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Review article

Fluoride in groundwater sources in Ghana: A multifaceted and country-wide review

Raymond Webrah Kazapoe [a], Ebenezer Ebo Yahans Amuah [b,*], Paul Dankwa [c], Obed Fiifi Fynn [d], Millicent Obeng Addai [e], Belinda Seyram Berdie [f], Nang Biyogue Douti [g]

[a] *Department of Geological Engineering, University for Development Studies, Tamale, Ghana*
[b] *Department of Environmental Science, Kwame Nkrumah University of Science and Technology, PMB, Kumasi, Ghana*
[c] *Research Department, Green Africa Youth Organization, Accra, Ghana*
[d] *Water Research Institute, Council for Scientific and Industrial Research, Accra, Ghana*
[e] *Department of Geography, University of Education, Winneba, Ghana*
[f] *Department of Earth Science, C. K. Tedam University of Technology and Applied Sciences, Navrongo, Ghana*
[g] *Department of Environmental Science, C. K. Tedam University of Technology and Applied Sciences, Navrongo, Ghana*

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ABSTRACT

A large portion of Ghana's population, particularly in rural areas, lack reliable access to safely managed water. Many of these communities rely on groundwater as their primary drinking water source. Distinguished by its thorough examination of F$^-$ occurrences in Ghana, this study complements previous studies by meticulously analyzing groundwater-soil and –plant dynamics, global implications, and region-specific insights, notably in the high-risk Bongo area. The study showed that Fluoride contamination in Ghana is evident in various regions, with primary data showcasing concentrations ranging from 0.05 mg/L^{-1} to 13.29 mg/L^{-1}. The Bongo District in the north exhibits elevated fluoride levels, surpassing WHO safety limits of 1.5 mg/L^{-1} [62]. Additional studies in Sekyere South and Nalerigu disclose concentrations from 0.3 mg/L^{-1} to 4.0 mg/L^{-1} and 0.35 mg/L^{-1} to 3.95 mg/L^{-1}, respectively. Contamination probabilities range from 50 % to 90 % in the north and northeast. While southern areas lack extensive data, the identified hotspots necessitate further investigation. Geological factors significantly influence fluoride levels, emphasizing the urgent need for comprehensive monitoring, mitigation, and public awareness. The identified contamination poses risks to public health, urging immediate action for sustainable solutions and ensuring safe drinking water in affected regions. The health implications of fluoride toxicity on the residents of regions prone to fluoride exposure are noteworthy. As a result, an inevitable surge in instances of dental and skeletal fluorosis can be anticipated. Notwithstanding the challenges, research indicates optimistic prospects for mitigating fluoride pollution in drinking water. Techniques like the utilization of "Bone Charcoal" and the "Contact Precipitation" approach offer promise for remediation. These methods can be implemented at a household level and some are economically viable, making them advisable for adoption in fluoride-prone areas of Ghana.

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[*] Corresponding author.
E-mail address: amuahyahans@gmail.com (E.E. Yahans Amuah).

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1. Introduction

Access to clean water remains a pressing challenge in Africa, with millions of people lacking reliable sources for drinking water and sanitation [1]. Factors such as inadequate infrastructure, pollution, climate change, and population growth exacerbate the problem [2]. Rural areas and informal settlements are disproportionately affected, facing limited access to safe water and proper sanitation facilities [3]. In Ghana, access to safe water services is limited, with only 41.41 % of the population having access to safely managed water as of 2023, which represents a modest increase of 1.71 % since 2019 [4]. Unfortunately, a significant 14 % of the population has little to no access to clean water sources [5]. This situation is particularly more severe in rural areas predominantly in the northern parts of the country, where indigenes rely almost solely on groundwater for their domestic activates [6]. However, a concerning problem in Ghana is the presence of anomalously high concentrations of natural fluoride in some groundwater sources.

Moderate fluoride consumption can reduce dental cavities and enhance bone development. However, prolonged intake of high fluoride levels can disrupt calcium and phosphorus metabolism in the human body, leading to calcium deficiency and skeletal fluorosis [7–10]. Fluoride (F-) is recognized as a crucial trace element important for human well-being [11]. It plays a vital role in preventing dental cavities, making it a significant contributor to oral health [12].

Studies have shown that approximately 65 % of global endemic fluorosis cases are due to elevated levels of F^- in drinking water [13,14]. The World Health Organization (WHO) recommends a permissible drinking water fluoride level of 1.5 mg/L^{-1} for maintaining health [15]. Within this optimal range, fluoride is beneficial for dental health and essential for bone growth and maintenance [16,17]. However, when fluoride concentrations exceed 1.5 mg/L^{-1}, it can lead to severe health issues, including dental discoloration, skeletal fluorosis, physiological disorders, and kidney malfunctions, among others [18–20]. It is worth noting that fluoride concentrations within the range of 0.0–0.5 mg/L^{-1} in the human body can result in dental cavities [21]. F^- exhibits an affinity for accumulating in the body's mineralizing tissues. In young individuals, it tends to amass in bones and teeth, while in older individuals, bones remain the primary storage site. The incorporation of fluoride into the tooth matrix during their development serves as a protective measure against dental caries [12]. Alarmingly, Rasool et al. [22] reported that approximately 200 million people across 25 countries worldwide are afflicted by the burdensome issue of fluorosis. India and China, the two most populous nations globally, face the most severe consequnces of this condition. African countries such as Ethiopia, Tunisia, Ghana, South Africa, Sudan, Somalia, Uganda, Algeria, Kenya, Tanzania, Senegal, Nigeria, Morocco, and Egypt are recognized for their considerable exposure to elevated fluoride levels in groundwater sources [23].

Fluoride is a naturally occurring element in the environment, often associated with different rock types and volcanic activity [8]. Another study by Sunkari and Abu [19] stated that rocks that have granitic configurations contain a lot of fluoride-bearing minerals such as micas (muscovite and biotite), apatite and amphibole. Sunkari et al. [8] also affirm that the dissolution of these minerals releases calcium and fluorine ions into groundwater systems which eventually increases the fluoride content. The process involves the weathering of the host rocks which contain the fluoride-bearing minerals. The fluorine element in the minerals dissolves gradually into the groundwater sources due to its high solubility and becomes one of the trace elements in the groundwater resources [24].

It has been established that fluoride mainly gets through to the human body through drinking water, most precisely groundwater sources [25]. Although several researchers including Jha et al. [26] and Rizzu et al. [27] suggest other sources such as cultivated foods. However, their assertion about cultivated foods may not be the case in Ghana as crop farming is rain-fed. The occurrence of fluoride in groundwater in Ghana has been well documented. Research by Salifu et al. [16], Sunkari et al. [8], Zango et al. [14], and Sunkari and Abu [19] throws light on the occurrence of F^- in groundwater sources in Ghana. Although these authors shed light on the occurrence of fluoride in Ghana, they focus on specific areas of the country, especially fluoride-endemic areas. This study seeks to conduct a holistic nationwide review of the occurrence of fluoride in the environment, especially groundwater with a special focus on Ghana.

This review on fluoride occurrence and movement in Ghana builds upon the foundation laid by previous research while adopting a more comprehensive approach. Unlike earlier studies that focused on specific regions or aspects of fluoride contamination, this study delves into the intricate mechanisms underlying fluoride concentration in various environmental compartments, including groundwater, soils, and plants, and the gaps alike. By synthesizing insights from previous studies and integrating new data, we aim to provide a holistic understanding of migration pathways and environmental factors influencing contamination levels nationwide. In particular, this study extends beyond the mere identification of hotspots to analyze the known and potential health impacts of excess fluoride intake, with a specific focus on endemic areas such as the Bongo district. This targeted examination allows us to assess the unique challenges and implications of fluoride contamination in highly affected regions, contributing valuable insights for targeted interventions and public health policies. Furthermore, this research incorporates a comparative analysis of global fluoride occurrence trends, enabling us to contextualize Ghana's situation within the broader global landscape. By examining geospatial predictors and spatially modeling fluoride concentrations, we aim to provide actionable insights for policy planning and public health interventions, thereby contributing to evidence-based strategies for mitigating health risks associated with fluoride contamination.

Ultimately, the findings of this study are expected to have scientific, policy, and practical relevance, informing evidence-based policies, interdisciplinary collaboration, and targeted efforts to ensure clean and safe drinking water for all Ghanaians. By addressing fluoride contamination in groundwater and its health implications, it contributes to SDG 3 by promoting good health and well-being through identifying and mitigating health risks. Furthermore, the study supports SDG 6 by shedding light on the challenges related to clean water and sanitation, with a focus on ensuring the availability of safe drinking water. The research findings provide critical insights that can lead to targeted public health interventions and improved water resource management, thus advancing progress toward these Sustainable Development Goals in Ghana.

2. Materials and methods

2.1. Description of study area

Ghana is located in the geographical coordinates between 4° W and 2° E in longitude and 4° N and 11° N in latitude (Fig. 1). The country is administratively divided into 16 regions and is bordered to the north by Burkina Faso, to the south by the Gulf of Guinea, and to the east and west with Togo and Cote d'Ivoire respectively [28]. Ghana's population stood at approximately 31 million as at 2020. Ghana experiences a predominantly equatorial tropical climate in the southern regions and a semi-arid climate in the north. In the southern areas, temperatures remain consistently high throughout the year, with average daily temperatures ranging from 21 to 30 °C. The northeast region experiences the highest temperatures between February and April where peak temperatures of between 35 and 40 °C are recorded. Rainfall levels decrease as one moves northward, varying from approximately 1900 mm per year in the southwest to around 800 mm in the northern regions [29]. The geology of the northern part of Ghana is mainly composed of the Voltaian sedimentary basin as well as the Paleoproterozoic rocks of the Birimian and its associated granitic rocks. The southern geological province of the country is similarly made up of the Birimian formations and Middle Precambrian rock formations with the coastal sediments outcropping close to the southern shores of the country. The terrain in the country is predominantly gentle, with less than 1 % of the land having slopes exceeding 5 %. The altitude ranges from sea level to 885 m at Mount Afadjato. Extensive studies on the presence of F^- in groundwater have been conducted in Ghana.

