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REVIEW PAPER

A review of global outlook on fluoride contamination in groundwater with prominence on the Pakistan current situation

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Abstract Several million people are exposed to fluoride (F^-) via drinking water in the world. Current review emphasized the elevated level of fluoride concentrations in the groundwater and associated potential health risk globally with a special focus on Pakistan. Millions of people are deeply dependent on groundwater from different countries of the world encompassing with an elevated level of fluoride. The latest estimates suggest that around 200 million people, from among 25 nations the world over, are under the dreadful fate of fluorosis. India and China, the two most populous countries of the world, are the worst affected. In Pakistan, fluoride data of 29 major cities are reviewed and 34% of the cities show fluoride levels with a mean value greater than 1.5 mg/L where Lahore, Quetta and Tehsil Mailsi are having the maximum values of 23.60, 24.48, > 5.5 mg/L, respectively. In recent years, however, other countries have minimized, even eliminated its use due to health issues. High concentration of fluoride for extended

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time period causes adverse effects of health such as skin lesions, discoloration, cardiovascular disorders, dental fluorosis and crippling skeletal fluorosis. This review deliberates comprehensive strategy of drinking water quality in the global scenario of fluoride contamination, especially in Pakistan with prominence on major pollutants, mitigation technologies, sources of pollution and ensuing health problems. Considering these verities, health authorities urgently need to establish alternative means of water decontamination in order to prevent associated health problems.

Keywords Pakistan scenario · Fluoride pollution · Drinking water · Mechanism · Sources of pollution

Introduction

Fluoridation of water has been a common practice in various countries like Australia, Brazil, Malaysia, USA, India and Vietnam. Most European countries do not fluoridate their water, but different parts of the world which are subject to high risk of water contaminant; this technique is most likely the best option to be implemented. Fluorine belongs to halogen family in the periodic table being the lightest member and most electronegative and reactive of all elements (Rafique et al. 2015). Due to its high reactivity, it does not found in elemental form and readily reacts to form an inorganic and an organic compound is known as fluoride (Manahan 2002). It ranked 13th most abundant element covering 0.06–0.09% of the total earth crust (Armienta and Segovia 2008). The concentration of fluoride in surface water reported 0.01–0.3 mg/L, while on the groundwater it is well under 1 to more 35 mg/L (Msonda et al. 2007). Generally, fluoride can enter the human body mainly by drinking water (Li et al. 2014). Ingestion of F below 1.5 mg/L may help to prevent the incidence of dental carries and enhance the growth of bone (Harrison 2005). However, the concentration of fluoride above 1.5 mg/l causes dental fluorosis or mottled enamel, and concentration above 3.0 mg/L may cause skeletal fluorosis (Dar et al. 2011). The World Health Organization (WHO) has set 1.5 mg/L as the maximum limit for fluoride in drinking water (Organization 2011). One cannot reveal the concentration of fluoride in water unless it is tested by employing a proper procedure or method (De Zuane 1997).

Fluoride pollution of drinking water is a great challenge for various nations of the world. Both of these pollutants are recognized as most dangerous inorganic pollutants (Smedley and Kinniburgh 2002; Wang et al. 2004; Su et al. 2006). Fluoride poisoning causes skeletal and dental fluorosis, and even loss of mobility such as arthritic joints, or more serious problems whether acute or chronic (Su et al. 2006). There is a high probability of co-occurrence of fluoride in groundwater of arid and semiarid regions in the world, where the aquifer is characterized by calcareous unconsolidated sediments to bedrock or alkaline groundwater (Semedley and Kinniburg 2002; Pauwels and Ahmed 2007; Kim et al. 2012). Especially, fluoride contamination of groundwater in sedimentary unconsolidated aquifers, most see as Vietnam, USA, Cambodia, India, Argentina and China (Kim et al. 2012; Smedley and Kinniburgh 2002), while in arid and semi-arid regions for example, California and Arizona (Robertson 1989), Yuncheng Basin in China (Currell et al. 2011) and Pakistan (Farooqi et al. 2007a) which are categorized by oxidizing environment.

