



Groundwater fluoride contamination in Ghana and the associated human health risks: Any sustainable mitigation measures to curtail the long term hazards?

Emmanuel Daanoba Sunkari^{a,b,*}, Salaam Jansbaka Adams^{c,d}, Moses Boakyee Okyere^a,
Prosun Bhattacharya^e

^a Department of Geological Engineering, Faculty of Geosciences and Environmental Studies, University of Mines and Technology, P.O. Box 237, Tarkwa, Ghana

^b Department of Geological Engineering, Faculty of Engineering, Niğde Ömer Halisdemir University, 51240, Niğde, Main Campus, Turkey

^c School of Natural and Environmental Sciences, University of Environment and Sustainable Development, PMB, Somanya, Eastern Region, Ghana

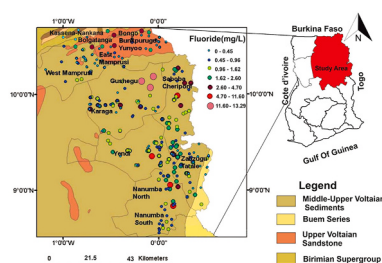
^d School of Nuclear and Allied Sciences, College of Basic and Applied Sciences, University of Ghana, P.O. Box LG 80, Legon, Accra, Ghana

^e Department of Sustainable Development, Environmental Science and Engineering, KTH Royal Institute of Technology, Teknikringen 10B, SE-100 44, Stockholm, Sweden

HIGHLIGHTS

- The fluorosis endemic parts of Ghana are only restricted to northern Ghana.
- Groundwater fluoride concentrations above 13.0 mg/L are reported in northern Ghana.
- Highly fluoridated groundwater in Ghana is largely due to geogenic processes.
- Children are the hypersensitive population with the highest non-carcinogenic risks.
- Sustainable defluoridation techniques are recommended to curtail the menace.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reviewed groundwater fluoride and the associated human health risks in Ghana. The physical and chemical properties of fluorine that make it soluble in the soil and aquifer materials were carefully reviewed. The pathways through which fluoride gets into groundwater were also reviewed. Fluoride concentrations in groundwater can be as high as 67 mg/L. Its natural concentration in water depends largely on the nature of the geologic formations; fluoride-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-), pH, temperature and residence time of waters within a particular formation. High F^- concentrations in groundwater are due to geogenic and anthropogenic sources. The fluorosis endemic parts of Ghana are only restricted to northern Ghana, where elevated groundwater fluoride concentrations (0.05–13.29 mg/L) in the North East Region, Northern Region, Upper East Region, and surrounding communities have been reported. The elevated groundwater fluoride concentrations are as a result of intense water-rock interaction, ion exchange reactions, and mineral dissolution from the Bongo Granitoids and Voltaian sediments. Children in the fluorosis endemic parts of Ghana are exposed to the intake of more fluoridated water than the other age groups and thus, children have higher non-carcinogenic risks. Although, almost all the age groups show evidence of dental fluorosis, children are

* Corresponding author. Department of Geological Engineering, University of Mines and Technology, Faculty of Geosciences and Environmental Studies, P.O. Box 237, Tarkwa, Ghana.

E-mail address: edsunkari@umat.edu.gh (E.D. Sunkari).

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the hypersensitive population. It is recommended that sustainable defluoridation methods such as adsorption, precipitation, membrane separation and ion exchange techniques be employed to curtail the menace of dental fluorosis.

1. Introduction

Fluorine is a halogen that naturally exists in the form of fluoride (F^-) due to its high reactivity and electronegativity (Ganyaglo et al., 2019; Zhang et al., 2020; Murray et al., 2021). It constitutes about 0.06–0.09% of the earth's crust, been the 13th most abundant element (Rusiniak et al., 2021).

Fluoride (F^-) occurs in waters in varied concentrations (Jacks et al., 2005; Brindha and Elango, 2011; Dar et al., 2011; Vithanage and Bhattacharya, 2015a, b). Its natural concentration in waters depends largely on the nature of the geologic formations; fluoride-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-), pH, alkalinity, temperature and residence time of waters within a particular formation (Saxena and Ahmed, 2001; Sunkari et al., 2018; Sunkari et al., 2019; Zango et al., 2019). Some of the minerals that have the greatest impact on the hydrogeochemistry of fluoride are: fluorite, apatite, mica, amphiboles, some clay minerals (such as illite, montmorillonite and kaolinite) and villiamite (Dar et al., 2011; Sunkari et al., 2018). Fluoride is colourless, tasteless or scentless when dissolved in water thereby making it difficult to be determined through physical examination. Its concentrations in waters can only be determined by chemical analysis (Brindha and Elango, 2011).

Fluoride causes health problems in people all over the world. A concentration of at least 0.6 mg/L promotes growth of human teeth and bones (Narbutaitė et al., 2007). Intake of groundwater with fluoride levels exceeding 1.5 mg/L will eventually lead to dental fluorosis (Sunkari et al., 2019; Kimambo et al., 2019; Aravinthasamy et al., 2020; Zango et al., 2021; Ijumulana et al., 2021). A further consumption of higher concentration will result in skeletal fluorosis (Brindha and Elango, 2011; Ijumulana et al., 2020, 2021). There are several ways of mitigating fluoride contamination in groundwater. These methods include: dilution of the groundwater contaminated with fluoride,

adsorption, ion exchange, and precipitation among others. Preference of any of these methods depends on the: affordability, magnitude of the contamination of groundwater as well as the origin of the contaminants; whether it is natural or anthropogenic (Bannerman and Ayibotele, 1984; Apambire et al., 1997; Abugri and Pelig-Ba, 2011; Brindha and Elango, 2011; Kimambo et al., 2019).

