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A review on source, impacts and mitigation measures of groundwater fluoride contamination: a major health issue

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A B S T R A C T

Fluoride (F^-) in groundwater is one such ion that makes the groundwater unsuitable for drinking purposes and responsible for serious human health problems such as dental, skeletal, and non-skeletal fluorosis in more than 25 countries worldwide. Recent studies estimated that cases of fluorosis are prevalent in 67 million people in 19 out of the 32 states of India due to intake of fluoride-enriched groundwater ranging from 0.01 to 37.0 mg/l affecting 8 and 18 million people among them by skeletal and dental fluorosis, respectively. The distribution of fluoride in groundwater varies due to geogenic or anthropogenic sources or combined factors. The various geological and artificial factors that govern the F^- prevalence in aquifers have been discussed. Different types of adverse health hazards of fluoride on humans and plants have also been enlightened. Since fluoride occurrence above 1.0 mg/l (BIS) or 1.5 mg/l (WHO) in groundwater can produce endemic health issues, there is an essential requirement to monitor groundwater fluoride levels frequently. Higher concentration in water needs treatment to bring them under the guideline value. Some available fluoride removal techniques from groundwater have been deliberated in study. Groundwater fluoride contamination is generally natural and unpreventable. However, most people unintentionally consume the untreated groundwater in developing countries leading to a widespread problem worldwide. A prominent solution is to educate and aware people about this issue. Frequent monitoring and defluoridation of the contaminated groundwater must be needed before consumption for a healthy world. The present review work is a step toward this fluoride hazard awareness with compact information about its various sources, status, removal technologies, and their relation with the environment.

Keywords: Groundwater · Fluoride contamination · Weathering · Health issue · Mitigation measure

1. Introduction

Fluoride is an inorganic, monatomic anion of fluorine with the chemical formula F^-, salts of which are typically white or colourless [1]. Fluorine (F) is the first element in the halogen group (Group-17) in the modern periodic table and is found to be the 15th most abundant element on the earth's crust [2], which disperses naturally in the form of fluoride. Fluoride (F^-) is the lightest and highly electronegative element present naturally in trace quantities in water bodies [3]. The natural processes like ion-exchange capacity, oxidation-reduction, residence time, geogenic process, and rock types contribute to contaminating the groundwater and surface water [4,5]. Many parts of the world are facing a significant problem due to the consumption of fluoride contaminated groundwater affecting 1.5 billion people directly or indirectly [6]. The ionic form of Fluorine (F^-) is easily soluble in the water system. The natural or geogenic sources, mainly fluoride bearing rock-minerals, are the leading cause of fluoride contamination in groundwater than any anthropogenic sources [7], such as the release of industrial effluents, onsite sanitation, and use of chemical (phosphatic) fertilizers [8-10]. The microorganisms play an essential role in fluoride contamination of groundwater during weathering of minerals. There are numerous sources and pathways for fluoride richness in human health and exerts significant toxic effects on biota [11].

2. Overview of fluoride contamination in groundwater: the source, impacts and mitigation measures

2.1. World scenario

In the context of the world, several researchers reported the problem of fluoride concentration at high level in groundwater in China, Southern Algeria, Mexico, Canada, Norway, Ghana, Kenya, Korea, Japan, Sri Lanka, Iran, Pakistan, Turkey, Italy, Brazil, Ethiopia and USA [12,13]. Among them, the United States, the South-East of Africa, Korea, Kenya, Middle East of Asia, Pakistan, China and India, are the most affected regions by groundwater fluoride [13]. The main governing factor that played a role in this groundwater fluoride distribution is the chemical, physical, geological properties of the aquifer.

2.2. Indian scenario

Indian earth crust has 12 million tons estimated fluoride deposits out of 85 million tons in the world [1]. In India, 85% of the available groundwater is used to meet the need for drinking water, and 80% of rural and 50% of the urban population are directly dependent on groundwater for drinking and domestic purposes [14]. From this data, we can imagine the intensity of fluoride causing health hazards in India, i.e., alarming and widespread. Cases of endemic fluorosis were observed since 1937 in the Prakasam district of Andhra Pradesh [15]. According to a recent study, some 67 million people in India are consuming groundwater having high fluoride concentrations, and 8 million people among them have been affected by skeletal fluorosis and 18 million people by dental fluorosis all over the country [16]. Fluoride rich

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groundwater and its health hazards have been documented in 200 districts, spread over in 19 Indian States. High fluoride levels in drinking water have been found in 50-100% of districts of Gujarat, Rajasthan, Andhra Pradesh, and Telangana. The groundwater of 30-50% of districts of Bihar, Jharkhand, Karnataka, Maharashtra, Madhya Pradesh, Haryana, Tamilnadu, Odisha, Punjab, Telengana and Uttar Pradesh are affected by fluoride. The value is less than 30% in the case of Delhi, Chhattisgarh, Kerala, and West Bengal) [17,18].