2.2. Research approach

This study offers an in-depth analysis of how environmental policies and global trends have been utilized to address the pressing health risks associated with fluoride in groundwater sources across Ghana. By employing a triangulation of information from a diverse range of sources, including scholarly journals, articles, and comprehensive reports, the research explores both pre-existing conditions and anticipated future developments related to fluoride contamination and its health implications. It systematically examines primary sources while considering the factors influencing fluoride levels in Ghana's groundwater sources, as well as proposing potential strategies to mitigate this widespread health risk. In alignment with the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines [30], a rigorous data collection process was employed, with a meticulous aggregation and cross-referencing of information from various reputable academic databases like Google Scholar, PubMed, Science Direct, ProQuest, Web of Science, and Scopus. A combination of search terms encompassing "Fluoride contamination in groundwater in Ghana" OR "Groundwater fluoride levels in Ghana" AND "Fluoride in environmental media" OR "Health risks from fluoride exposure in Ghana"

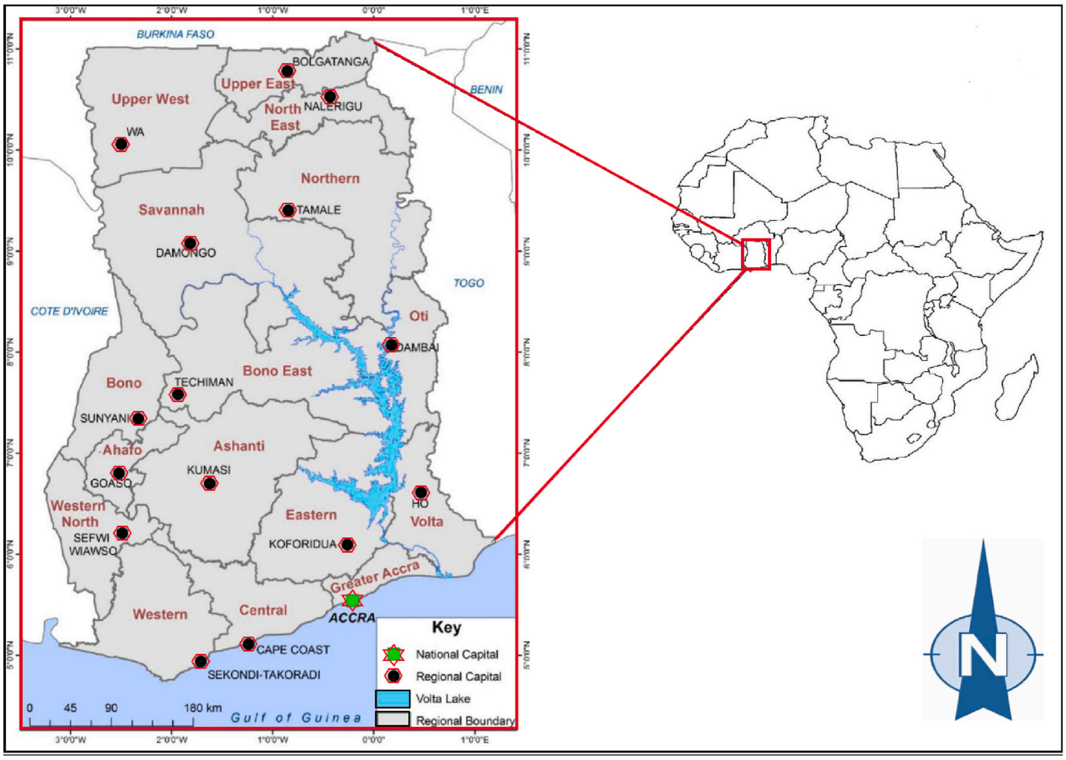

Fig. 1. Description of Ghana: study area.

OR “Geogenic fluoride in Ghana’s groundwater” OR “Ghana water quality and fluoride” OR “Geographic distribution of fluoride in Ghana” OR “fluoride in groundwater in Ghana” OR “health risks” OR “global trends of fluoride” were thoughtfully used to maximize the sensitivity and specificity of the search. Building upon the approach employed by Amuah et al. [31,32] and Kazapoe et al. [33], this systematic literature review involved a detailed assessment of 301 scholarly materials, with a focus on their relevance to the research’s main components: titles and keywords, abstracts, content significance, and the novel concepts and insights they offer regarding fluoride contamination in Ghana’s groundwater sources.

Each component underwent a thorough evaluation according to the following criteria.

- Title and Keywords (TiK): This component’s score considered the appropriateness of the title (Ti) and the relevance of keywords (Kw), with each accounting for 15 % of the total score.
- Abstract (As): The assessment of abstracts was based on the study’s stated purpose (Pu) (50 % weight), the clarity of the research approach/design (Rad) (50 % weight), and the comprehensive summary of findings (Saf) (70 % weight).
- Content assessment (CoA): This component involved the examination of several aspects, including the presentation of statistics (Sp) (40 % weight), the alignment with existing literature (Cl) (30 % weight), the inclusion of graphical elements like maps, charts, and figures (mcf) (20 % weight), the depth of result interpretation and contextual analysis (Ric) (50 % weight), and the soundness of the conclusion(s) drawn (Cs) (20 % weight).
- Concept assessment (Ca): The assessment of this component considered the novelty of the methodology (nm) (50 % weight), the parameters examined (Pe) (40 % weight), and the relationship between research question(s), objective(s), or hypothesis(es) (Rq) (50 % weight).

The final selection of literature was determined by aggregating these components into an overall score (Os) (weighted at 500 %) and subsequently converting them to a 100 % scale using the provided equations (Eqns. (1)–(6)) and the scale delineated in Table 1. Based on this evaluation, materials were categorized as ranging from suitable to extremely suitable for inclusion in the study.

$$\mathrm{Tik} = \mathrm{Ti} + \mathrm{Kw} \tag{1}$$

$$\mathrm{As} = \mathrm{Pu} + \mathrm{Rad} + \mathrm{Saf} \tag{2}$$

$$\mathrm{CoA} = \mathrm{Sp} + \mathrm{Cl} + \mathrm{mcf} + \mathrm{Ric} + \mathrm{Cs} \tag{3}$$

$$\mathrm{Ca} = \mathrm{mn} + \mathrm{Pe} + \mathrm{Rq} \tag{4}$$

$$\text{Sum of ratings by 5 experts } (\mathrm{Os}) = 5 \times [\mathrm{Tik} + \mathrm{As} + \mathrm{CoA} + \mathrm{CA}] \tag{5}$$

$$\text{Scaling to } 100\% = \mathrm{Sr} \times 0.2 \tag{6}$$

Ultimately, a total of 23 materials were deemed pertinent and met the criteria for inclusion in this study, as illustrated in Fig. 2. These components underwent rigorous scrutiny to ensure the selected literature sources were of high quality and relevance.

2.3. *Eligibility criteria*

Eligibility criteria for Inclusion: This review considered scholarly articles, research papers, reports, and authoritative sources published in reputable journals and academic databases, with a specific focus on fluoride levels in groundwater sources across Ghana. English-language publications or those with English-language abstracts were included, provided that their content directly addressed various aspects of fluoride concentration in Ghana’s groundwater sources, including sources, distribution, health risks, and potential mitigation strategies.

Exclusion criteria: This review excluded studies conducted outside the geographical boundaries of Ghana and non-peer-reviewed sources like editorial articles, opinion pieces, and news articles. Literature unrelated to fluoride levels in Ghana’s groundwater sources, such as studies not pertaining to fluoride sources, distribution, health implications, regulatory mechanisms, and mitigation strategies, were excluded. These criteria were applied to maintain the focus and reliability of the review.

Table 1
Criteria for evaluating and rating literature sources.

Rating (%)	Description
0–15	Poor
16–30	Fair
31–45	Moderate
46–60	Suitable
61–75	Very suitable
76–90	Highly suitable
>90	Extremely suitable

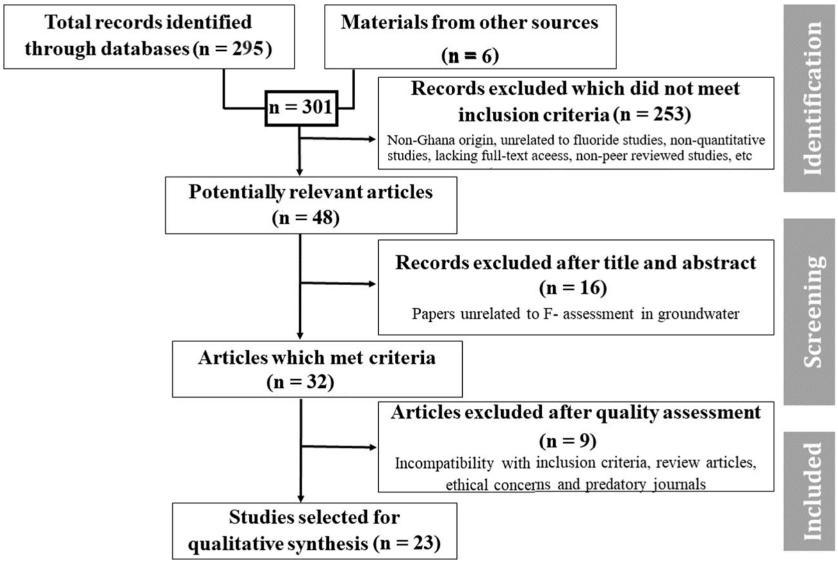

Fig. 2. PRISMA flowchart illustrating the search process.

2.4. *Data extraction*

Initially, a preliminary test of the data extraction form was performed by one reviewer, and necessary refinements were implemented to include crucial information, such as author details, study type, study location, and specifics regarding air quality in Ghana. Following this refinement phase, the subsequent data extraction and review procedures were independently conducted by three distinct authors. In cases of discrepancies or disagreements, the reviewers worked together to reach a collaborative resolution.

2.5. *Data analysis*

Data analysis for this study followed a narrative synthesis approach, systematically examining and integrating the findings from the selected research works, with a specific focus on the outcomes of interest pertaining to fluoride in groundwater sources in Ghana. It is important to note that all the studies included in this review were of a quantitative nature. However, it is worth mentioning that a meta-analysis was not conducted as part of this review.

3. Results and discussion

3.1. *F^- occurrence and movement in groundwater*

Fluoride can be found in natural waters across a wide range of concentrations, spanning from minute levels to those exceeding established consumption standards [25]. The presence of fluoride in natural water sources is influenced by numerous factors. According to Zango et al. [14] and Kazapoe et al. [34], these factors encompass climatic conditions, aquifer composition, geological host rock composition, the geochemical environment, the mixing of diverse recharge waters, and the prevailing hydrogeological conditions. In addition to these factors, Yidana et al. [25] also asserted that pH, temperature, anionic exchange capacity, and the presence or absence of Ca^{2+} and HCO_3^- ions in the water contribute to fluoride occurrence. Zango et al. [14] further emphasized that the high electronegativity and solubility of fluoride, combined with various geochemical processes, make it readily accessible in groundwater. It is worth noting that elemental fluorine in its free state is unstable and does not play a role in toxicology, as it quickly reacts to form fluoride compounds [24].