Fluoride is one of the most toxic and ubiquitous elements in the environment. Groundwater contamination by fluoride is one of the most important and serious environmental issues for the developing world due to high toxicity and serious health problems even at very low concentration (Mandal and Suzuki 2002). More than 70 countries of the world have drinking water supplies naturally contaminated with fluoride, and mostly countries belong to the Southeast Asia and South Asia (Ravenscroft et al. 2009; Rasool et al. 2015). In several countries of the world such as Chile, Taiwan, India, Bangladesh, Mexico and Hungary, the elevated level of fluoride (> 1.5 ppm) has been reported (Smedley et al. 2002; Ndiaye et al. 2005; Dolar et al. 2011). Like, other developing countries, Pakistan are facing a deficiency of water along with fluoride contamination (PCRWR 2005). Probably 1.1 billion population lack access to safe drinking water, no entree to proper sanitation about 2.5 billion, and every year more than 5 million people die of water-related diseases (Hinrichsen and Tacio 2002; Waghmare et al. 2015). Water quality of rivers, aquifers and lakes in Pakistan is assumed not good for human consumption. Drinking water availability in Pakistan according to various national reports revealed that only 57% of the total populations of Pakistan have access to safe water (Farooq et al. 2007b; Ullah et al. 2009).

Conversely, in accord with the international reports, only 25.61% of the population has drinkable water in Pakistan (Rosemann 2005). Drinking water seems heavily contaminated due to various anthropogenic and natural activities in many large cities of Pakistan such as Karachi, Islamabad, Lahore, Qasur, Faisalabad and Rawalpindi (Bhutta et al. 2002). However, in Pakistan majority of the population is affected by water-related health problems due to fluoride contamination in drinking water. The aim of this review is to highlight the possible sources and to provide an insight into the available mitigation technologies for removing fluoride contamination from drinking water globally, with a special focus on Pakistan. This analysis is carried out to establish an in-depth understanding of the impact of fluoride on health, which can help health authorities in their policy-making activities concerning fluoridation of water in the future.

Co-occurrence of fluoride

The coincidental F^- occurrence in the groundwater suggested a common pathway or source for both of these pollutants (Farooqi et al. 2007a). Coincidental occurrence of elevated fluoride in groundwater might be explained by the coal combustion at brick factories scattered in air pollutants (Farooqi et al. 2007b) as well as mineralized coal burning produced toxic elements (Finkelman et al. 2002). There are various natural and anthropogenic sources of fluoride responsible for groundwater contamination throughout the world. Tahir and Rasheed (2012) analyzed 747 water supply sources in 16 major cities of Pakistan and explored the fluoride toxicity. They observed at around 16% of monitored sources having fluoride value above the permissible limit. They reported that Punjab and Baluchistan as having maximum fluoride levels with ranges less than 0.05 to 19.70 and 0.1 to 24.48 mg/L, respectively (Tahir and Rasheed 2012). Fluoride levels in water sources of 29 cities of Pakistan are summarized in Table 2. Fazlul et al. (2002) reported that of all fluoride concentration levels in Bangladesh, groundwater sources had the lowest concentrations as they ranged from 0.22 to 2.32 mg/L with a mean value of 0.56 mg/L. The fluoride-bearing minerals are fluorite, fluorapatite, cryolite and apophyllite, ferro-magnesium silicates (amphiboles and micas) and clay minerals (Guo et al. 2007; Dey et al. 2011). Other, fluoride is anthropogenically sourced from aluminum refining, fertilizer and semiconductor manufacturing, glass and ceramic production, coal combustion, brick manufacturing, nickel, copper and steel smelting (Pickering 1985; Rahaman et al. 2011).

Fluoride controlling factors in groundwater

There are some factors which control enrichment of fluoride in groundwater. These factors include pH, temperature, anion exchange capacity (OH^- for F^-), the solubility of fluorine-bearing minerals, contact time of water with rocks, the solubility of fluorine-bearing minerals, the absence of complexion or precipitating ions and colloids and type of geological formation traversed by water (Farooqi 2007a). Climatic conditions (temperature and rainfall) greatly affect the fluoride concentration in groundwater in arid and semiarid regions. Arid and semiarid climatic regions experience to receive low rainfall (225–400 mm per year) and high evaporation (> 2000 mm per year) and have low groundwater hydraulic conductivity (Su et al. 2006). The low rate of groundwater recharge sources such as rainfall in arid regions lead to prolonging water–rocks interaction which causes elevation of fluoride content in groundwater. On the other hand, high evaporation causes precipitation of lower solubility minerals ($CaCO_3$) which reduce the availability of calcium ions in groundwater and promote dissolution of fluorite minerals (Vithanage and Bhattacharya 2015). pH value is a major controlling factor for fluoride in groundwater which increases due to the release of ions such as Na^+ and $HCO_3{}^-$ and ultimately favors the dissolution of fluoride-bearing minerals (Rango et al. 2009). Fluoride at low pH forms complexes with aluminum and Fe in soil, and its adsorption on clay minerals (illite, chlorite and smectite mineral) below pH 4.0 is significantly high, while it decreases above pH 6.5. Under alkaline conditions ($pH > 7$), anion exchange occurs where OH^- can replace F^- from biotite and muscovite and clay minerals (Ng et al. 2003; Li et al. 2014).