Ghana is one of the fluorosis endemic countries in West Africa. The highly fluoridated parts of Ghana are mainly restricted to the northern fringes of the country, which are largely dominated by varying lithologies involving rocks belonging to the Birimian Supergroup and the Voltaian Supergroup (Fig. 1). These rocks are mainly volcanic and sedimentary rocks that are intruded by granitoids (Fig. 1). The fluorosis endemic parts of Ghana have been the focus of many researchers in the past decades (Apambire et al., 1997; Anku et al., 2009; Atipoka, 2009; Salifu et al., 2012; Yidana et al., 2012; Firempong et al., 2013; Alfredo et al., 2014; Craig et al., 2015, 2018; Anornu et al., 2017; Tay, 2017; Sunkari et al., 2018; Donzagla et al., 2019; Ganyaglo et al., 2019; Sunkari et al., 2019; Zango et al., 2019, 2021; Zakaria et al., 2021). Most of these studies are localized to specific communities, districts, municipalities and districts in northern Ghana. However, there is no comprehensive review on the fluoride menace to the groundwater resources in the entire country. This study aims at reviewing all studies previously conducted in Ghana, especially in the highly fluoridated parts of northern Ghana to elucidate the: groundwater fluoride levels, sources of fluoride enrichment in groundwater, extent and severity of fluorosis, and sustainable mitigation measures of high groundwater fluoride.

2. Mineralogy and geochemistry of fluorine

Fluorine (F) has a higher concentration of about 850–1200 mg/L in intermediate igneous rocks under terrestrial conditions (Kabat-Pendias and Pendias, 1992; Abugri and Pelig-Ba, 2011; Vithanage and

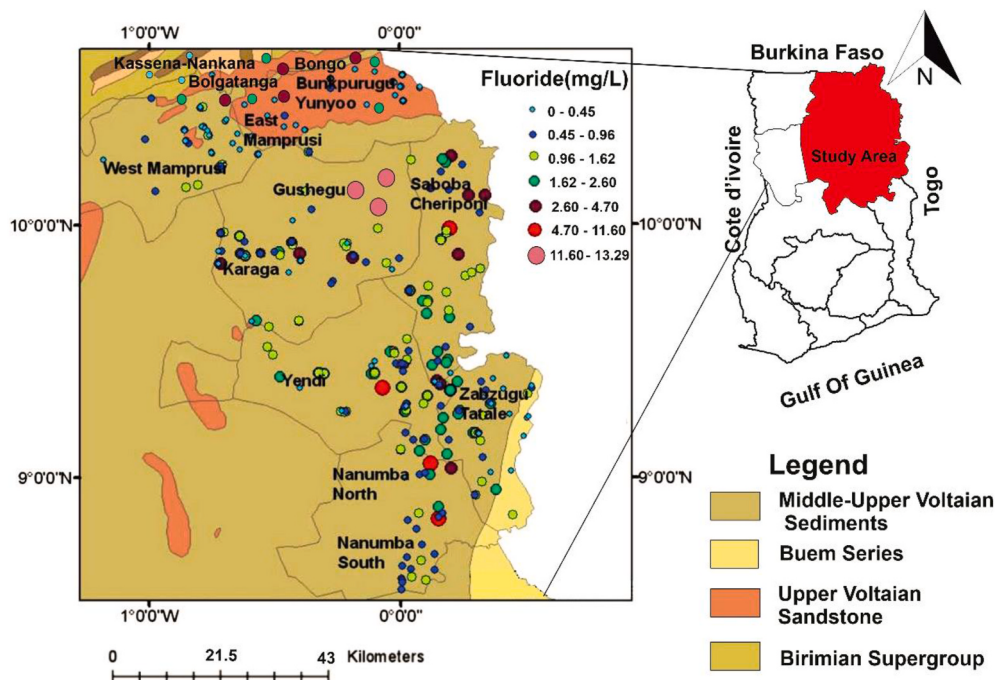
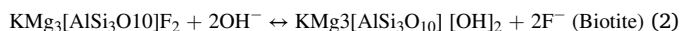


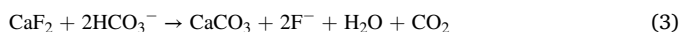
Fig. 1. Location and spatial distribution map of groundwater fluoride in northern Ghana (modified after Salifu et al., 2012).

Bhattacharya, 2015a, b). The commonest F⁻-bearing minerals involved in the mechanism of F⁻ enrichment in water are: fluorite (CaF₂), fluoroapatite (Ca₅(PO₄)₃F), biotite (KMg₃[AlSi₃O₁₀]F₂), muscovite (KAl₂[AlSi₃O₁₀]F₂), cryolite (Na₃AlF₆), villiaumite (NaF), amphiboles, (Ca,Na,K)_{0.1}(Ca,Fe,Li,Mg,Mn,Na)₂(Al,Cr,Fe,Mg,Mn,Ti)₅(Al,Si,Ti)₈O₂₂(OH,F,Cl)₂ and topaz (Al₂(SiO₄)F₂) (Kabata-Pendias and Pendias, 1992; Ozsvath 2009; Abugri and Pelig-Ba, 2011; Rao, 2017; Sunkari et al., 2018; Jha and Tripathi, 2021). Fluoride is largely adsorbed by the soil mineral components at an acidic pH, usually at pH range of 6–7 (Larsen and Widdowson, 1971; Perroilt et al., 1976; Chhabra et al., 1980; Omuetti and Jones, 1980; Abugri and Pelig-Ba, 2011). High groundwater F⁻ concentrations are mostly related to alkaline environments that are characterised by high sodium and bicarbonate concentrations as well as low calcium concentrations (Handa, 1975; Rao et al., 1993; Kundu et al., 2001; Edmunds and Smedley, 2005; Jacks et al., 2005; Brindha and Elango, 2011). Alkaline conditions with pH range of 7.6–8.6 facilitate the dissolution and dissociation of fluoride-bearing minerals from the host rocks (Saxena and Ahmed, 2001; Brindha and Elango, 2011). At higher, pH ionic exchange occurs between F⁻ and OH⁻ ions in clay minerals (such as illite, kaolinite and montmorillonite) and in silicate minerals (such as mica and amphiboles) resulting in increase of F⁻ ion concentration in groundwater (Gupta et al., 2012). F⁻ solubility is lowest in acidic environments, especially at a pH range of 5–6.5 (Gupta et al., 2012).