Kumar et al. [35], employing petrographic analysis of host rock, attributed the elevated concentrations of F^- in groundwater sources in the Indo-Gangetic Alluvial plains of India to intense interactions between rocks and water, resulting in the dissolution of fluoride-bearing minerals. Rocks with granitic compositions are known to contain several fluoride-bearing minerals such as Amphibole, apatite, and micas like biotite and muscovite [19]. Sunkari et al. [8] have comprehensively documented the mechanisms underlying fluoride occurrence in these geological contexts. In their study, the authors revealed that the occurrence of fluoride in groundwater sources is achieved by two main reaction processes.

1. Dissolution of fluoride-bearing minerals such as fluorapatite ($Ca_5(PO_4)_3F$) in most magmatic and sedimentary terrains to release Ca^{2+} and F^-.

$$CaCO_3 + 2\,F^- + H^+ = CaF_2 + HCO_3^- \qquad (7)$$

2. The precipitation of calcite to remove Ca^{2+} from the solution according to the following reactions:

$$Ca^{2+} + CO_3^{2-} = CaCO_3 \tag{8}$$

$$Ca_5(PO_4)_3F + 3H^+ = 5Ca^{2+} + 3HPO_4^{2-} + F^- \tag{9}$$

The reaction described above leads to a reduction in the Ca^{2+} activity within the solution. Subsequently, the Ca^{2+} can be eliminated from the solution through ion exchange with Na^+ from clay minerals, thereby modifying the solution's saturation state. This alteration is coupled with an increase in fluorite/fluorapatite dissolution. In this context, fluorapatite dissolves, releasing both calcium and fluoride ions into the solution, while calcite, a carbonate mineral, sequesters the released Ca^{2+}, thereby enhancing the concentration of F^- in groundwater sources [8]. The dissolution of fluorapatite and the precipitation of calcite occur concurrently. Thus, the reduction of the activity of Ca^{2+} promotes the dissolution of fluoropatite which releases F^- into groundwater [8].

The aforementioned findings hold significant implications across various domains. From a public health perspective, this understanding is vital in identifying regions at risk of high fluoride concentrations and enables the implementation of measures to ensure safe drinking water. Moreover, it has environmental consequences, as elevated fluoride levels can adversely affect aquatic ecosystems and biodiversity. Water resource management benefits from these insights, allowing for informed decisions on groundwater extraction and quality preservation. In the realm of geological research, these findings contribute to knowledge about geochemical processes and mineral dissolution in granitic rock formations. Additionally, policymakers can utilize this knowledge to establish regulations and standards for fluoride concentration in drinking water. Lastly, educational and awareness initiatives can empower affected communities to make informed choices regarding their water sources. In essence, these findings have wide-ranging implications, influencing public health, environmental protection, water management, geological research, policy development, and community education, all contributing to the safe and sustainable use of groundwater resources.

3.2. F^- occurrence and movement in soils

Fluoride in soil manifests in both elemental fluorine and mineral compounds [36]. Its predominant residence is within the clay fraction of soil, a feature influenced by the clay and organic carbon content, as well as soil pH [37]. Typically, the average fluoride content in soil registers at 0.3 g/kg, falling within the normal range of 30–300 mg/L^{-1} [36]. This concentration level generally poses no harm to plants and animals [36]. Of biological significance to flora and fauna is the soluble fluoride content found in soil, a component that organisms can readily assimilate [37]. This soluble fluoride presence in soil stems from both natural processes and human-induced activities [38]. Among the principal natural processes are the weathering of source rocks containing fluoride-bearing minerals and volcanic activity, which contribute to the introduction of fluoride into soils [27]. Key mineral contributors include Apatite (CaF_2.3-$Ca_3(PO_4)_2$), Cryolite (Na_3.AlF_6), and Fluorospar (CaF_2) fragments [26,39,40].

Pickering [39] underscores that industries utilizing raw materials with trace fluoride contents hold the potential to release significant quantities of gaseous fluorides (SiF_4 and HF) and particulate fluorides, thereby augmenting soil fluoride levels in the vicinity. This influence extends to industrial operations encompassing brick manufacturing, coal-fired power generation, iron production, and fertilizer manufacturing. Moirana et al. [41] and Huang et al. [42] further noted that the application of phosphate fertilizers, pesticides, and sewage sludge to soil can substantially elevate soil fluoride levels, leading to increased phytoaccumulation.

Hong et al. [37] stated that over 90 % of natural fluoride in soils exists in insoluble or strongly bounded forms, closely associated with soil particles. Jha et al. [26] mentioned that fluoride in soil takes on various forms, including resin-extractable, water-soluble, and acid-extractable compounds. Aligning with this perspective, Pickering [39] also affirmed that the amount of F^- adsorbed by soils demonstrates variability based on soil parameters like pH and soil type. Edmunds and Smedley [21] added that soil particle adsorption of F^- thrives under slightly acidic conditions, with uptake in acidic soils potentially reaching tenfold that observed in alkaline soils. Contrarily, [37] asserted that a majority of fluoride in soils assumes insoluble states, rendering it less accessible to plants. Nevertheless, they acknowledged that low pH and the presence of clay and organic matter can elevate F^- concentrations in soil. Flühler et al. [43] also reported that the mobility of highly reactive fluoride in soils, and consequently the rate of accumulation, hinges upon intricate interactions between the liquid and solid phases of the soil matrix. The low affinity of organic matter for fluoride leads to a common trend of total soil fluoride content increasing with depth. It has been estimated that the global average fluoride content in soils stands at 320 mg/L^{-1} [26].

Understanding the presence of fluoride in soil, the sources, and chemical forms is crucial for agricultural practices [37]. However, in the context of Ghana, there seems to be noticeable scarcity research attention in this particular area. Despite the critical role of soil fluoride levels in influencing crop growth, productivity, and potential implications for food safety, there is a lack of comprehensive studies investigating the sources, distribution, and chemical forms of fluoride in the country. This research gap restricts the country's ability to develop targeted strategies to manage fluoride levels in soil, potentially impacting agricultural yields and the overall safety of food produced in these areas. Farmers and agricultural experts need to be aware of how fluoride levels in soil can affect crop growth and animal health. Additionally, they knowledged that over 90 % of natural fluoride in soils exists in strongly bounded forms can guide soil management strategies to minimize potential risks associated with elevated fluoride levels [44]. From an environmental perspective, recognizing the impact of industrial processes, such as brick manufacturing and power generation, on soil fluoride levels highlights the importance of regulating emissions and waste disposal to prevent soil contamination [45]. Moreover, the influence of phosphate fertilizers, pesticides, and sewage sludge on soil fluoride levels underscores the need for responsible and sustainable agricultural practices to avoid excessive phytoaccumulation [46].

The variability of fluoride adsorption by soils based on pH and soil type emphasizes the importance of soil testing and management tailored to specific agricultural and environmental contexts [47]. Soil pH adjustment and the incorporation of organic matter can help mitigate the risk of elevated fluoride concentrations in soils [37]. These findings are relevant for policymakers, farmers, and environmental agencies, as they provide insights into how to maintain soil quality, ensure food safety, and prevent soil contamination in regions where fluoride levels are a concern. Overall, the implications of this research extend to agricultural practices, environmental management, and public health, emphasizing the importance of informed decision-making and sustainable land use.

3.3. Fluoride: occurrence in plants

Fluoride has been known to be a cumulative substance in the foliage of plants (Fig. 3) [37]. Different plants have different tolerance levels for fluoride uptake [38]. Rizzu et al. [27] asserted that the most important factor for the uptake of F^- in soils by plants is the speciation of the F-. According to Senkondo [38], the high electronegativity of fluorine makes it combine readily with other elements to form stable compounds that are insoluble in soils. Kabata-Pendias and Szteke [48] reported that although plants can uptake fluoride from the soil, the increased concentration of it in plants is usually from airborne fluoride compounds. In the soil, the roots of plants passively absorb dissolved fluoride from the soil water and it is then moved via the xylematic conducts up to the stem, leaves, and fruits Rizzu et al. [27]. From the atmosphere, gaseous fluoride moves into the leaf through the stomata and then dissolves in the water that permeates the cell wall [26]. The fluoride then moves to the margins and tips of the leaf which are the sites of the greatest evaporation of the leaves. The excessive concentration of fluoride in vegetation leads to visible leaf injury [37]. In plants that are prone to fluoride toxicity, fluoride negatively affects reproduction, growth, germination, crop yield, and metabolism of amino acids [37].

F^- plants have significant implications for agriculture, environmental management, and food safety [49]. However, there appears to be a notable scarcity of research emphasis on the cumulative nature of fluoride in plant foliage in Ghana. This gap in research attention is critical given the potential risks associated with fluoride uptake in agricultural crops. Different plants have varying tolerance levels for fluoride, which highlights the importance of selecting suitable plant species for cultivation in regions with elevated soil fluoride levels [50]. The speciation of fluoride in soils and the uptake by plants underscore the complexity of fluoride movement within the plant system [51]. This knowledge is essential for farmers and agricultural experts to make informed decisions about crop selection and cultivation practices in areas with potential fluoride exposure. The impact of excessive fluoride concentration on plants, including visible leaf injury and detrimental effects on growth, germination, crop yield, and amino acid metabolism as stated by Panda [52], Baunthiyal et al. [53], Rizzu et al. [54] emphasizes the need for soil and water management to prevent fluoride toxicity in agricultural settings in Ghana. It also underscores the importance of monitoring and regulating industrial emissions that may contribute to airborne fluoride compounds in the country. These findings have practical relevance for agriculture and environmental policies as they inform agricultural practices to minimize the risks of fluoride toxicity in crops and highlight the importance of selecting appropriate plant varieties for specific regions. Additionally, these findings can guide efforts to regulate and reduce fluoride emissions from industrial sources to protect plant health and ensure food safety.

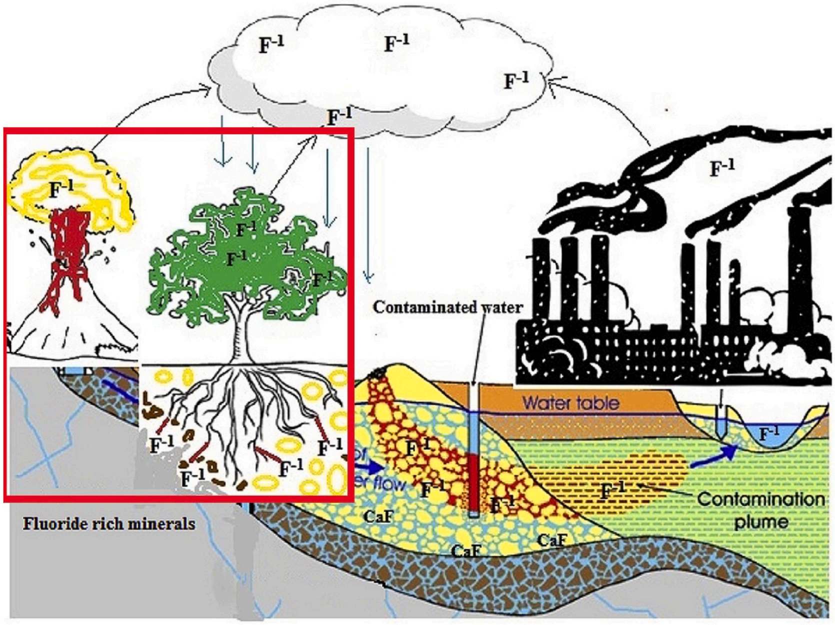

Fig. 3. Dynamics and contamination of F^- in soil (modified from Ref. [44]).