Fluoride-bearing minerals

(Srivastava and Lohani 2015) reported around 150 fluoride-containing minerals. Of these minerals, some are silicate some halides, and some are phosphate. (CaF_2), sellaite (MgF_2), fluorapatite ($Ca_5(PO4)_3F$), cryolite (Na_3AlF_6), villiaumite (NaF) and topaz ($Al_2(SiO_4)F_2$) are major fluoride-bearing minerals. In addition to these, some other minerals like mica and amphiboles can also contain F^- which replaces for an OH^- in the mineral structures (Edmunds and Smedley 2013). Certain clay minerals such as illite, chlorite and smectite characterized as best anion exchange media, where hydroxyl groups substitute fluoride ion due to similar ionic radii under alkaline condition (Ayoob and Gupta 2006). Rock–water interaction causes disintegration of fluoride-bearing minerals in bedrocks which result in accumulation of high fluoride in groundwater (Mamatha and Rao 2010). High concentration of fluoride ions in groundwater has been noticed in the areas that lie within low plain, whereas low concentration in the regions located on highland. This is due to the fact that contact time of water with aquifer materials in plain places was longer and exists slow groundwater movement compared to highlands (Dissanayake 1991). The concentration of fluoride is proportional to the degree of retention time in the aquifer and its interaction with geological materials (Czarnowski et al. 1996).

Hydro-chemical factors anion exchange

Due to anion exchange process, fluoride concentration in water goes up to 30 mg/L. This occurs largely in the sedimentary or igneous basin under alkaline conditions, where various types of clay minerals represent as a medium for replacement of hydroxyl ion (OH^-) with fluorine ion (F^-). The substitution of F^- in OH^- position readily occurs during magmatic fractions due to the similar ionic radius (Farooqi et al. 2007a). Fluoride ions are adsorbed on the surface of clay minerals at acidic pH between 5 and 6.5 and desorbed under alkaline conditions. Thus, an alkaline condition favors enrichment of fluoride ions in groundwater (Saxena and Ahmed 2003; Singh et al. 2015). Under alkaline conditions ($pH > 7$), anion exchange occurs where OH^- can replace F^- of fluoride-containing minerals such as biotite and muscovite (Li et al. 2014). (Farooqi et al. 2007a) reported a positive correlation between sodium and fluoride in the water with a low concentration of calcium, where the exchange of Ca^{2+} for Na^+ takes place accelerating the solubility of CaF to increase releasing high fluoride. The prolong water retention causes replacement of Ca^{2+} with Na^+ which leads to the formation of soft Na^+-rich water that favors leaching of fluoride in groundwater (Karro and Uppin 2013). High $HCO_3{}^-$ also promotes dissolution of fluoride-containing minerals (CaF_2) in groundwater (Handa 1988). The above reaction increases the pH value of water with increasing other water quality controlling factors such as EC, TDS and redox potential (Eh).

Spatial variation of fluoride concentration in groundwater

The fluoride concentration in recent studies as reported by Rasool et al. (2015) indicates much higher values than previously reported studies D. G khan (Malana and Khosa 2011), Qasur, Lahore (Farooqi et al. 2007a), Sialkot (Ullah et al. 2009) and Hudiara drain, Lahore, Punjab (Khattak et al. 2012). PCRWR has declared 6 cities recently, which are most affected areas of Pakistan such as Sindh, Bahawalpur, Multan, Lahore, Vehari and Muzaffargarh (PCRWR 2005). Spatial and occurrence of fluoride concentration in groundwater of Pakistan are shown in Table 2; Fig. 1. The coal burning industries could be a source of high-fluoride concentrations besides other natural sources.

Mechanisms of fluoride in groundwater

The occurrence of an elevated level of fluoride in groundwater categorized by a low concentration of Ca^{2+} and Mg^{2+} and a higher concentration of Na^+ (Farooqi et al. 2007b). Fluoride ions are adsorbed on clay using acidic solution, and they are desorbed in alkaline solution with high $HCO_3{}^-$ that promotes precipitation of Ca^{2+} as calcite (Sarma and Rao 1997). However, alkaline pH is helpful for fluoride dissolution (Saxena and Ahmed 2003). Two most important mechanisms were used to explain possible reasons for increased fluoride level in groundwater, and these procedures include ion exchange, evaporative concentration and dissolution of fluoride-bearing minerals (Agrawal et al. 1997; Saxena and Ahmed 2003).