In mica, for example, the hydroxyl ions replace F⁻ as shown in (Equations (1) and (2)) below:



According to Gupta et al. (2012) and Malago et al. (2017), the dissolution of F⁻ accounts for the presence of fluoride in groundwater in sandstone dominant aquifers. For example, the hydrolysis of aluminosilicate minerals in sandstone aquifers produces bicarbonate ion (HCO₃⁻), which can enhance fluorite dissolution (Equation (3)).



The sodium bicarbonate type of waters generally have high concentrations of fluoride (Handa, 1975; Chae et al., 2007; Brindha and Elango, 2011). The presence of high HCO₃⁻, Na⁺ and pH promotes the release of F⁻ from aquifer matrix into groundwater (Jacks et al., 2005; Brindha and Elango, 2011; Gupta et al., 2012).

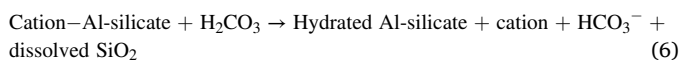
3. Mechanism of fluoride concentration and enrichment in groundwater

The mechanism of fluoride concentration and enrichment in groundwater is explicitly explained by Rao (2011) and Malago et al. (2017) below:

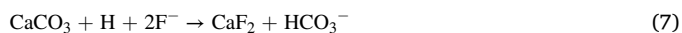
Precipitation waters get enriched in CO₂ from the air and soil as well as biochemical reactions of bacteria and organic matter during infiltration (Equations (4) and (5)), resulting in an increase in pH and subsequent over-saturation of CaCO₃.



The onset of evapotranspiration coupled with dry climatic conditions lead to the precipitation of CaCO₃ thereby leaving the soils to become alkaline, with higher sodium concentration. The carbonates can also be derived from the dissolution of silicate minerals through the action of H₂CO₃ (Equation (6)).

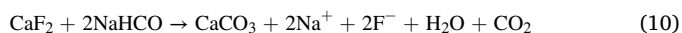
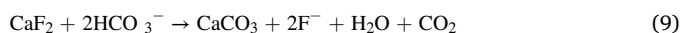


The CaCO₃ present in the soil or aquifer material can also get dissolved as illustrated in Equations (7) and (8);



Hence, the F-bearing minerals: apatite, biotite, fluorite, hornblende and muscovite, are considered the principal sources of F⁻ in groundwater, whereas phosphate fertilizers is the supplementary source of F⁻ in the water (both surface water and groundwater). Some clay minerals are also significant sources of high fluoride concentrations in groundwater due to ion exchange between F⁻ and OH⁻ (Rao, 2011; Malago et al., 2017).

As the alkaline water activates the processes of dissolution and dissociation of F⁻ from the soils and weathered rocks (Rao et al., 1993; Saxena and Ahmed, 2001; Jacks et al., 2005; Rao, 2011; Gupta et al., 2012; Malago et al., 2017), with a simultaneous precipitation of CaCO₃, there is a reduction in total hardness (in terms of Ca²⁺ and Mg²⁺ ions) and a dissolution of CaF₂ (Equations (9) and (10)).



From the above equations, the mechanism of high F⁻ concentration in groundwater is that F⁻ is mainly released from the F-bearing minerals during infiltration by geochemical reactions and that the groundwater in its pathway is subjected to evapotranspiration due to the influence of arid climate, resulting in precipitation of CaCO₃ and a reduction in the activity of total hardness so that there is a dissolution of F⁻ (Malago et al., 2017; Rao, 2011). Besides, the excess alkalinity activates the alkalinity in the presence of alkaline soils, causing the higher concentration of F⁻ in the groundwater (Malago et al., 2017; Rao, 2011).

4. Sources of fluoride in groundwater

High concentrations of fluoride in groundwater are derived from two main sources: natural (lithogenic/geogenic) and anthropogenic (Kim et al., 2010; Brindha and Elango, 2011; Rao, 2011; Ali et al., 2016). Geogenic sources include: the nature of aquifer material and volcanic ash (Brindha and Elango, 2011; Ijumulana et al., 2020, 2021). Anthropogenic sources include phosphate fertilizers and fly ash (Kim et al., 2010; Brindha and Elango, 2011).

4.1. Geogenic sources of fluoride contamination in groundwater

4.1.1. Aquifer material

Under normal temperature and pressure, fluoride-bearing minerals like cryolite and fluorite have lower solubility. However, when the pH becomes alkaline within a specific conductivity range of 750–1750 μS/cm, fluoride-bearing minerals tend to have higher solubility and thus, dissolve faster (Saxena and Ahmed, 2001; Brindha and Elango, 2011). The average content of F⁻ in granitoids is 810 mg/kg (Wedepohl, 1969; Brindha and Elango, 2011). The weathering, dissolution and dissociation of these rocks facilitate mobilization of F⁻ in groundwater. Subsequently, longer times of groundwater residence in aquifers dominated by fractured fluoride-rich rocks elevate the groundwater F⁻ levels (Brindha and Elango, 2011).