3.4. Fluoride: global occurrence and health implication

The global burden of endemic fluorosis, a health issue stemming from elevated F^- concentrations in drinking water, is estimated to account for a substantial 65 % [14]. Numerous countries across South America, Asia, Australia, and Africa have grappled with the predicament of fluoride contamination and its consequential health ramifications [12]; [55]. Argentina, positioned as one of the most severely affected regions in Latin America, alongside Mexico, Peru, and Chile, reports alarming fluoride levels, with Martinez et al. [56] documenting readings as high as 7.2 mg/L^{-1} to 10 mg/L^{-1} in many parts of the nation. Notably, Borgnino et al. [57] emphasize that an estimated 1.2 million Argentinians consume groundwater exceeding both national and international fluoride standards. Buchhamer et al. [58] contend that the occurrence of fluoride in Argentina exhibits a strong association with the presence of arsenic, a phenomenon corroborated by Guo et al. [59] in their research.

In Mexico, Reyes-Gómez et al. [60] revealed that a staggering 89 % of sampled water wells exceeded the standards set by the WHO for fluoride content. Elevated fluoride concentrations have also been reported in other countires, including the United States of America, Sweden, the Czech Republic, Canada, Poland, and Finland [26,61,62].

The issue of endemic fluorosis has profoundly affected two of the world's most populous countries, India and China. By 1995, approximately one-tenth of China's populace had been exposed to endemic fluorosis [63]. In the Kuitun area of China's Zhuiger Basin, fluoride levels as high as 21.5 mg/L^{-1} were recorded in 1997. A subsequent study in 2004 revealed that over 26 million Chinese individuals suffered from dental fluorosis, with an estimated one million more afflicted by skeletal fluorosis Srivastava and Flora, [64]. India grapples with a similar challenge, as reported by Chinoy [65] and Viswanathan et al. [66], with approximately 20 million Indians severely affected by fluorosis and an additional 40 million at risk due to factors such as population growth, limited awareness concerning water quality monitoring, and indiscriminate tube well drilling. Guo et al. [59] further documented excessive fluoride concentrations in numerous wells in Inner Mongolia.

Africa has experienced the repercussions of fluoride toxicity, with countries like South Africa, Tanzania, Sudan, Kenya, and Ghana (Fig. 4) grappling with cases of fluorosis [63]; [67]. Tanzania stands out as one of the most severely fluoride-affected areas globally [63]. The East African Rift Valley (EARV) has witnessed some of the highest recorded F^- levels in groundwater, exceeding 100 mg/L^{-1}, as reported by Rizzu et al. [27]. Surface water bodies in the region have even registered concentrations of 700 mg/L^{-1}. Vuhahula et al. [68] reported a staggering 100 % prevalence rate of dental fluorosis in the Arusha Region of Tanzania, attributing it to the intense volcanic activity characteristic of the EARV. This geological phenomenon, as expounded by Rizzu et al. [27], is among the few active rift valleys globally and is linked to the release of excessive fluoride into the surrounding groundwater. Other African countries encompassed by the EARV, such as Uganda, Ethiopia, Kenya, and Djibouti, all contend with fluoride toxicity issues [69]. In Uganda, research by Rwenyoni et al. [70] and Rwenyoni et al. [71] underscores the role of altitude in influencing the prevalence and severity of fluorosis in both low and high-fluoride regions. Ethiopia, featuring the highest percentage of the African rift valley, exhibits an unsurprising trend of excess fluoride concentrations near active and sub-active regional fields characterized by acidic volcanics within the high-temperature rift floor, as discovered by Ayenew [72]. In parts of Ethiopia like Wonji and Awassa, Olsson [73] conducted a study revealing that 99 % of sampled children aged 6–7 years exhibited dental fluorosis. Furi et al. [74] also identified fluoride levels exceeding WHO permissible limits in 60 % of samples from the Middle Awash Basin. Additional studies on fluorosis in Ethiopia have

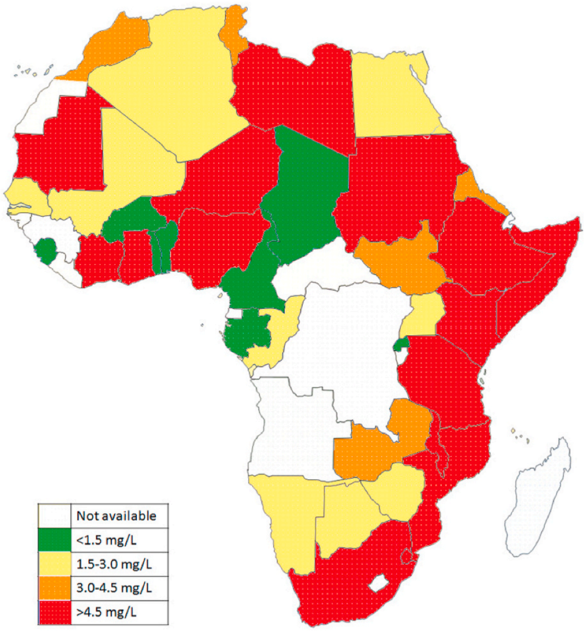

Fig. 4. Distribution of F^- in groundwater in Africa [78].

been documented by Ali et al. [75] and Tekle-Haimanot et al. [76]. Nigeria also grapples with fluoride contamination, as evidenced by research conducted by Dibal et al. [77]. Their findings indicate fluoride concentrations ranging from 0.03 to 10.3 mg/L^{-1} in basement aquifers and 0–5 mg/L^{-1} in sedimentary rocks. Dibal et al. [77] conducted a comparative study of groundwater fluoride concentrations in Northcentral Nigeria's Langtang area, revealing higher levels in the dry season compared to the rainy season, with fluoride levels increasing with depth.

A more detailed report is presented by Brindha and Elango [79] and Abanyie et al. [55] who highlighted the global distribution of F^{-}. The distribution of F^{-} in groundwater spanned from the southwestern part of South American continent, particularly in Chile and northern and eastern Argentina. In North America, regions like Mexico (including Oaxaca, Mexico City, Toluca, Leon, Potosi, Zacatecas, Monterry, San Antanio, Austin, and Chihauhua) and Canada (such as Labrador City, Williston, Calgary, Swift Current, Prince Albert, among others) exhibit high F^{-} contents in their groundwater. Similarly, several African countries like South Africa, Lesotho, Senegal, Somalia, Swaziland, southern Mozambique, southeastern Zimbabwe, Namibia, central Tanzania, Niger stretching downwards into Nigeria, northern Tunisia through Libya, Egypt, Israel, Jordan, Lebanon, Syria, Iraq, Iran, Turkmenistan, and Turkey portray significant F levels. Notably, high F content is observed in the southeastern part of Pakistan, extending into India, as well as in Brunei, Indonesia, Thailand, Japan, Laos, Cambodia, Vietnam, and the central parts of Russia and China. Additionally, regions in the north- and southwestern and northeastern areas of Australia, as well as specific areas in Europe such as Spain, Norway, Germany, and Turkey, exhibit noteworthy levels of F in their groundwater [55,79]. Moreover, countries like Sri Lanka, Malawi, Brazil, and Ghana have also been identified to possess significantly high levels of F in their groundwater systems [55].

The global prevalence of high fluoride concentrations in drinking water, leading to endemic fluorosis, presents a widespread and severe health challenge across various regions. Millions of people in countries such as Argentina, Mexico, India, and China suffer from dental and skeletal fluorosis due to excessive fluoride exposure. This issue underscores the critical importance of monitoring water sources and implementing effective water treatment processes to ensure safe drinking water. Geological and hydrogeological factors, notably in regions with volcanic activity like the East African Rift Valley, contribute to elevated fluoride levels, necessitating a better understanding of these processes for mitigation. Public awareness and education programs are essential to inform communities about the risks and mitigation strategies. Factors like altitude and seasonal variations further complicate the problem, emphasizing the need for tailored approaches to address the issue in different contexts. The relevance of these findings extends to public health, environmental management, and water resource policies. They call for immediate actions to address water quality issues, regulate industrial activities that contribute to fluoride contamination, and implement sustainable water treatment and management practices to safeguard the health of affected populations. Additionally, these findings emphasize the importance of geological and hydrogeological factors in understanding and addressing fluoride contamination on a global scale. These findings support the urgency of coordinated efforts to protect public health and ensure clean water sources globally.

3.5. F^{-} occurrence in groundwater in Ghana

Ghana grapples with the pervasive challenge of fluoride toxicity, a subject that has garnered substantial research attention from scholars such as Apambire et al. [23], Sunkari et al. [19], Zango et al. [20], Yidana et al. [25], and Firempong et al. [80]. These investigations have primarily honed in on specific geographic areas, primarily within Northern Ghana. The focal point of these studies predominantly revolves around the intricate interplay between rocks and water as a pivotal contributor to fluoride contamination in groundwater. Notably, a significant portion of this research has concentrated on the Bongo District, situated in northeastern Ghana. This focus on the Bongo District is primarily due to its geological characteristics, which make it a hotspot for fluoride-related issues. A

Table 2
Some studies on F^{-} levels in groundwater in Ghana.