In West Bengal, fluorosis was first observed in 1983, from Nasipur village of Birbhum district. Extensive research works were also carried out on fluoride geochemistry of groundwater in Nalhati-1 block of the Birbhum district, West Bengal [19]. Continuous monitoring also reported that groundwater in other parts of the states is also affected by fluoride contamination [20]. 225 villages in 43 blocks of West Bengal, spread over seven districts viz; Puruliya, Birbhum, Maldah, Bankura, Uttar Dinajpur, and Dakshin Dinajpur, South 24 Parganas are identified as fluoride affected (contamination level of 1.06-17.6 mg/l) regions, where people are at risk of endemic fluorosis [21,22]. According to the PHED 2013, 7,400,000 people (11.9% of the rural population) of West Bengal facing the risk of fluoride contamination in drinking water. In 2003, the PHED constituted a fluoride committee with the involvement of several organizations for a rapid assessment of fluoride levels in groundwater throughout West Bengal. The survey was carried out over 107 blocks in 12 districts and reported that 43 blocks in seven districts have enriched fluoride concentrations of more than 1.5 mg/l [23]. Subsequent testing of all hand-pumped tube wells in the 43 blocks found 3.88% exceeding the acceptable government standard.

3. Research Methods

A systematic review of literature was done to find out the possible sources, impacts, and mitigation measures of groundwater fluoride contamination. Many parts of the world are presently facing a significant problem due to the consumption of fluoride contaminated groundwater. Weathering of fluoride-bearing rocks contributes to elevate fluoride content in groundwater. Rapid growth of different industries raised the fluoride concentration in the environment. Natural and anthropogenic sources of fluoride were also evaluated in this review work. The intake of high fluoride (F^-) contaminated groundwater causes significant health issues. Health effects of fluoride on human body and plants were investigated properly. Methodologies like coagulation and precipitation, adsorption, ion-exchange and membrane process for toxicant removal from groundwater were also reviewed in this study.

4. Results and discussion

4.1. Fluoride in groundwater

Worldwide, groundwater is considered as the primary source of drinking water and is used for various domestic purposes without any physical or chemical treatment. However, naturally or anthropocentrically, groundwater contains some undesirable elements such as fluoride, arsenic *etc*., which may lead to several health disorders.

4.1.1. Natural sources

Natural source of fluoride is mainly the fluoride bearing minerals, which comprises about 0.32% of the earth's crust and is the greatest contributor of fluoride contamination for groundwater [24]. Volcanic eruption or volcanic ash having high hydrogen sulfide (HS) and marine aerosols are also natural sources of fluoride that can reach the water bodies through the hydrological cycle [25]. Most of the fluoride-rich minerals are found in igneous and metamorphic rocks. Sedimentary rocks contain a smaller amount of fluoride, but the presence of fluorapatite can significantly raise the fluoride concentration in them [26,27]. Granitic-Gneiss complex also contains fluoride-rich minerals such as amphiboles, muscovite, biotite, and hornblende, which are some key fluoride sources in arid and semi-arid regions [28].

Granitic rocks, a typical fluoride source for groundwater, contain an average of 810 mg/kg fluoride [29]. The average fluoride content in other rock minerals is given in Table 1. The weathering of these fluoride-bearing rocks contributes to elevated fluoride content in

Table 1. Major rock types and their fluoride content capacity [30].

Rock types	Fluoride content range (ppm)	Average fluoride content (ppm)
Phosphorite	24000-41500	31000
Granite-Gneiss	20-2700	870
Shales and Clays	10-7600	800
Basalt	20-1060	360
Limestone	0-1200	220
Sandstone	10-880	180
Coal	40-480	80

ground water. The longer the residence time of groundwater fractured rock aquifers, the higher the fluoride levels in the groundwater.