4.1.2. Volcanic ash

As mentioned, volcanic rocks contain high amount of F⁻. Hydrogen fluoride is one of the gases that easily dissolves in magmas and is partly dissipated during volcanic eruption (D'Alessandro, 2006; Brindha and Elango, 2011). During volcanic eruption, F⁻ is emitted in the form of volcanic ash. This falls out as particulate F⁻ and also together with precipitating water. Percolating and infiltrating waters will finally mobilize F⁻ into groundwater. This accounts for the F⁻ contamination in

areas where volcanic eruption is common, for example Iceland (Fridriksson, 1983; Steingrímsson, 1998; Brindha and Elango, 2011; Walser et al., 2020). The solubility of volcanic ash is very high and hence the risk of F^- contamination in groundwater is very high. It has been established that volcanic sources are the main cause of groundwater F^- contamination in Kenya (Gaciri and Davies, 1993; Brindha and Elango, 2011). The F^- concentration in ash from Hekla eruption in 2010 was found to be in the range of 23–35 mg/kg (Matvælastofnun, 2010; Brindha and Elango, 2011).

4.1.3. Calcretes, sepiolite and palygorskite

Calcretes are common in regolith overlying granitic rocks and are composed of microcrystalline calcite with variable concentration of Mg (<3 mol % $MgCO_3$) (Reddy et al., 2010). They are reported as a common source of F^- in groundwater. For example, Jacks et al. (2005) reported fluorine concentrations of calcretes in India ranging from 510 to 9000 mg/kg. Jacks et al. (2005) suggested that the fluorine is released from solution by co-precipitation with calcite and dolomite. Moreover, Fan et al. (2003) also indicated that sorption of fluorine on calcite surfaces is also a mechanism of fluorine mobilization in calcretes and subsequently in groundwater. Another possible site for the sorption of fluorine is the presence of sepiolite and palygorskite in calcrete deposits (Reddy et al., 2010). Sepiolite is less stable and palygorskite easily weathers into smectite (Singer et al., 1995). These clay minerals are Mg-hydroxylsilicates and are reported to contain significant amounts of F^- in the OH-positions (Reddy et al., 2010). For instance, about 1.3% of F^- in a Spanish sepiolite, which is in equilibrium with 2 mg/L of F^- in groundwater was reported by Torres-Ruiz et al. (1994). Similarly, fluoride-rich sepiolite and palygorskite in sandy soils in South Africa and Iran were reported by Singer et al. (1995) and Khademi and Mermut (1999), respectively. In both cases, the authors suggested that formation of the fluoride-rich sepiolite and palygorskite occurred after calcrete precipitation under alkaline soil conditions. This suggests that alkaline pH plays a major role in mobilization of F^- in sepiolite and palygorskite.

4.2. Anthropogenic sources of fluoride contamination

4.2.1. Phosphate fertilizers

The application of phosphate fertilizers on agricultural lands increases F^- contamination in soil and groundwater (Motalane and Strydom, 2004; Farooqi et al., 2007; Brindha and Elango, 2011). Analysis of F^- content in phosphate fertilizers yielded the following: superphosphate (2750 mg of F/kg), potash (10 mg of F/kg) and NPK (Nitrogen Phosphorous Potassium) (1675 mg of F/kg), all contain reasonable amounts of F^- (Brindha and Elango, 2011).

4.2.2. Fly ash

Combustion of fossil fuels produces fly ash, which also accounts for high F^- contamination in soil and for that matter in groundwater worldwide. Combustion of coal, especially those used in firing power plants is estimated to also produce about 150 million tons of fly ash worldwide annually (Prasad and Mondal, 2006; Piekos and Paslawski, 1998; Brindha and Elango, 2011). Churchill et al. (1948) reported that coal contains 40–295 mg of F/kg. They however observed that the F^- content of coal depends on the type and amount of coal being burnt. The use of coal by brick kilns for burning is also not a negligible source for F^- contamination (Jha et al., 2008; Brindha and Elango, 2011). Improper disposal of fly ash may cause leaching of F^- into soil and groundwater (Brindha and Elango, 2011).

5. Socio-economic and health implications of high groundwater fluoride

Water for domestic purposes, especially drinking water is the major source of F^- intake in humans (Antwi et al., 2011). Most of the people affected by highly fluoridated groundwater are low income earners and

they largely live in the tropical countries (arid and semi-arid regions), where the per capita consumption of water is high due the dry climatic conditions (Kim et al., 2010). In Ghana for instance, the daily consumption of water is about 3–4 L/day per adult, which is higher than the WHO estimated daily consumption of 2 L/day per adult (Apambire et al., 1997; Kim et al., 2010), indicating that people are more exposed to the threat of fluorosis. The intensity is also higher in densely populated countries like India and China (Gupta et al., 2006; Kim et al., 2010).

The WHO recommends a minimum of 0.6 mg/L and a maximum of 1.5 mg/L as the permissible limits of F^- intake into the human body (WHO, 2008). Any intake of F^- concentration below or above these limits will result in the associated negative health impacts. The most common impact is fluorosis - a health condition caused by intake of F^- greater than 1.5 mg/L. Children below the age of eight are the most affected (Antwi et al., 2011). Fluorosis comes in different forms; dental, skeletal and crippling fluorosis (Narbutaitė et al., 2007; Antwi et al., 2011; Annan, 2018; Ijumulana et al., 2021). Dental fluorosis (1.5–4 mg/L of F^-) is characterised by staining and pitting of the teeth and may eventually lead to damage of the enamel in severe cases (WHO, 2008; Antwi et al., 2011; Annan, 2018). A further accumulation of F^- (>4 mg/L) in the bones over years will lead to skeletal fluorosis, crippling fluorosis (>10 mg/L), thyroid changes (>50 mg/L), growth retardation (>100 mg/L) and kidney problems (>120 mg/L) as they facilitate the formation of kidney stones (WHO, 2001; 2002; Antwi et al., 2011; Annan, 2018). Also, an intake of F^- concentration of 0.5 mg/L or less into the human body has the potential of causing dental caries (Antwi et al., 2011; Annan, 2018).