Authors (Year)	Fluoride Range	District/Region
Apabire et al. [23]	0.11 mg/L^{-1} – 4.60 mg/L^{-1}	Bongo District/Upper East
Yidana et al. [25]	0.15 mg/L^{-1} – 8.12 mg/L^{-1}	Northern Ghana
Salifu et al. [16]	1.0 mg/L^{-1}> − <1.5 mg/L^{-1}	Gushegu District/Northern Region
Oyelude et al. [81]	0.01 mg/L^{-1} – 0.37 mg/L^{-1}	Kassena-Nankana
Dongzagla et al. [82]	0.6 mg/L^{-1} – 1.5 mg/L^{-1}	Jirapa
Dongzagla et al. [82]	0.6 mg/L^{-1} – 2.0 mg/L^{-1}	Kassena-Nankana
Alfredo et al. [7]	4 % of samples >1.5 mg/L^{-1} (278 functioning and 8 capped boreholes)	Bongo District/Upper East
Firempong et al. [80]	0.95 mg/L^{-1} – 2.36 mg/L^{-1}	Bongo District/Upper East
Sunkari et al. [8]	(1.71 mg/L^{-1} – 4.0 mg/L^{-1})	Bongo District/Upper East
	(0.3 mg/L^{-1} – 0.8 mg/L^{-1})	Sekyere South/Ashanti
Zango et al. [14]	0.05 mg/L^{-1} – 13.29 mg/L^{-1}	Nalerigu/North East
Sunkari and Abu [19]	1.71 mg/L^{-1} – 4.0 mg/L^{-1}	Bongo District/Upper East
Zango et al. [20]	0.35 mg/L^{-1} – 3.95 mg/L^{-1}	Vea Catchment/North Eastern Ghana
Sunkari et al. [19]	0.05 mg/L^{-1} – 13.29 mg/L^{-1}	North Eastern Ghana
Ganyaglo et al. [83]	0.46 mg/L^{-1} – 2.37 mg/L^{-1}	Kassena-Nankana West (existing wells)
	0.11 mg/L^{-1} – 4.27 mg/L^{-1}	Kassena-Nankana West (newly drilled wells)
	0.54 mg/L^{-1} – 1.98 mg/L^{-1}	Bongo (existing wells)
	0.29 mg/L^{-1} – 3.74 mg/L^{-1}	Bongo (newly drilled wells)
Sunkari et al. [8]	0.3 mg/L^{-1} – 0.8 mg/L^{-1}	Sekyere South
Sunkari et al. [84]	0.43 mg/L^{-1} – 3.61 mg/L^{-1}	Bongo District/Upper East

comprehensive overview of research endeavours related to fluoride contamination of drinking water resources and recorded fluorosis cases in Ghana is presented in Table 2. While extensive efforts have been dedicated to studying F^{-} in Ghana, certain uncharted areas, as depicted in Fig. 5, beckon further research scrutiny.

Significant regions with high likelihoods of fluoride contamination are discernible across the country, with the northeastern part emerging as the most profoundly impacted, boasting probabilities ranging from 50 % to 90 % [5]. Additionally, Araya et al. [5] underscored that this affected region spans from Eastern Gonja through to the northernmost precinct of Bongo, except a low-probability corridor nestled from the Mamprugu Moagduri to the Bunkpurugu Yonyo districts. In the northwestern expanse, encompassing the Sawla-Tuna-Kalba and Bole districts, the probability of groundwater fluoride contamination hovers around 50 %–70 %. Fluoride contamination in northern Ghana has garnered considerable attention within the academic literature. The Northern Region, as depicted in Fig. 6, has earned notoriety for its elevated F^{-} levels, primarily attributed to the geological formations of the Oti Pendjari Group (in the Saboba and Chereponi Districts), with reported F^{-} levels exceeding 4.0 mg/L^{-1} [85].

The findings of Tay [86] in the Savelugu-Nanton district showed an exceedance of F– in 10.8 % of groundwater sources analyzed with F– ranging between <0.5 mg/L^{-1} and 3.0 mg/L^{-1}. The study detailed that Dohi, Zetigu, Manguli, Naprisi and Fazhini were the communities with very high levels (1.5 mg/L^{-1} to 3.0 mg/L^{-1}). Similar to these claims, a recent study by Sunkari et al. [87] in the Saboba area revealed that F– content in groundwater exhibited variability, with an average concentration of 1.33 mg/L^{-1} and ranging from 0.6 to 4.7 mg/L^{-1}. Natchan, Boagban, Kunkunzoli, District Assembly, Boakpalb, Gbaln and Gbong showing elevated concentrations of F–, projecting high occurrence in the northwestern part of the district. The main contributors to groundwater fluoridation were identified as micas and fluorite. In the Kassena-Nankana Municipality, Oyelude et al. [81] reported low 0.01 mg/L^{-1} to 0.81 mg/L^{-1}. Similarly, low F– have been recorded in Jirapa (0.6 mg/L^{-1} – 1.5 mg/L^{-1}) whereas in the Kassena-Nankana area some groundwater systems had F– reaching 2.0 mg/L^{-1} [82]. In the Kassena Nankana West District, newly drilled wells exhibited a wide range of fluoride concentrations, ranging from 0.11 mg/L^{-1} to 4.27 mg/L^{-1} (avg. 1.18 mg/L^{-1}). Particularly high fluoride levels were found in Naveem (2.10 mg/L^{-1}), Kalivio CHPS compound (3.70 mg/L^{-1}), Akania (4.27 mg/L^{-1}), and Aneo (1.89 mg/L^{-1}). Existing wells, on the other hand, showed lower fluoride concentrations ranging from 0.46 mg/L^{-1} to 2.37 mg/L^{-1}. Some wells, such as Kalivio Gugoro (2.37 mg/L^{-1}) and Banyui (2.15 mg/L^{-1}), exceeded the WHO guideline value of 1.5 mg/L^{-1}, representing about 15 % of the sampled groundwater. Overall, newly drilled wells had slightly higher average fluoride levels (1.18 mg/L^{-1}) compared to existing wells (1.14 mg/L^{-1}), largely due to many existing wells with high fluoride values being capped. The spatial distribution revealed higher fluoride concentrations in the eastern and western parts of the study area [83].

Notably, high F^{-} concentrations are also observed in the northwestern quadrant of Ghana, chiefly within the precincts of the Savannah region, where studies by Arhin and Affam [88] and Loh et al. [89] have reported concentrations surpassing 1.5 mg/L^{-1}.

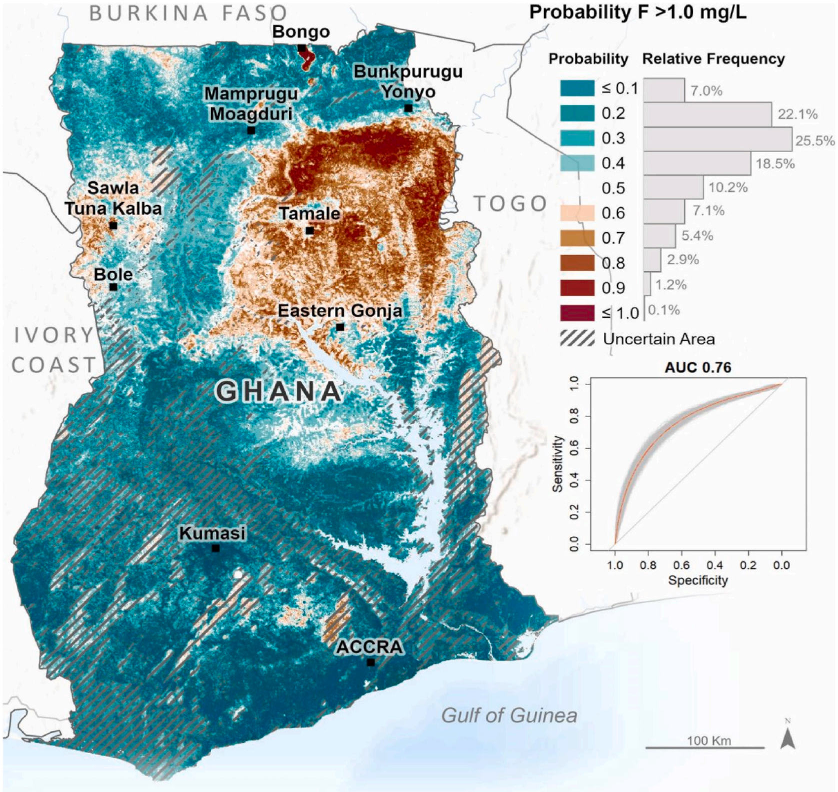

Fig. 5. F^{-} levels in groundwater in Ghana [5].

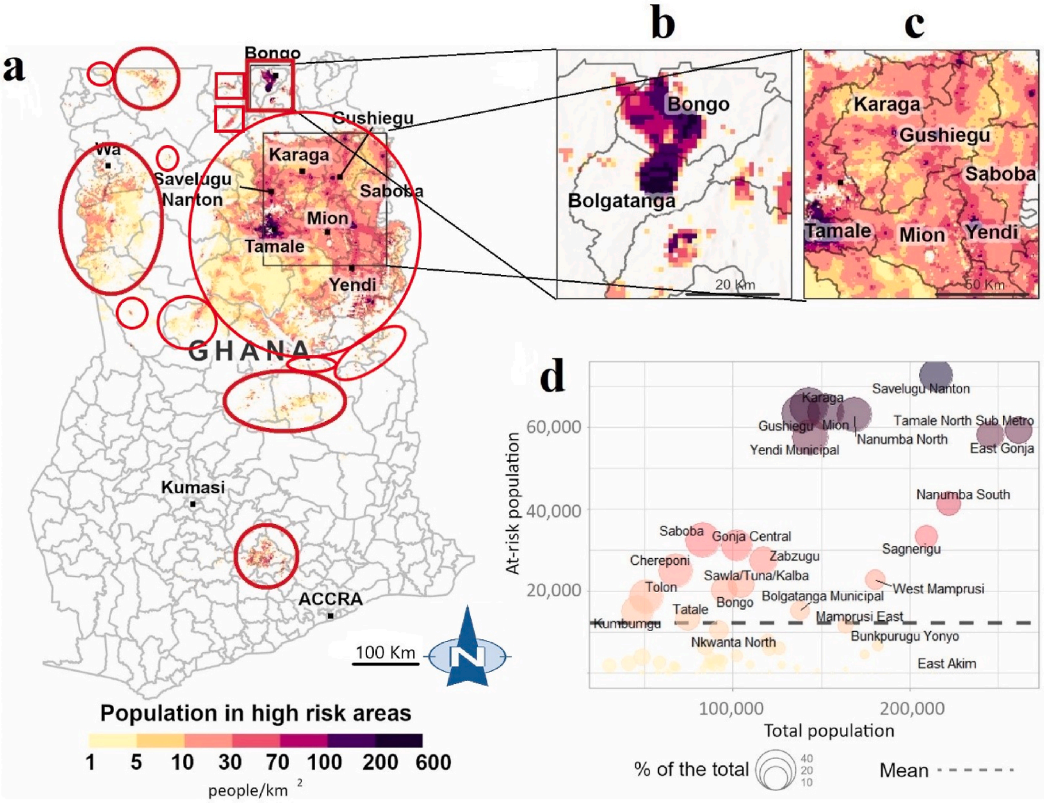

Fig. 6. (a) Hotspot F^- areas relating to groundwater in Ghana (exposure risk of above 1.0 mg/L^{-1}, probability cutoff at 0.49) (b) Bongo (c) Karaga and Tamale and (d) Population data for each district was compared with the at-risk population, excluding areas with high uncertainty (3 % of at-risk population) (modified from Ref. [5]).