4.1.2. Anthropogenic sources

The rapid growth of different industry types in the country currently raised the fluoride concentration in the environment. The major industry such as thermal power (burning of coal), oil refining, steel manufacturing, chemical fertilizer production, clay production, aluminum smelting, glass and enamel production, brick and ceramic manufacturing, the nuclear industry (production of uranium hexafluoride and uranium trifluoride) *etc*. are the primary anthropogenic sources of fluoride. In addition, wastes (sewage and sludge), agricultural fertilizers, and pesticides are some other sources of fluoride in groundwater [30-32]. Coal contains 40 ppm to 480 ppm of fluoride (Table 1). During burning of coal, it produces fly ash, which ultimately reaches the groundwater and contaminates with fluoride. The application of rock phosphate contains high level of fluoride. Its repeated use in the crop field has significantly increased (50–100 kg P2O5/ha/year). It can add 5-10 ppm fluoride into the soil, a significant anthropogenic fluoride source for groundwater [33,34].

The fluoride content, present in gaseous and particulate form, contributed by the volcanic ash and fly ash, returns to the soil through atmospheric dry/wet deposition and contaminates groundwater during percolation [12, 35]. Sometimes an open surface of fluoride-containing rock helps to elevate the fluoride concentration in the atmosphere during its weathering [36]. The meteorological factor such as temperature, rainfall, wind direction, speed, and turbulence play a significant role in fluoride distribution and deposition in the atmosphere. The gaseous forms of fluoride are hydrogen fluoride, sulfur hexafluoride, silicon tetrafluoride, and fluorosilicic acid and particulate forms of fluoride are mainly calcium fluoride, aluminum fluoride, lead fluoride, sodium hexafluorosilicate, and calcium phosphate fluoride [37]. The atmospheric air contains fluoride in the range of 0.01 to 0.4 ug/m^3, and precipitation (rainwater) contains a fluoride limit to 0.089 mg/l, which lastly reaches to aquifer during groundwater recharge [38].

4.2 Health effects of fluoride

4.2.1. Effects on Human being

The intake of excess fluoride (F^-) causes significant health issues in different parts of the world. Climatic factors also play an important role in fluoride intake capacity in the human body, the guideline value for fluoride consumption also differs in different countries based on climatic factors. The consumption of fluoride >1.0 mg/l may cause various health problems like abdominal pain, nausea, dental enamel degradation, and damage to organs and tissues [21,23,39]. Further increase in the concentration of fluoride (>4 mg/l) can be responsible for osteosclerosis, crippling deformities of the spine and major joints, calcification of ligaments, skeletal fluorosis, intellectual impairment in children, mental retardation, miscarriage, birth abnormalities, loss of mental stability and often cancer in human body [40-42]. In addition, excessive intake may cause various other health disorders such as salivation, severe gastroenteritis, tachycardia, anorexia, ventricular abnormalities, dyspnoea, sweating, stiffness, restlessness, and muscle weakness [43]. Out of these most prevalent health problems are dental and skeletal fluorosis. Dental fluorosis is an aesthetic and social problem rather than being a health problem.

Dental fluorosis is hypoplasia or hypo-mineralization of tooth enamel due to exposure to fluoride. It may result in discoloration and pit formation in the enamel. The discoloration of teeth may change the colour from white, yellow-brown to black. The discoloration may be in spots, streaks invariably horizontal in orientation, as during the development of new layers of the matrix are added horizontally [21]. Skeletal fluorosis is not easily recognizable until the disease has developed to an advanced stage. It results from excessive fluoride deposition in the skeleton, the deposition is more in cancellous bone than cortical bone. Changes in the bone can be observed through radiographs. Maximum ill effects of fluoride are found in the neck, spine, knee, pelvic and shoulder joints, hardening of joints, and calcification [1]. It also affects small joints of the hands and feet, leading to pain in the neck, back, joints and rigidity begin in regions where cancellous bones predominate. When calcium fluorapatite deposition takes place in the bone, the bone's density mass gets increased. In the backbone, the perforations through which nerves and blood vessels pass are constricted, leading to pressure on nerves and blood vessels, culminating in paralysis and excruciating pain.