Other health implications that could occur owing to the intake of highly fluoridated water include; low haemoglobin levels, muscle fibre degeneration, excessive thirst, deformities in RBCs, skin rashes, headache, nervousness, depression, neurological manifestations, gastrointestinal problems, urinary tract malfunctioning, nausea, abdominal pain, reduced immunity, tingling sensation in fingers and toes, low IQ, male sterility, repeated abortions or still births and other genotoxic effects (Li et al., 1988; Tang et al., 2008; Brindha and Elango, 2011).

6. Groundwater fluoride hotspots in Ghana

A summary of the groundwater F^- concentrations in northern Ghana is given in Table 1. The occurrence of high F^- concentrations in groundwater has been reported in parts of the Savelugu Municipality (Tay, 2017) and parts of the Gushiegu Municipality (Maxwell et al., 2012) both in the Northern Region of Ghana (Fig. 1; Table 1). The Bongo District and its surrounding areas (parts of the Bolgatanga Municipality) in the Upper East Region of Ghana (northeastern Ghana) are of epidemic levels (Apambire et al., 1997; Pelig-Ba, 1987; Apambire et al., 1997; Abugri and Pelig-Ba, 2011; Antwi et al., 2011; Yidana et al., 2012; Sunkari et al., 2018; Sunkari et al., 2019) (Fig. 1). Recently, Zango et al. (2019) reported extremely high F^- concentrations (0.05–13.29 mg/L) in groundwater resources within the newly-created North East Region of Ghana (Fig. 1; Table 1). They suggested that the high groundwater F^- is due to the semi-arid climatic conditions of the region, alkaline nature of the water, water-rock interaction, mineral dissolution, and ion exchange reactions. Tay (2017) found high concentrations of F^- in the northern part of the Savelugu Municipality from Zoosali to Nyoglo in the range of 1.5–3.0 mg/L, high above the WHO accepted maximum value of 1.5 mg/L (Fig. 1; Table 1). Anim-Gyampo et al. (2018) established the relation between F^- concentration and sericite composition. They established a positive relationship between F^- concentration and modal composition of sericite and as such sericite is the major contributor of F^- contamination with carbonate minerals been the minor contributors in parts of the Gushiegu Municipality. They concluded that, the Voltaian Supergroup is of marine environment as suggested by Affaton et al. (1990).

High F^- contamination (1.71–4.4 mg/L) in groundwater has been reported in the Bongo District and surrounding communities (Fig. 1;

Table 1

Summary of groundwater fluoride concentrations in northern Ghana (BDL = Below Detection Limit).

Location	Groundwater fluoride concentration (mg/L)	Analytical Method	Reference
Vea Catchment	0.35–3.95	DIONEX ICS 90 Ion Chromatography	Zango et al. (2021)
Kwahu-Bombouaka Group, North East, Ghana	0.01–8.40	DIONEX ICS 90 Ion Chromatography	Sunkari et al. (2020)
Bongo District, Upper East Region	0.30–5.84	Metrohm 861 Ion Chromatography/Fluoride Ion Selective Electrode	Atipoka (2009); Firempong et al. (2013); Alfredo et al. (2014); Sunkari et al. (2018); Sunkari et al. (2019)
North East Region	0.05–13.29	DIONEX ICS 90 Ion Chromatography	Zango et al. (2019)
Upper East Region	0.30–5.00	Fluoride Ion Selective Electrode/DIONEX ICS 90 Ion Chromatography	Craig et al. (2015); Ganyaglo et al. (2019)
Northern Region	BDL - 11.6	Fluoride Ion Selective Electrode	Anku et al. (2009); Salifu et al. (2012); Yidana et al. (2012); Zakaria et al. (2021)
Anayari Catchment, Upper East Region	0.10–2.00	Hach DR 900 Colorimeter	
Savelugu-Nanton District, Northern Region	0.10–4.10	Hach DR 900 Colorimeter	Tay (2017)
Gushiegu District, Northern Region	BDL - 1.97	DIONEX ICS 90 Ion Chromatography	Salifu et al. (2017)
Kassena-Nankana West, Upper East Region	0.46–2.37	DIONEX ICS 90 Ion Chromatography	Ganyaglo et al. (2019)
Bawku Municipality, Upper East Region	0.10–1.50	DIONEX ICS 90 Ion Chromatography	Anim-Gyampo et al. (2014)
Atankwidi Basin, Northeastern Ghana	0.38–1.95	Shimazu SIL-10AF Ion Chromatography	Anornu et al. (2017)
White Volta River Basin of Ghana	0.04–3.79	Shimazu SIL-10AF Ion Chromatography	Anornu et al. (2017)
Upper Regions of Ghana	0.11–4.60	DIONEX ICS 90 Ion Chromatography	Apambire et al. (1997)
Namoo, Upper East Region	0.30–4.50	Fluoride Ion Selective Electrode	Craig et al. (2018)
Jirapa and Kassena-Nankana Municipalities	0.70–1.50	Portable Palintest Visual Standard Comparator Kit	Dongzagla et al. (2019)
Bunkpurugu-Yunyo District	0.10–0.13	DIONEX ICS 90 Ion Chromatography	Anim-Gyampo et al. (2014)