However, in a similar certain of the Maluwe catchment, Abu et al. [90] reported low F– levels except in Tinga. In a distinct southern enclave near Accra, the likelihood of fluoride contamination registers at approximately 50 %–60 %. As indicated by Araya et al. [5], a mere 1.2 % and 16.5 % of the country's expanse exhibit probabilities exceeding 80 % and 50 %, respectively, of groundwater fluoride concentrations surpassing 1.0 mg/L^{-1}. The model confers a 50 %–60 % probability of F^- above 1.0 mg/L^{-1} only in specific areas (Eastern Region), with these concentrations predominantly linked to delimited areas within the Eburnearn supergroup. However, in the southern swathes of the nation, particularly in the Western, Western North, and Ahafo regions, the model encounters diminished certainty, attributable to the paucity of F^- studies [5]. Furthermore, this study acknowledges the influence of temperature on F^- distribution, particularly in the context of climate change projections. As temperatures rise due to climate change, there is an anticipated impact on the distribution of F-, potentially leading to the emergence of new endemic F^- areas within Ghana. This aspect is crucial to consider as it highlights the dynamic nature of F^- contamination and underscores the need for proactive measures to address emerging challenges associated with climate-induced changes in F^- distribution.

In the North East Region, Zango et al. [14] conducted a study involving eighty-eight (88) groundwater samples to assess the hydrochemical factors and evaluate the potential human health risks associated with groundwater fluoride and boron levels in the study area. The research findings indicated that the fluoride content in the groundwater sources varied within the range of 0.05 mg/L^{-1} to 13.29 mg/L^{-1}, with an average concentration of 3.26 mg/L^{-1}. Importantly, the maximum concentration exceeded the WHO's recommended threshold. The study disclosed that 61 out of the borehole samples, which accounted for 75 %, exhibited significantly elevated fluoride contamination. Furthermore, the research pointed out that the alkaline pH of the groundwater played a crucial role in contributing to the heightened levels of F^- in the groundwater samples. The study further explained that the surplus OH- ligands in the groundwater, combined with the alkaline pH, led to the replacement of exchangeable F^- within the muscovite and biotite minerals found locally in the study area. As a result, the groundwater's fluoride concentration increased.

Salifu et al. [16] also focused on the F^- constituent in water within the Gushegu district of northern Ghana. The study considered the origin of elevated fluoride content in the groundwater sources (saturated and unsaturated zones of the underlying aquifer) of the study area. The authors' application of factor analysis and hierarchical cluster analysis revealed that the use of phosphate and sulfate fertilizers in the area is the root source of fluoride contamination in the groundwater. The source of the fluoride as stated by the study varied from Zango et al. [14] which discussed that the rock-water interaction with muscovite and biotite minerals was the source of the groundwater fluoride. This is quite surprising because the study areas for both research falls within the same geologic formation. However, the difference could be due to the different approaches used to explain the source of the fluoride as Zango et al. [14] opted for a more hydrogeochemical approach as opposed to Salifu et al. [16] which applied statistical methods to assess the source of the fluoride concentration. The results obtained by Salifu et al. [16] were similar to the findings of Yidana et al. [25] in the same area.

Focusing on the southern part of the country, Sunkari et al. [8] assessed the F^{-} levels of groundwater samples in the Sekyere South district showing contrast results to that of the Bongo District. The authors determined that the F^{-} contents in the groundwater samples spanned between 0.4 mg/L^{-1} and 0.6 mg/L^{-1}. These concentrations are well below the WHO guideline limit for F^{-} in drinking water sources. The authors attributed the presence of F^{-} in the groundwater samples to muscovite minerals within the geology of the study area.

Research on F^{-} levels in various regions of Ghana have revealed notable implications. Regional disparities in water quality become evident, with some areas facing significant challenges due to elevated F^{-} concentrations in groundwater. These disparities highlight the need for targeted interventions in high-risk regions. The studies also shed light on the sources of F^{-} contamination, which can vary from geological interactions to agricultural practices, emphasizing the importance of understanding local factors. Elevated F^{-} levels in groundwater pose health risks, particularly for dental and skeletal fluorosis. Furthermore, the research underscores the need for interdisciplinary collaboration, additional studies, and effective mitigation strategies to ensure access to safe drinking water, considering the complexities of water quality issues.

The afore-stated findings in Ghana reveal a pervasive challenge, primarily affecting the northeastern and northern regions of the country. Elevated fluoride levels in groundwater, often exceeding safe limits, have been observed in specific areas such as the Bongo District. The geological characteristics of these regions play a significant role in fluoride contamination. These findings emphasize the need for comprehensive monitoring and mitigation efforts, particularly in areas with high probabilities of groundwater fluoride contamination. Public health awareness and education programs should be implemented to inform communities about the risks associated with fluoride exposure and promote safe drinking water practices. Additionally, further research is warranted to explore areas with limited data, particularly in the southern regions of Ghana, to gain a comprehensive understanding of the extent of fluoride contamination and its implications on public health.

3.6. F^{-} levels in the Bongo area: Ghana's most endemic F^{-} area

The Bongo area in Ghana stands as one of the most profoundly affected regions, earning its distinction of being the country's most endemic area for elevated F^{-} levels in groundwater [19]. In this enclave, the pervasive issue of F^{-} toxicity has garnered considerable attention from researchers and health authorities [8]. The unique geological and hydrogeological characteristics of the Bongo District, situated within the Upper East Region of Ghana, have contributed to the heightened prevalence of F^{-} in its groundwater resources [91]. The presence of fluoride in groundwater within the Bongo District is linked to distinct geological formations found in the area, including the Birimian metavolcanics, metasediments, granitoids, and the Bongo granitic rocks [23,6]. This introductory glimpse sets the stage for a closer examination of the challenges and dynamics surrounding F^{-} levels in the Bongo area, shedding light on the extensive research efforts and ongoing concerns in this endemic region.

Apambire et al. [23] described the geochemistry, genesis, and health concerns of the fluoriferous groundwater of the Bongo District of Ghana to the geology of the area. In the research, the authors gave the range of F^{-} levels of groundwater sources flowing through each of the four geologic types in the district (Table 3). The study identified that the areas of high F^{-} were skewed in favour of the Bongo granitic rock suite. Sunkari and Abu [19] had a near-same value range for the F^{-} levels in the groundwater in their research in the same study area. The study discussed an F^{-} range of 1.71 mg/L^{-1} to mg/L^{-1}. It should be noted that dissimilar to Apambire et al. [23], Sunkari and Abu [19] did not consider the concentrations of F^{-} in groundwater of the different geologic formations. It must be pointed out also that both studies attempted to ascertain the F^{-} content in groundwater sources within the study area in contrast with the geologic background of the area. Apambire et al. [23] reported F^{-} concentrations in the study area were high at the northern and southern edges of the area whereas Sunkari and Abu [19] described higher concentrations within the central portions of the district. The geospatial distribution of F^{-} within the Bongo District as determined by Sunkari and Abu [19] was similar to Sunkari et al. [8] with almost the same values for the F^{-} concentrations. The results obtained by Sunkari and Abu [19] and Sunkari et al. [8] were different from Apambire et al. [23]. However, this contradiction could be attributed to different sampling sizes as Apambire et al. [23] sourced 371 groundwater systems and Sunkari and Abu [19] and Sunkari et al. [8] studied 30 sources.

Table 3

Geology of the Bongo District and their fluoride content.

Rock type	Formation	Range	Average	Reference(s)
Bongo granite	Bongo granitic suite	200–2000 mg/L^{-1}	792 (12) mg/L-1	Murray [92] and Apambire et al. [23]
Sekoti granodiorite	Bongo granitic suite	1000–1600 mg/L-1	825 (4) mg/L-1	Murray [92]
Birimian horblende granodiorite	Upper Birimian Granitoids	tr-500 mg/L-1	100 (10) mg/L-1	Murray [92] and Apambire et al. [23]
Birimian Biotite granodiorite	Upper Birimian Granitoids	tr-500 mg/L-1	225 (4) mg/L-1	Murray [92]
Birimian Biotite Gneiss	Upper Birimian Granitoids	tr-100 mg/L-1	33 (3) mg/L-1	Murray [92]
Birimian phyllite	Upper Birimian Metasediments	200–500 mg/L-1	350 (4) mg/L-1	Murray [92] andApambire et al. [23]
Birimian greenstone	Upper Birimian Metavolcanics	tr-537 mg/L-1	365 (3) mg/L-1	Murray [92] and Apambire et al. [23]
Birimian Metavolcanics		0.11 mg/L^{-1} - 0.92 mg/L^{-1}	0.29 mg/L^{-1}	
Birimian Metasediments		0.25 mg/L^{-1} - 0.92 mg/L^{-1}	0.46 mg/L^{-1}	Apambire et al. [23]
Birimian Granitoids		0.12 mg/L^{-1} - 0.95 mg/L^{-1}	0.49 mg/L^{-1}	
Bongo Granite		0.61 mg/L^{-1} - 4.60 mg/L^{-1}	2.29 mg/L^{-1}	

Firempong et al. [80] also hosted a groundwater study in the Bongo District and reported an average F-level above the acceptable limit (1.50 mg/L^{-1}). Contrary to this, the study aimed to explore the correlation between fluoride ions in drinking water sources and the prevalence of dental fluorosis. The research involved the examination of two hundred (200) children and their respective drinking water samples to establish a connection between the fluoride concentration in their drinking water and dental fluorosis, assessed using Dean's specific index. The findings revealed that 63.0 % of the children within the main Bongo townships suffered from dental fluorosis, whereas only 10.0 % of those outside the townships experienced this issue. Furthermore, a statistically significant disparity was observed in the occurrences of dental fluorosis in relation to the fluoride levels in the drinking water sources across the communities.

In the Bongo area, considering 13 boreholes, Tiimub et al. [93] measured F^- concentrations varying from 0.02 mg/L^{-1} to 1.65 mg/L^{-1}. Similarly, Obiri-Nyarko et al. [94] also stated that the F^- levels in the area ranged between 1.9 mg/L^{-1} and 6.5 mg/L^{-1}. Recent insights by Sunkari et al. (2023) and Ashong et al. [95] also reported 0.43 to 3.61 mg/L^{-1} (avg. 1.89 mg/L^{-1}) and 0.75 mg/L^{-1} to 2.50 mg/L^{-1}, respectively. Similar to the findings obtained in the Kassena-Nankana West, Ganyaglo et al. [83], in the Bongo District, newly drilled wells showed a wide range of F concentrations, ranging from 0.29 mg/L^{-1} to 3.74 mg/L^{-1} (avg. 1.43 mg/L^{-1}). Elevated levels were found at locations like Aberingabisi CHPS Compound (3.74 mg/L^{-1}), Sambolo Basic School (3.46 mg/L^{-1}), Atampiisi CHPS Compound (2.34 mg/L^{-1}), Bongo Senior High School (2.62 mg/L^{-1}), and St. Ann Primary School (2.76 mg/L^{-1}), accounting for around 26 % of the sampled groundwater. For existing wells, fluoride concentrations varied from 0.54 mg/L^{-1} to 1.98 mg/L^{-1} (avg. 1.31 mg/L^{-1}). Higher values were noted at Aberingabisi (1.97 mg/L^{-1}), Anafobisi Zuen (1.96 mg/L^{-1}), and St. Ann Primary School (1.98 mg/L^{-1}), representing about 27 % of the sampled groundwater.