Fluoride cannot be directly permeable in the biological cell membrane, it binds with Ca^{2+} ions to form Ca-ionospheres, and then it is permeable to the cell membrane [44]. After absorption into blood vessels, it is diffused throughout the body and is accumulated into calcium-rich areas such as bone and teeth. It produces reactive oxygen species (ROS) within cellular mitochondria and reduces the cellular antioxidant defences against oxidative damage [45]. It causes inhibitory effects on Na^+/K^+–ATPases of the glycolytic pathway and the Krebs cycle. It also prevents ATP production and cellular respiration by combining with the functional groups of amino acids of the enzyme used in the glycolytic pathway and the Krebs cycle [46]. It also induces apoptosis. Fluoride exposure decreases protein synthesis by affecting the vesicular traffic in Golgi bodies and endoplasmic reticulum (ER) in cells [47].

4.2.2. Effects on Plants

Long-term exposure of plants in water containing fluoride showed various ailments such as necrosis and chlorosis along the leaf veins. A histochemical study of fluoride contamination showed that chlorosis of leaf occurs due to disruption of chloroplast in both spongy mesophyll and palisade cells [48]. It also reduces the germination ability, inhibits catalase activity, growth parameters, respiration, metabolism of amino acids, protein synthesis, and photosynthesis *etc*. [49,50]. It strongly reduces the process of photosynthesis, affects pigment synthesis, and causes chloroplast degradation [51]. It also inhibits the enzyme that has cofactors like fluoride and requires cofactors like Ca^{2+}, Mg^{2+}, and Mn^{2+} ions [48]. After absorption of fluoride, when it is translocated to the shoot, it causes biochemical, physiological, and structural damage to the cell [52].

4.3 Mitigation techniques of fluoride from groundwater

To overcome the fluoride contamination in water, different techniques or methods for de-fluoridation are available. Some major popular techniques such as precipitation and coagulation, adsorption, ion exchange, and membrane (nanofiltration membrane, reverse osmosis and electrolysis) are discussed here.

4.3.1. Coagulation and precipitation

The National Environment Engineering Research Institute (NEERI), Nagpur, has developed a technique for de-fluoridation of water called the Nalgonda technique. In this process, coagulants like lime and alum (aluminum salts) are used for the removal of fluoride contamination from water [53]. The Indian Institute of Science (IISc), Bangalore, recently has proposed a simple defluoridation technique using magnesium oxide and sodium bisulfate.

As lime helps to remove fluoride 8.0 mg /l, it is used only in conjunction with alum treatment to ensure the proper fluoride removal [54,55]. In the first stage, precipitation occurs by lime dosing, followed by a second step in which alum is added to cause coagulation. After the addition of alum into the water, basically, two reactions undertake. The first reaction produces insoluble aluminium hydroxide [Al(OH)3] to react between alum and alkalinity. In the second stage, alum reacts with fluoride ions present in the water. The best fluoride removal is accomplished at a pH range of 5.5–7.5 [56]. Lime serves to shape bigger and denser flocs for fast settling. Bleaching powder is included for cleansing at the rate of 3 mg/l [57]. It is the most generally utilized de-fluoridation method, especially at the community level.

4.3.2. Adsorption

Adsorption is a process where molecular species are attached to the solid surface by attraction force. Adsorption technique is simple, economical, adaptable, available in a wide range, and suitable for drinking water treatment. The adsorption process is economical when a low-cost adsorbent is used as an alternative to the activated carbon. On the other hand, low-cost adsorbents are more economical to dispose of than regeneration. The tested adsorbents for the removal of fluoride are activated alumina, charcoal, activated carbon, calcined clay (fired clays, coated clay), bleaching earth, red mud, bone char, calcium, etc. [58-64]. Some natural plant-based defluoridation agents are seeds of the Drumstick, roots of Vetiver grass, Tamarind seeds, tea ash, and eggshell powder.

The capacity of adsorbents for fluoride removal depends on the pH and concentration level of fluoride in water. Activated carbon as a fluoride adsorbent effectively works at a pH of less than 3 [65]. The major advantage of the adsorption process is that it is fast and more efficient (90%) for fluoride deduction. Low-cost adsorbents like hydroxyapatite, fluorspar, calcite, quartz, and quartz, activated by ferric ions and found the adsorption capacity in the order of hydroxyapatite > fluorspar > quartz [66]. The depending factor such as contact time, pH of the solution, and adsorbent concentration played important roles in the removal process. The adsorbent such as alum-impregnated alumina showed a high efficiency (99% at pH 6.5) to remove fluoride from the water system. The bio-sorbent, such as algal spirogyra, was effective at low pH for fluoride adsorption [67]. Activated carbon derived from the royal Gulmohar fruit shell was used to remove fluoride from the aqueous solution [68].