Table 1), which is significantly higher than the WHO (2017) standard value of 1.5 mg/L for drinking water (Smedley et al., 1995; Atipoka, 2009; Abugri and Pelig-Ba, 2011; Sunkari et al., 2018; Sunkari and Abu, 2019; Abanyie et al., 2020; Zango et al., 2021). The Bongo District forms part of the Birimian Supergroup of Ghana with the Bongo Granitoids been the major rocks outcropping there. There are high and low fluoride

concentrations in the Birimian Supergroup (Fig. 1) due to the variation in composition of the Birimian rocks. Areas dominated by the Birimian metavolcanic and intrusive rocks that contain abundant micas (biotite and muscovite) show higher groundwater fluoride concentrations than those largely overlain by Birimian metasediments that contain lesser amounts of micas (Sunkari et al., 2018; Sunkari et al., 2019). The topography of the area is generally flat. About 40% of the land surface is covered with granite outcrops thereby making farming and other activities very difficult (Bongo District Assembly). The major minerals in the granite are quartz, plagioclase, microcline, muscovite, and biotite with considerable amounts of amphiboles, especially hornblende. Zirconium and apatite occur as accessory minerals, whereas sericite and epidote are also reported locally as secondary minerals (Sunkari et al., 2018).

The mechanism of the release of F^- from the F-bearing minerals is explained using a model by Sunkari et al. (2018). The F^- released from the regolith can be drained into neighbouring catchments and may remain within the regolith for a long time. This may eventually pollute water being tapped from such reservoirs/aquifers. Ozsvath (2006) also indicated that albite dissolution and ion exchange reactions can result in high F^- levels in groundwater. Thus, the positive relationship of F^- with Na^+ and $(K^+ + Na^+)/ (K^+ + Na^+ + Ca^{2+} + Mg^{2+})$ ratio reveal the influence of F^- mobility (Sunkari et al., 2018). Hence, the high concentration of F^- in groundwater in the Bongo District could be as a result of the presence of albite (accounting for pinkish colouration) and biotite in the Bongo Granitoids and pegmatite veins in the granitoids (Ozsvath, 2009; Sunkari et al., 2018).

7. Human health risks associated with fluoridated groundwater in Ghana

Studies on human health risk assessment of fluoridated groundwater in Ghana are not readily available. Most of the studies only predict the presence of dental fluorosis without a detailed health risk assessment. However, at the time of writing this review, only Ganyaglo et al. (2019) and Zango et al. (2019) conducted human health risk assessment of high groundwater fluoride in the fluorosis endemic parts of Ghana. Whilst Ganyaglo et al. (2019) studied the Upper East Region, Zango et al. (2019) studied the North East Region of Ghana. These studies generally appraised the estimated daily intake of fluoridated water and the non-carcinogenic human health risks associated with the various age groups; infants, children, teenagers, and adults. Accordingly, children in northern Ghana drink more fluoridated water (0.00–1.13 mg/kg/day) than the other age groups (Fig. 2). This implies that children are more exposed to the human health risks associated with fluoridated groundwater than the other age groups. As a result, previous studies have indicated that children are exposed to higher non-carcinogenic human health risks like dental fluorosis in northern Ghana than the other age groups (Fig. 3). The non-carcinogenic human health risks were assessed by computing the hazard quotients (Ganyaglo et al., 2019; Zango et al., 2019), where if the hazard quotient exceeds 1, a potential non-carcinogenic human health risk is envisaged for the consumption of fluoridated water. Therefore, children in northern Ghana, who have hazard quotients ranging from 0.07 to 18.8 (Fig. 3), are the hypersensitive population. Although almost all the age groups show evidence of dental fluorosis, children are the most affected since they drink more fluoridated groundwater.

8. Sustainable mitigation measures

Various measures proposed by researchers for mitigation of F^- contamination in water are summarised in a schematic chart in Fig. 4. They are classified into in-situ and ex-situ measures (Fig. 4). In-situ methods aim at mitigating the concentration of F^- in the aquifer through artificial recharge (Bhagavan and Raghu, 2005; Brindha and Elango, 2011). The ex-situ methods aim at the decontamination of water

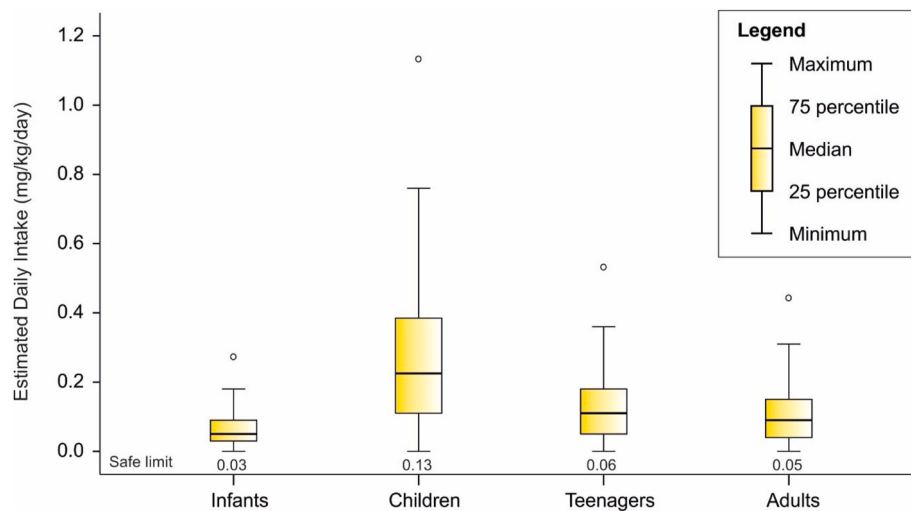


Fig. 2. Estimated daily intake of fluoridated groundwater by the various age groups in northern Ghana (smaller circles above the whiskers indicate outliers).