These highlights the heterogeneous nature of groundwater fluoride levels in the region. Such variability can stem from several factors, including geological differences, hydrological processes, and anthropogenic activities. Geological formations rich in fluoride-bearing minerals, such as micas and fluorite, can contribute to elevated fluoride levels in groundwater. Additionally, variations in water-rock interactions, groundwater flow patterns, and recharge rates can influence fluoride concentrations. Anthropogenic factors, such as agricultural practices, industrial activities, and improper waste disposal, can also impact fluoride levels in groundwater. These activities may introduce contaminants or alter hydrological conditions, leading to fluctuations in fluoride concentrations. The variation in groundwater fluoride levels in the Bongo area can be attributed to geological factors, hydrogeological conditions, anthropogenic activities, seasonal variations, and sampling locations. Geological formations and structures may naturally contain varying levels of fluoride, while aquifer characteristics and human activities like illegal mining can impact groundwater quality. Seasonal changes and the specific locations of boreholes also contribute to observed variations. This complex interplay of factors underscores the heterogeneous nature of fluoride concentrations in groundwater within the same geographic area, highlighting the importance of comprehensive understanding for effective water resource management and health risk mitigation.

The high levels of F^- in the Bongo area of Ghana highlight a significant public health concern. This region is considered the most endemic area for elevated F^- levels in groundwater in the country. This poses a serious health risk to the local population. The link between F^- levels in drinking water and dental fluorosis is evident, underscoring the urgent need for interventions and public health initiatives in the area. It is imperative to provide safe drinking water sources and raise awareness about the risks associated with high F^- levels to mitigate the health implications of fluoride contamination in the Bongo area. Public health awareness and education programs should be implemented to inform communities about the risks associated with F^- exposure and promote safe drinking water practices. Also, non- and governmental organization should ensure that fluoride-dominated areas are provided with alternative sources of drinking water. Further research is warranted to explore areas with limited data, particularly in the southern regions of Ghana, to gain a comprehensive understanding of the extent of fluoride contamination and its implications on public health.

3.6.1. *Geology of the Bongo District*

Grasping the geology and its associated fluoride levels is essential when crafting solutions for fluoride contamination in the area's water sources. This data is also crucial for areas facing similar fluoride concerns, offering a deeper understanding of the geological influences and informing measures to provide safe drinking water to residents. The mobilization of F^- in groundwater in the area primarily stems from weathering processes, ion exchange reactions, and the dissolution of minerals containing F^- in the aquifers. Geochemical modeling revealed that the groundwater is notably undersaturated concerning several minerals, including calcite, dolomite, fluorite, gypsum, anhydrite, aragonite, halite, and quartz. This undersaturation signifies that the groundwater has the potential to dissolve or consume these minerals in the surrounding geological formations (Sunkari et al., 2023). The geological makeup of this region includes (i) Upper Birimian Metasediments, (ii) Upper Birimian Volcanics, (iii) Granitoids linked to the Upper Birimian Formation, and (iv) Bongo granitic sets [23]. A previous study by Murray [92] revealed that the geological composition of the Bongo area predominantly comprises Bongo granite and porphyritic microgranite. Additionally, the region features greenstone, lava amphibolite, tuff, and occasional occurrences of phyllite and schist. There are also altered formations such as hornblende granodiorite, biotite granodiorite, and adamellite, with lesser extents of areas covered by foliated hornblende-biotite granodiorite and tonalite. As noted by Sunkari and Abu [19], the Upper Birimian Metasediments consist of elements like biotite schist, greywacke, and quartz-muscovite schist, while the Upper Birimian Volcanics feature extensive layers of basaltic lavas, tuff, and more. Bongo granitic formations, with their unique alkali-rich nature and elevated fluoride levels, are specifically found in Ghana's Bongo District [23,92]. Apambire et al. [23] further stated that the rock formations across the area exhibited varying levels of F-, ranging from trace levels to 2000 mg/kg. The fluoride concentration in the water interacting with the Birimian metavolcanics, metasediments, and granitoids was generally low, measuring less than 1 mg/L^{-1}. In contrast, the fluoride levels in the water interacting with the Bongo granitic rocks ranged from 0.61 to 4.6 mg/L^{-1}. In a study by Atipoka et al. [6] which evaluated F^- indifferent geological formations of the Bongo area showed that the granite formation area, 94 % of boreholes exhibited fluoride concentrations above 1 mg/L^{-1}, regardless of their depth, indicating a high risk of fluoride ingestion from boreholes for residents in this region. Conversely, in the igneous/metamorphic geologic zone, only around 19 % of boreholes had fluoride concentrations exceeding 1 mg/L^{-1} at depths ranging from 40 to 60 m, suggesting a lower risk compared to the granite formation area. Although fewer boreholes were drilled in the greenstone formation zone, there are still risks of fluoride concentrations exceeding 1 mg/L^{-1} in boreholes deeper than 40 m. The aforementioned findings suggest that the presence and dominance of F^- in the groundwater system of the Bongo area is strongly influenced by geological factors. Table 3 showcases the geologies of Ghana's Upper East Region which host Bongo and their fluoride levels.

3.7. Insights of F^- levels in Ghana

The issue of F^- in drinking water sources is a global canker. Studies have shown that some countries have more urgent problems with fluoride contamination than others. Countries like India, China, Argentina, Sri Lanka, Ethiopia, Tanzania, and Kenya are some of the severely affected areas [75]. Most of the available literature on fluoride pollution is focused on the geogenic interactions as a means of fluoride release into the environment. Drinking water, and for that matter groundwater is the most researched environmental medium for F^- contamination because it usually makes contact with F–bearing minerals which dissolve to release F^- into the groundwater sources. A major quality of fluorine that enables its persistence in water resources is its high electronegativity. The high electronegativity of fluorine ensures that it bonds perfectly well with chemical compounds in water to form stable molecules and thus explains its movement in water. Water is not the only known media for fluoride contamination of the environment, soils and plant also accumulates fluoride in them. Research has discovered that fluoride found in the soil is not readily available to plants for absorption due to the speciation of the chemical compounds they form in the soil. Pickering [39] and Kabata-Pendias and Szteke [48] revealed that fluoride bonds with chemicals in soils to form compounds that are strongly absorbed by soil mineral surfaces. They also form large compounds that are huge enough to make plant uptake of it difficult. The literature also suggests that F^- in soils is mostly associated with industrial pollution or the application of phosphate and sulfate fertilizers to farmlands. Studies including Dabeka and McKenzie [96] and Rizzu et al. [54] have attempted to identify sources of fluoride in food items such as milk, rice, and meat.

Issues of F^- contamination in water resources in Ghana arose when Murray [92] undertook a study to discover the geology of "Zuarungu". The research revealed high concentrations of fluoride in the geology of the area. This research proceeded with a gamut of research to assess drinking water risk to F^- level within the Region. The majority of these researches have proven that indeed most water resources within the region have been contaminated by fluoride. Due to the high concentration of F^- in the underlying geology, most researchers attempt to ascertain the geogenic causes of the high fluoride in the groundwater resources in the area. Research has also determined that the geology of the Bongo District is endemic to the area and thus explains why fluoride toxicity in Ghana is skewed towards that area. Despite this, certain areas within the North East Region such as Nalerigu have also been determined to be affected by fluoride contamination. However, research shows that the fluoride toxicity in the area is a result of the application of phosphate and sulfate fertilizers onto farmlands that degrade to release fluoride into the surrounding environment.

Also, most research conducted on fluoride toxicity in Ghana are related to groundwater resources as opposed to surface water resources, soils, and plants. Although some researchers take a look at the fluoride content in surface water bodies, they are not mainstream fluoride research work but consider fluoride as part of the physicochemical studies. This is so because usually, fluoride contamination of soils and plants is from industrial activities and due to the low industrialization of Ghana, explains why there is less research on fluoride contamination of plants and soils.

3.8. Suggested treatment systems for fluoride removal

Fluoride removal from groundwater is of paramount importance, particularly in regions affected by high F^- concentrations. Thus, various treatment systems have been proposed to address this issue. One widely employed method is the use of semi-permeable membranes, utilizing techniques like reverse osmosis and electrodialysis. These technologies have gained global recognition for their effectiveness in reducing F^- levels in water, making them suitable for both large-scale and small-scale applications [79,91,6,97]. Their cost-effectiveness and relatively simple installation process render them particularly valuable in resource-constrained, rural communities in developing regions.

In Ghana, several innovative approaches to fluoride removal have been proposed, taking into account local conditions and cost considerations. Antwi et al. [98] introduced a solar water distillation method for fluoride treatment within the Bongo district of Ghana. Their approach demonstrated promising results, with an average reduction of 96.3 % in F^- levels in the raw borehole water. This method leverages solar energy to distill water, effectively removing fluoride from the water source.

Another noteworthy development in fluoride removal was the bench-scale integrated bone and biochar bed treatment system, which was specifically designed for addressing geogenic fluoride contamination in groundwater within the Bongo district of Ghana, as investigated by Kumi et al. [91]. This method exhibited remarkable efficiency, achieving a 100 % removal rate for fluoride, even when dealing with high initial concentrations of 3.6 mg/L^{-1} F-. Furthermore, the treatment process was characterized by a relatively short development time, typically ranging from 15 to 27 min, making it an expedient solution for local communities grappling with fluoride-contaminated water sources.

These innovative fluoride removal technologies not only serve to enhance the quality of drinking water but also contribute to the overall well-being of communities affected by fluoride contamination, particularly in regions with limited resources. The utilization of solar water distillation and integrated bone and biochar bed treatment exemplifies the adaptability of fluoride removal solutions to suit the unique challenges and conditions faced by communities in Ghana and other affected areas, offering a ray of hope for improved water quality and public health.