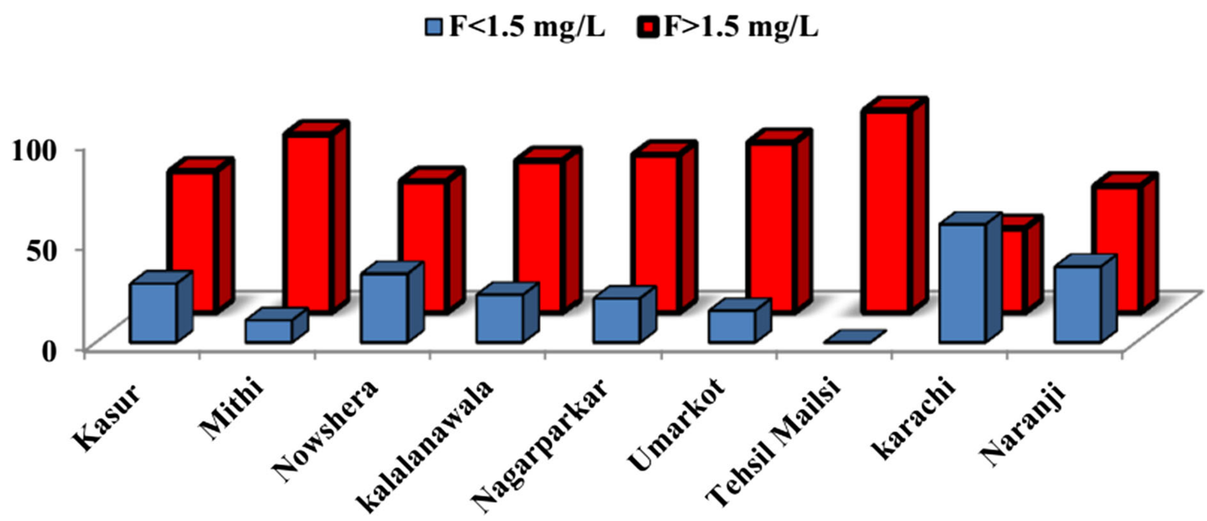

Fig. 1 Distribution of fluoride contaminations in different cities of Pakistan data from

Probably, one of the mechanisms of higher F concentration in water from arid and semiarid regions is the condensation of soluble components due to evapotranspiration and evaporation (Jacks et al. 2005).

However, mechanisms in a recent study by Rasool et al. (2015 explain oxidative–evaporative processes due to the dissolution of fluoride-bearing minerals. There are various natural and anthropogenic sources responsible for high fluoride levels in water which include minerals leaching of fluoride bearing (Shah and Danishwar 2003; Naseem et al. 2010), coal industries waste, agricultural fertilizer (Siddique et al. 2006), brick production and coal combustion into air which goes down due to rain into soil (Farooqi et al. 2007b). As currently reported, the possible sources for high-fluoride concentration in groundwater are agricultural fertilizers, industrial wastes and soil enrichment with fluoride-bearing minerals, as the study area is a major agricultural and industrial unit.

Global perspectives of fluoride especially Pakistan

The elevated fluoride concentration in groundwater globally with exceeding WHO permissible limits of 1.5 ppm is shown in Table 1; Fig. 2. The worldwide result shows that most affected countries with a high concentration of fluoride are Tanzania, Germany, Argentina, China, Kenya, Mexico, India, USA and Pakistan (Table 1). Fluorides are naturally released into groundwater though dissolution of F-containing soils and rocks. In the earth crust, fluoride abundant (625 mg/kg) which was because of fumarolic gasses, geography and volcanic activity (Edmunds and Smedley 2013). Likewise, fluoride concentration increased due to the natural dissolution of minerals, fertilizer plants, metallurgical industries, semiconductor production generated with high-fluoride contents globally; as well as in the case of phosphate production, fluoride effluents could reach up t0 3000 ppm (Ndiaye et al. 2005; Dolar et al. 2011). However, same situation present in Pakistan, a high concentration of F have been reported in many areas of Pakistan are shown in Table 2, Fig. 3.