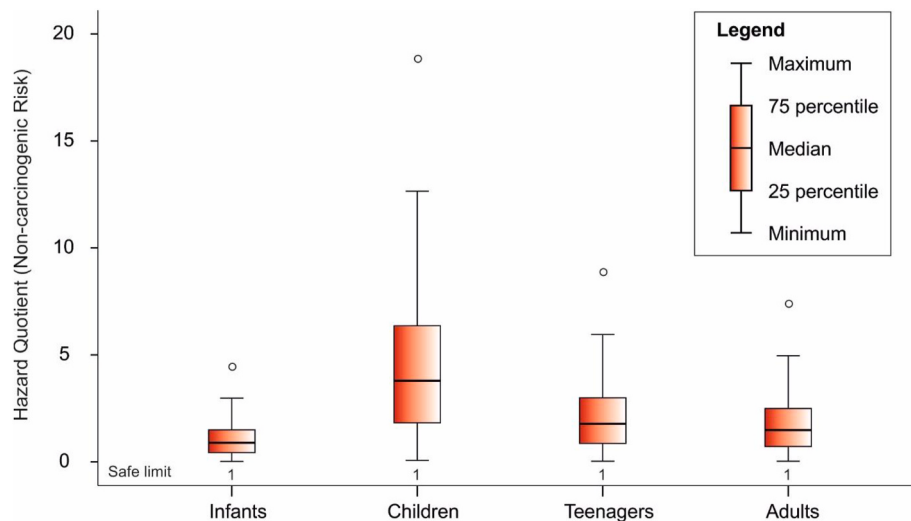


Fig. 3. Hazard quotient (non-carcinogenic risks) of fluoridated groundwater associated with the various age groups in northern Ghana (smaller circles above the whiskers indicate outliers).

at the household or community level (Brindha and Elango, 2011).

8.1. In-situ treatment methods

Check-dams constructed in Anantapur District, India were useful in reducing F^- content in groundwater (Bhagavan and Raghu, 2005). According to Brindha and Elango (2011), rainfall recharge or rainwater harvesting can be adopted using percolation tanks and recharge pits. Recharge of rainwater after filtration through the existing wells can also be planned to improve the groundwater quality of a particular aquifer. This method may prove useful if it is carefully planned and constructed.

8.2. Ex-situ treatment methods

The most common ex-situ techniques for defluoridation are adsorption, membrane separation, precipitation, and ion exchange (Abugri and Pelig-Ba, 2011; Brindha and Elango, 2011).

8.2.1. Adsorption technique

This method of F^- decontamination involves channelling water via a contact bed in which the F^- is adsorbed onto the matrix. Chidambaram

et al. (2003) and Chauhan et al. (2007) intimated that the commonly used absorbents are activated charcoal and activated alumina. Other absorbents that have the potential of de-fluoridating groundwater are char, brick, bone, serpentine, waste mud, red mud, rice husk, charfines, bentonite, kaolinite, and ceramic (Brindha and Elango, 2011). Effective de-fluoridation by these absorbents is contingent on the initial F^- concentration, pH, contact time, absorbent type and its size.

8.2.2. Precipitation technique

This method involves addition of calcium to fluoride contaminated waters, which precipitate fluoride as fluorite. An alternative is the use of aluminium salts, lime or alum. Precipitation methods are simple and cost effective (Brindha and Elango, 2011).

8.2.3. Membrane separation technique

Membrane separation technique comprises of reverse osmosis and electrodialysis. Both methods employ the use of a semi-permeable membranes that are capable of eliminating dissolved solutes from the water when they pass through them. However, the two techniques are quite distinct because reverse osmosis operates with pressure whereas electrodialysis operates with direct potential. Reverse osmosis is also

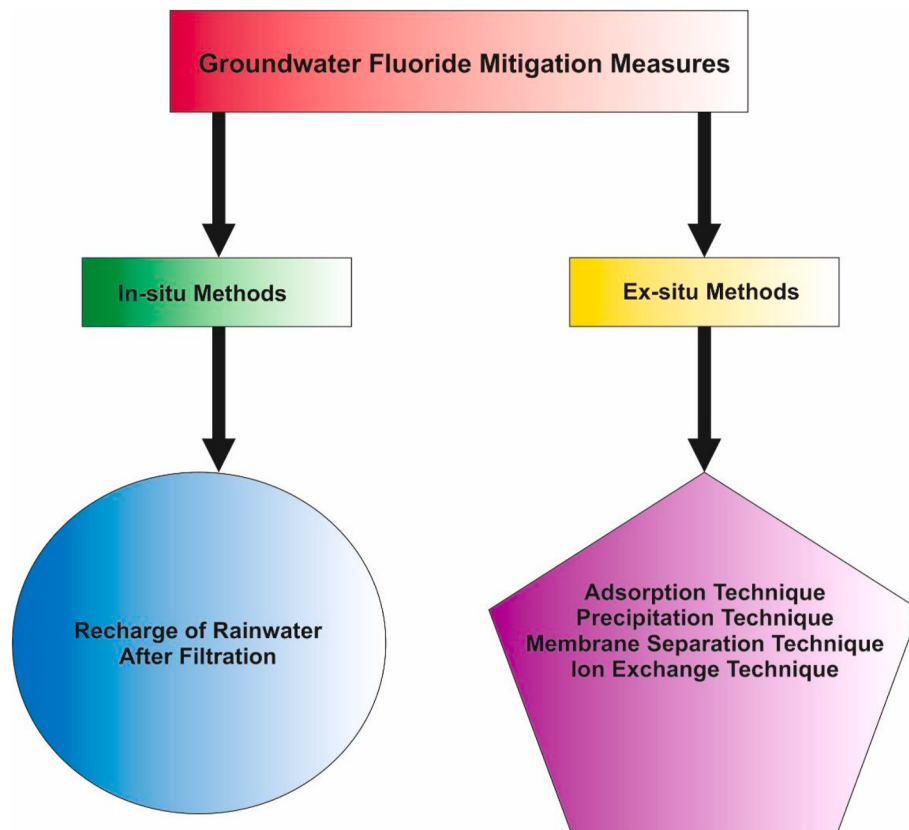


Fig. 4. Schematic chart of sustainable groundwater fluoride mitigation measures.

