consequently, the interpretation of the data was limited by an inability to measure individual fluoride exposures over long periods of time, or to measure exposure to other known risk factors such as smoking or other cancer-causing substances.

In response to the concerns raised by the NTP 1990 study, EPA requested that NRC review the available toxicological and exposure data on fluoride to determine whether the current drinking water standard of 4 mg/L was sufficient to protect public health. In 1993, NRC completed an extensive literature review concerning the association between fluoridated drinking water and increased cancer risk. Although NRC concluded that the data did not demonstrate an association between fluoridated drinking water and cancer, it did suggest that more research should be undertaken (especially research that examined individual, rather than population, exposures).

Dental fluorosis:

When EPA promulgated the fluoride regulation in 1986, it did not differentiate between mild and severe dental fluorosis, and broadly considered fluorosis of the dental enamel to be a cosmetic effect. In contrast, 10 of the 12 NRC committee members concluded that severe enamel fluorosis is an adverse health effect, not simply a cosmetic effect. The committee members explained that severe enamel fluorosis involves enamel loss, and that loss compromises the function of tooth enamel, the purpose of which is to protect the tooth against decay and infection. Because severe enamel fluorosis occurs in roughly 10% of children in communities with water fluoride concentrations at or near the current standard of 4 mg/L, the committee unanimously agreed that the MCLG should be set to protect against this condition, and that EPA's standard of 4 mg/L is not adequately protective.

Skeletal fluorosis:

As noted, EPA set the fluoride MCLG and MCL to protect against the adverse health effect of crippling skeletal fluorosis (stage III skeletal fluorosis). In this latest review, the NRC committee concluded that stage II skeletal fluorosis, the symptoms of which include sporadic pain, joint stiffness, and abnormal thickening (osteosclerosis) of the pelvis and spine, also constitutes an adverse health effect. Based on comparison of bone ash concentrations of fluoride and related evidence of skeletal fluorosis, the committee further found the data to suggest that Fluoride at 2 or 4 mg/L might not protect all individuals from the adverse stages of the condition.

However, this comparison alone is not sufficient evidence to conclude that individuals exposed to fluoride at those concentrations are at risk of stage II skeletal fluorosis. There is little information in the epidemiologic literature on the occurrence of stage II skeletal fluorosis in U.S. residents, and stage III skeletal fluorosis appears to be a rare condition in the United States. Therefore, more research is needed to clarify the relationship between fluoride ingestion, fluoride concentrations in bone, and stage of skeletal fluorosis before any firm conclusions can be drawn.

Carcinogenicity:

In the 2006 report, NRC noted that the question of whether fluoride might be associated with bone cancer continues to be debated and analyzed, and that further research should be conducted. Most committee members held the view that the 1992 cancer bioassay that found no increase in osteosarcoma (a rare bone cancer) in male rats lacked sufficient power to counter the overall evidence of a positive dose-response trend found in the 1990 rat study. After reviewing the studies available to date, the NRC committee concluded that “the evidence on the potential of fluoride to initiate or promote cancers, particularly of the bone, is tentative and mixed,” and that, overall, the literature does not clearly indicate that fluoride either is or is not carcinogenic in humans. NRC noted that the Harvard School of Public Health was expected to publish a large, hospital-based case-control study of osteosarcoma and fluoride exposure in 2006, and that the results of that study might help to identify research needs. The NRC review did include an assessment of pre-publication data from an “exploratory analysis” of a subset of the Harvard data

that found an association between exposure to fluoride in drinking water and the incidence of osteosarcoma in young males. The subsequent study evaluated whether bone fluoride levels were higher in individuals with osteosarcoma. In this study, reported in 2011, some of the researchers detected no significant association between bone fluoride levels and osteosarcoma risk. It was noted that “the major advantage of this study is the use of bone fluoride concentrations as the measure of fluoride exposure, rather than estimated fluoride exposure in drinking water.”

Remediation:

There are basically two approaches for treating water supplies to remove fluoride: flocculation and adsorption. In the former method fluoride is removed through reaction with chemicals (generally hydrate aluminium salts) that coagulating into flocs settle at the bottom of the container. The other method is to filter water down through a column packed with a strong adsorbent, such as activated alumina, activated charcoal or ion exchange resins. Both methods can be used for community or household treatment plants but often their exercise costs are too high for third world countries. Recent research highlighted the strong fluoride sorption properties of volcanic soils, which are readily available in volcanic areas [20, 21]. The high content of amorphous phases of aluminium (allophane, imogolite), clay minerals and organic bound aluminium enhance fluoride adsorption properties. Volcanic soils exert their defluoridation properties also naturally. Bellomo et al. [22] evidenced that the soils of Mt. Etna adsorb about 70% of the magmatic fluorine deposited on its flanks protecting the huge groundwater resources and maintaining the fluoride concentration always below the safe drinking water level.

Conclusion:

Fluorosis is generally not considered in the volcanic hazard evaluation of volcanic systems. Nevertheless fluorosis related to volcanic activity affects probably, at the global level, nearly some million of people. In the majority of cases this brings more sufferance or even only aesthetic problems (dental fluorosis) but in the worst cases it can bring to complete inability (skeletal fluorosis). Problems of fluorine contamination have to be managed in different ways. It has to be highlighted that while in the more evolved nations fluorosis is generally declining because there are enough economic resources to find alternative water sources in the less evolved nations the problem is still increasing. Furthermore in some of these countries, which often suffer for arid climate and consequent water shortage problems, emphasis is usually on water availability rather than quality. By taking the above remedies which was indicated in this paper like flocculation and adsorption procees in purifying the drinking water we can control the contamination of fluorine in drinking water. By this we can control the some of the health impacts caused by the fluorosis.

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