Although in Khyber Pakhtoonkhwa fluoride concentration in spring water recorded can be up to 13.52 ppm as reported by Shah and Danishwar (2003). Likewise, the Thar Desert in NagarParkar 35.4 ppm was recorded (Naseem et al. 2010). Farooqi et al. (2007a) reported that fluoride concentration in Khalanwala, Punjab, is 21.1 ppm, which concluded 75% of the samples analyzed to be above WHO limits. The current study in Tehsil Mailsi shows the highest concentration of fluoride in groundwater around 5.5 ppm (Rasool et al. 2015). The overall representation of elevated fluoride in groundwater needs managements and monitoring through the world. Fluoride increased concentration in water creates a harmful effect on the human body which depends on uptake duration (Fawell et al. 2006). Detailed studies carried out in India, China, Tibet and Pakistan indicated increased instances of skeletal fluorosis and dental

Table 1 Worldwide distribution of fluoride in groundwater

Locations	Fluoride concentration (ppm)	Fluoride sources	References
Tehsil Mailsi (Punjab, Pakistan)	> 5.5	Groundwater	Rasool et al. (2015)
Lahore and Kasure districts (Punjab, Pakistan)	2.47–21.1	Groundwater	Farooqi et al. (2007a)
District Tharparkar (Sindh, Pakistan)	13.8–49.3	Underground water	Brahman et al. (2013)
District Nagarparkar (Sindh, Pakistan)	18.5–35.4	Irrigated surface water	Brahman et al. (2014)
North-West India	< 19	Groundwater	Agarwal et al. (1997)
South India	< 20	Groundwater	Fawell et al. (2006)
Jilin Province, China	> 2–< 10	Groundwater	Zhang et al. (2003)
Shanxi province, China	< 8.3	Groundwater	Wang et al. (2009)
Muenster region, Germany	< 8.8	Wells water	Queste et al. (2001)
Southeast regions, Argentina	3.8–182	Wells water	Paoloni et al. (2003)
Middle and eastern parts, Turkey	< 13.7	Drinking water	Azbar and Turkman (2000)
Rift Valley, Kenya	< 180	Groundwater	Gaciri and Davies (1993)
Ethiopia	10–68	Wells water	Rango et al. (2012)
South Africa	< 40	Groundwater	Muller et al. (1998)
Shinyanga Region, Tanzania	< 250	Groundwater	Ghiglieri et al. (2012)
Arusha Region, Tanzania	< 330	Groundwater	Ghiglieri et al. (2012)
Mexico	3.7	Groundwater	Carrillo-Rivera et al. (1996)
USA	< 4.3	Groundwater	Segreto et al. (1984)

fluorosis, due to consumption of an excessive amount of water (Cao 2005). In Yuncheng Basin, China, fluorosis is a widespread problem; almost 20% of people living in the basin are being affected by this disease during the last two decades (Gao et al. 2007).

Environmental sources of fluoride

Fluoride enters the environment via both anthropogenic and natural sources (Table 3). In the majority of cases, natural sources have been identified as the main cause for high levels of F in groundwater (Gaciri and Davies 1993). Natural sources which cause fluoride contamination of groundwater include volcanic eruption, weathering and erosion of fluoride-bearing rocks (Brindha and Elango 2011). There are some common fluorine-bearing minerals which contribute fluoride in groundwater include fluorite (CaF2), sellaite (MgF2), fluorapatite (Ca5(PO4)3F), cryolite (Na3AlF6), villiaumite (NaF) and topaz (Al2(SiO4)F2). Some other minerals like mica and amphiboles can also contain F^- which replaces for OH^- in the mineral structures (Edmunds and Smedley 2013). On the other hand, coal combustion and waste production by various industries, including steel, aluminum, copper and nickel smelting, and the production of glass, phosphate fertilizers, brick and tile are worth mentioning anthropogenic sources (Fig. 4) of fluoride in groundwater (Farooqi et al. 2007a). The main natural source of fluoride in groundwater is weathering of rocks bearing minerals, leaching rock contamination in groundwater reserves (Hem 1985). Probably, most reactive fluorine naturally found as calcium fluoride (CaF2) (Handa 1988), which include topaz, fluorite, fluorapatite, phosphorite, cryolite and chlorapatite. Mostly, higher concentrations of fluoride are present in shale than limestone and sandstone, while a high concentration of fluoride found in alkaline rocks (1200 to 8500 mg/kg) (Dey et al. 2011).