3.9. Known and potential health impacts relating to excess intake of F^-

Excessive fluoride intake, often through high levels in drinking water, can lead to various chemical reactions within the human body. These reactions can have adverse health effects, ranging from gastrointestinal irritation to disruptions in cellular processes and bone integrity. In this context, it is important to explore the established and potential interactions that occur in the body after the consumption of water containing high fluoride levels. Understanding these is crucial for assessing and mitigating health risks associated with elevated F^- exposure.

- Excessive fluoride intake results in a wide range of toxic effects on the body. Primarily, fluoride exposure induces oxidative stress, leading to consequences such as cell cycle arrest and apoptosis. Although the precise mechanisms behind fluoride toxicity remain elusive, these stress-related outcomes are commonly associated with protein inhibition, organelle disturbances, changes in pH levels, and disruptions in electrolyte balance [99].
- Suppression of metalloproteins by ionized fluoride: F^- interacts with vital metals, forming highly durable and frequently insoluble compounds. Furthermore, F^- can generate ternary complexes that involve both metal and phosphate, displaying increased stability in comparison to metallo-fluoride complexes [100]. This interaction leads to the inhibition of numerous pathways, including vital processes like glycolysis, cellular respiration and nutrient transport. It is presumed that this inhibition occurs primarily through the inactivation of metalloproteins, contributing to the multifaceted effects of F^- exposure on various cellular functions [101,102].
- Inhibition of proteins by metallo-fluoride substrate mimics: The interaction of fluoride with metals, particularly aluminum and beryllium, results in highly toxic complexes that inhibit enzymes involved in phosphoryl transfer [103]. These metallo-fluoride complexes can crystallize with numerous enzymes, primarily ATPases, GTPases, or kinases, and their impact depends on factors like pH and interactions with specific amino acids [104]. In addition to direct inhibition, these complexes can alter phosphorylation states, particularly by mimicking the action of GTP. By binding to GDP and stabilizing the "on" conformation, these metallo-fluorides disrupt the regulation of proteins, leading to dysregulation of functions such as cell signaling, transport, and cytoskeleton integrity [102]. It is noteworthy that free fluoride can also affect protein activity by modifying phosphorylation states, often involving the presence of magnesium to create phosphate mimics [105].
- Induces pH and electrolyte imbalance: Fluoride exposure induces acidification and disrupts electrolyte balance at both the single-cell and multi-cellular levels. Although the precise mechanism remains unclear, prolonged exposure to elevated fluoride levels in vertebrates leads to decreased calcium and magnesium levels in the bloodstream while increasing potassium levels [106].
- Drop in intracellular pH: F^- exposure results in a decline in intracellular pH. Functioning as a weak acid, fluoride primarily enters cells in the form of HF and then dissociates, releasing a proton alongside each fluoride ion. Consequently, higher F^- levels within a cell lead to increased cytoplasmic acidity. However, it is worth noting that fluoride-induced intracellular acidification surpasses what can be solely attributed to proton transport [107].
- Disturbance of the Endocrine System: Exposure to F^- has been linked to a decrease in thyroid hormones, specifically triiodothyronine (T3) and thyroxine (T4). Studies that report significant reductions in T3 and T4 levels due to fluoride exposure typically involve patients with dental fluorosis or mammals exposed to F^- concentrations ranging from 30 to 80 mg/L-1 (2–4 mM) for a minimum of 2 months [108]. At the cellular level, fluoride exposure triggers a range of adverse effects on the thyroid, including DNA damage, membrane disruption, and the induction of mitochondrial and endoplasmic reticulum stress, in addition to oxidative stress signaling [109]. Importantly, when cells are exposed to both excessive F^- and I, there is a synergistic effect that activates endoplasmic stress, IRE1 signaling, and DNA damage [108].
- Formation of fluorapatite in teeth: When exposed to elevated fluoride levels, a chemical reaction takes place in the developing enamel of teeth. Fluoride ions can substitute hydroxyl ions in hydroxyapatite, the principal mineral constituent of tooth enamel [12]. This leads to the creation of fluorapatite ($Ca_5(PO_4)3F$), a compound that exhibits increased resistance to acid and lower solubility. The reaction can be represented as follows:

$$\text{Hydroxyapatite} + \text{fluoride} \rightarrow \text{Fluorapatite} + \text{Hydroxide}\ 3Ca_5(PO_4)3OH + 2F^- \rightarrow 3Ca_5(PO_4)3F + 6OH^- \tag{10}$$

This incorporation of fluoride into tooth enamel can cause dental fluorosis, leading to discoloration and structural changes in the teeth.

- Inhibition of enzymes: Fluoride ions can inhibit enzymes that play crucial roles in various metabolic pathways [110]. For example, fluoride can inhibit enolase, a key enzyme in glycolysis, by binding to its active site [111]. This interference disrupts the glycolytic pathway and inhibits the production of energy (ATP) from glucose.
- Formation of CaF2 precipitates in bones: The accumulation of fluoride ions in bones can result in the creation of CaF2 precipitates [112]. This can reduce bone density and increase bone fragility. The reaction can be represented as:

$$Ca^{2+}\ (\text{in bone}) + 2F^- \rightarrow CaF_2\ (\text{precipitate}) \tag{11}$$

It is crucial to emphasize that the impact of fluoride on the body depends on the dosage, and the actual responses can differ based on variables like fluoride concentration, exposure duration, and individual sensitivity. The adverse health effects mentioned earlier can occur when fluoride exposure exceeds recommended levels. These impacts should be assessed in fluoride-burdened areas in Ghana and beyond.

3.10. Policy plan for reducing the impacts of F^- on public health

Apambire et al. [23] indicated that due to the consistently high average temperatures of 32 °C in the Upper Region of Northern Ghana, adults can consume water at rates of 3–4 L/day. This consumption is 1.5–2 times more than what the WHO estimated for daily water intake in 2017. As a result, Apambire et al. [23] suggested a maximum safe fluoride level in drinking water to be 1.0 mg/L^{-1}. Considering the increased fluoride exposure in Ghana's population, Craig et al. [113] introduced age-specific guidelines for fluoride consumption. Younger individuals, particularly during tooth enamel development, face a higher risk of non-carcinogenic effects like permanent dental fluorosis. Ingested fluoride is retained more by children (80–90 %) than by adults (60 %). Additionally, liquids account for approximately 90 % of absorbed fluoride, while solids contribute to 30–40 % [114].

Given the cost of failed borehole drilling, construction and development, the possibility of integrating appropriate water treatment into the investment and maintenance costs of the existing water source should be looked at and discussed in detail. In the wake of fluoride-related findings in cultivated crops (Jha, 2011), it is thus prudent to enshrine a buffer along the course of river bodies to avert the possible negative impact of fluoride on groundwater. Equally, the concentrations of fluoride in fertilizers applied to crops within heavily affected areas should be scaled down to prevent its unforeseen effects.

4. Conclusion

Fluoride in drinking water has been found to have detrimental effects on human health, particularly in areas where groundwater sources are contaminated with high F^- concentrations. This review has highlighted the occurrence, movement, and health implications of F^- in groundwater, soils, and plants, with a focus on the situation in Ghana. The presence of F^- in natural waters is influenced by various factors, including geology, geochemical environment, hydrogeological conditions, climate, and human activities. In Ghana, regions such as the Upper East and Northern Regions have been identified as fluoride-endemic areas due to the geological composition of these regions, leading to high F^- concentrations in groundwater. F^- can also accumulate in soils, mainly in the clay fraction, and its availability to plants depends on factors such as pH, organic carbon content, and the specific forms of F^- in the soil. F^- uptake by plants can have adverse effects on their growth and development, and some plant species are more tolerant to F^- than others. The global occurrence of F^- contamination in drinking water has been documented in several countries, including India, China, Argentina, and various African nations. These regions have experienced health issues related to F^- exposure, such as dental and skeletal fluorosis. In Ghana, the Bongo District in the Upper East Region has been identified as one of the most severely affected areas in Ghana. Research in Ghana has primarily focused on groundwater F^- levels, with limited attention given to surface water, soils, and plants. Various treatment methods for F^- removal have been explored, ranging from membrane techniques to adsorption using locally available materials. These methods have shown promise in reducing F^- levels in water, but their feasibility and effectiveness may vary depending on the specific conditions and resources available in different regions. F^- level in drinking water sources is a significant public health concern globally, and efforts should be made to monitor and mitigate its impact, especially in fluoride-endemic areas like the Bongo District in Ghana. Public awareness and education on the risks associated with F^- exposure and the importance of access to safe drinking water are also essential components of addressing this issue.

Future research focus is needed in the following areas.

- Better understanding of the sources, distribution, and health effects of F^- in different environmental media and to develop cost-effective treatment methods for F^- removal in affected regions.
- Conduct extensive hydrogeological surveys across various regions of Ghana to map the distribution of fluoride in groundwater.
- Evaluate the health impacts of long-term exposure to fluoride-contaminated water in Ghanaian communities. Conduct epidemiological studies to assess dental fluorosis, skeletal fluorosis, and other potential health issues.
- Research and develop cost-effective and sustainable fluoride removal technologies suitable for Ghanaian rural communities.
- Examine the potential impacts of climate change such as altered rainfall patterns, temperature variations, and changes in aquifer recharge rates might influence the concentration and distribution of fluoride.
- Risk assessment for long-term chronic health effects of fluoride through dental and skeletal fluorosis.
- Techniques for the suppression of water fluorides which may be inconspicuous but are significant hindrances to rural water supplies.
- Studies towards developing a long-term strategic action plan for mitigating the effects of climate change on fluoride concentration and distribution in groundwater.

4.1. Limitations

This work provides an account of the health impacts of high fluoride intake, however, there are some limitations to the study. There are still many questions concerning the specific mechanisms of fluoride toxicity and the ways in which it affects metal ions when combined with other factors. Further analysis is necessary regarding genetic and behavioral factors influencing the population variance in relation to fluorides. However, there are limited published studies on the factors that affect the bioavailability of fluoride in the environment, and the feasibility of preventing such incidents has not been thoroughly analyzed in the policy context. The research from Ghana may not be generalized to other areas; therefore, future researches should consider comparisons.

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CRediT authorship contribution statement

Raymond Webrah Kazapoe: Writing – original draft, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **Ebenezer Ebo Yahans Amuah:** Writing – original draft, Resources, Methodology, Formal analysis, Data curation, Conceptualization. **Paul Dankwa:** Writing – review & editing, Software, Methodology, Investigation, Conceptualization. **Obed Fiifi Fynn:** Writing – review & editing, Visualization, Methodology, Data curation, Conceptualization. **Millicent Obeng Addai:** Writing – review & editing, Investigation, Data curation, Conceptualization. **Belinda Seyram Berdie:** Writing – review & editing, Conceptualization. **Nang Biyogue Douti:** Writing – review & editing, Methodology, Conceptualization.

Declaration of competing interest

The authors have not disclosed any competing interests.

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