economical and the equipment can be installed at homes but electro-dialysis involves a complex and massive set-up and hence more expensive. It is best fit for the community level. Both membrane techniques involve the removal of essential ions for the human body (Brindha and Elango, 2011). Abugri and Pelig-Ba (2011) are of the opinion that the membrane techniques are the appropriate technology for poor, rural areas in developing countries due to their cost, fouling issues, operational sophistication, and difficulty of intermittent operation. Meanwhile, Brindha and Elango (2011) are suggested that membrane techniques are comparatively costly due to their nature.

8.2.4. Ion exchange technique

According to Brindha and Elango (2011), in this method of defluoridation, water passed through a column containing ion exchange resin, which enables the fluoride ions to replace calcium ions in the resin. When the resin is saturated with the fluoride ions, it is backwashed with solution containing chloride such as sodium chloride. The chloride ions will then replace the fluoride ions in the resin and the water is ready for reuse. However, the backwash is rich in fluoride and hence care should be taken in disposing this solution so that it does not re-contaminate the defluoridated water.

8.3. Advantages and disadvantages of sustainable groundwater fluoride mitigation measures

The proposed sustainable groundwater fluoride mitigation measures have both advantages and disadvantages (Ingle et al., 2014), which are summarised in Table 2. Therefore, adoption of any of them should be with caution. Both the advantages and disadvantages should be a guide to which technique is suitable for mitigating high groundwater fluoride menace in aquifers.

Table 2

Advantages and disadvantages of the sustainable groundwater fluoride mitigation measures.

Technique	Advantages	Disadvantages
Adsorption technique	Can potentially remove fluoride up to 90%. Effective and economical.	It largely depends on pH over a pH range of 5–6. Presence of carbonate, sulphate or phosphate causes ionic competition.
Precipitation technique	Contact time is minimal for complete defluoridation. It is indigenously available and cheap. Can be used at household level. It is cost-effective.	Highly skilled personnel is required for operation. Treatment is ineffectual if TDS is > 1500 mg/L. Day-to-day operation requires a trained operator. Excess aluminium can contaminate the water.
Membrane separation technique	It has a very simple design, construction, operation and maintenance. Very effective for removing fluoride. It maintains the quality of the water. Effective over a wide pH range. No competition with other ions.	Discarding the sludge poses serious environmental problems. Brine disposal is a major problem. It is expensive when compared with the other techniques. It results in acidic water and needs pH adjustment. A lot of water is wasted as brine.
Ion exchange technique	Can potentially remove 90–95% fluoride. It retains the color and taste of water. Can be used for communities, districts and larger cities.	Its potency is reduced when phosphate, sulphate, and carbonate ions are present. Due to the cost of resin, it is expensive. Low pH and high chloride levels are common in the treated water.

9. Conclusion, recommendations and research gaps

The presence of F^- -bearing minerals in the host rocks and water-rock interactions in an alkaline environment under dry climatic conditions have been established to be the main causes of F^- enrichment and contamination in groundwater. Chemical processes such as decomposition, dissociation, and dissolution are also responsible for the mobility and transport of fluoride in groundwater. Chemical weathering under arid to semi-arid conditions with relatively high alkalinity and long residence time favours high concentrations of fluoride in groundwater. The high groundwater F^- contamination in northern Ghana can be attributed to the above mechanism due to the presence of albite and biotite in the Bongo Granitoids and pegmatite veins. The Bongo Granitoids contain from 2 to more than 20 times the amount of fluorine in the surrounding rock formations. The groundwater fluoride contamination has resulted in dental fluorosis, particularly in children since they drink more fluoridated water than other age groups.

The following are recommended to mitigate high fluoride concentrations in groundwater and their impact on human health in Ghana and other high fluoride zones worldwide:

1. The people of northern Ghana should avoid the use of phosphate fertilizers as they contribute to the anthropogenic sources of groundwater fluoride contamination: they should adopt organic farming.
2. Afforestation should be encouraged. A good vegetation cover will reduce evapotranspiration and hence deposition of fluoride-bearing salts in the unsaturated zone and their subsequent infiltration into groundwater will be impeded.
3. The people of northern Ghana and other similar high fluoride zones should resort to the use of fluoride-free toothpaste. This will reduce the amount of fluoride intake into their bodies.
4. The Government should complement the efforts of researchers and Non-governmental organizations to establish defluoridation plants in Northern Ghana.

A lot of research has been done on fluoride contamination in groundwater and in identifying high fluoride zones globally. But the problem of defluoridation of these fluoride waters (especially groundwater) still remains unsolved to a large extent, especially how to reduce the high cost of the sustainable fluoride mitigation measures and make them affordable to households. Most of these defluoridation methods are ex-situ measures with the accompanying high cost. A careful look into the in-situ measures where the problem is solved from the source can be of great help. Since fluoride contamination in groundwater is largely confined to arid and semi-arid regions globally (especially Africa and Asia), future research should clearly establish the link between climate change and fluoride contamination. The cost of analysing water samples is increasingly high and overburdens the limited resources of researchers. As such, future research should consider coming out with models to predict levels of fluoride in groundwater, mobilization of fluoride, residence time and fluoride migration.

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.

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