4.3.3. Ion-exchange

The ion-exchange process is supportive for fluoride removal from water bodies with great level. In this process, the artificial or industrial made chemical resins such as anion and cation exchange resins *e.g.*, Polyanion (NCL), Tul-sion A-27, Deacedite FF (IP), Amberllte IRA 400, Lewatit MIH-59, and Amberlite XE-75 have been used for fluoride removal. The strongly anion-exchange nature of resins removes fluoride from water [54,69,70]. In the following reaction, fluoride ions are replaced by chloride ions of the resin, and this process goes until all the sites of the resin get occupied by fluoride. The strong electronegativity of the fluoride ions replaces the chloride ions from the resin [54]. The removal of fluoride takes place in the following reaction: $\text{Matrix-NR}_3\text{-Cl}^- + \text{F}^- \rightarrow \text{Matrix-NR}_3\text{-F}^- + \text{Cl}^-$

Here, the fluoride removal efficiency depends on the exchange capacity of resins and the ratio of fluoride to the total anions of water. After completion of fluoride removal, the resin is again back-washed with sodium chloride supersaturated water. As a result, fluoride ions are replaced by new chloride ions, and resin is recharged to repeat the process.

4.4.4. Membrane process

In the last decade, the popularity of membrane separation/filtration processes such as nanofiltration (NF), reverse osmosis (RO), Donnan dialysis, electrodialysis *etc*. has increased for industrial importance in the treatment of wastewater, seawater desalination as well as potential fluoride technique from water [69]. NF removes mostly the larger dissolved solids having relatively low-pressure requirements [69]. In contrast, RO is a physical process that needs higher pressures for greater rejection of all dissolved solids. Many researchers reported that membrane processes have an efficiency of up to 98% in fluoride removal. The efficiency depends on different factors such as water chemistry, temperature, pressure, regular monitoring, and maintenance. Donnan dialysis or diffusion dialysis is similar to the ion exchange process and different from electro-membrane process in the way that here driving force is not an electrical current but the concentration of the solutions followed by complexation with Al^{3+} ions [69]. Electrodialysis is an electrolytic process for separating an aqueous electrolyte solution into a concentrated brine and dilution by means of an electric field and ion-selective membrane.

5. Conclusions and recommendations

A fluoride level of <0.5 mg/l in drinking water is essential to cure dental carries, bone deformity for healthy teeth and bones. Whereas, concentration above the recommended limit of WHO, i.e., 1.5 mg/l and BIS, i.e., 1.0 mg/l, can produce trifling dental fluorosis to crippling skeletal fluorosis depending on the dissolved quantity and exposure duration. However, fluoride can cause several health disorders apart from fluorosis due to the ingestion of fluoride-enriched drinking water. Weathering of fluoride-bearing rocks and their interaction with water with prolonged residence time is the prime source of high fluoride in groundwater. High sodium and bicarbonate with low calcium content is the typical water chemistry of fluoride-enriched groundwater. The foremost anthropogenic sources of fluoride are volcanic ash, combustion of coal, and chemical fertilizers containing agricultural runoff. Many defluoridation techniques such as coagulation and precipitation, adsorption, ion exchange, electrodialysis, and reverse osmosis are used to remediate the groundwater from high fluoride content. Among them, reverse osmosis has a simple design, cost-effective, local, easily accessible materials, has a rural focus, and is considered the best available technology. Artificial groundwater recharge, recharge of water table using harvested rainwater through existing wells, constructing check dams, percolation ponds *etc*., are some onsite defluoridation treatments to minimize the fluoride level through dilution. It can be assumed that the explanation of fluoride hydrogeochemistry, its spatial prevalence, proper mitigation measures *etc*., discussed in this article will be helpful to increase the knowledge and awareness about the fluoride problems to fit in the circumstances and be accepted by rural mass.

Conflict of interests

The authors declare there is no conflict of interests.

Data availability

The authors confirm that all data collected or analyzed during this study are included in this published article.

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