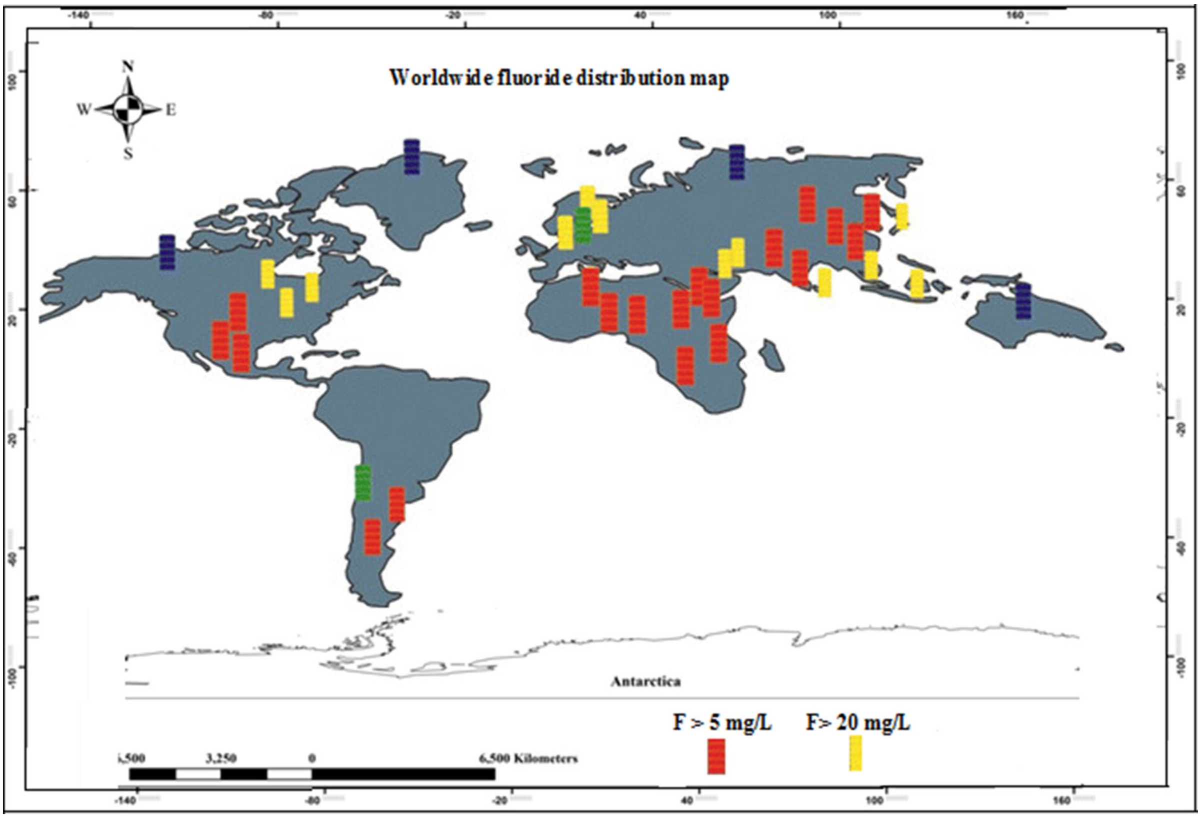

Fig. 2 Status of fluoride (mg/L) contamination in groundwater all over the world

Table 2 Special distribution of fluoride in Pakistan

Locations	Province	Max. concentration (ppm)	References
District D.G. Khan	Southern Punjab	1.5	Malana and Khosa (2011)
Lahore and Kasur districts	East Punjab	22.8	Farooqi et al. (2007b)
Lahore and Kasur districts	East Punjab	21.1	Farooqi et al. (2007a)
District Sialkot	Punjab	0.99	Ullah et al. (2009)
District Tharparkar	Sindh	49.3	Brahman et al. (2013)
District Nagarparkar	Sindh	35.4	Brahman et al. (2014)
District Khairpur Mir	Sindh	5	Baig et al. (2012)
Manchar lake, district Jamshoro	Sindh	1.14	Kazi et al. (2009)
Tehsil Mailsi	Punjab	> 5.5	Rasool et al. (2015)

Geological and anthropogenic contamination of fluoride in groundwater: Pakistan scenario

Varying concentrations of fluoride pollutant has been found in groundwater from different places of Pakistan (Azizullah et al. 2011). Pakistan Council for Research in Water Resources (PCRWR) carried out a detailed study to explore the possibility of fluoride toxicity in the drinking water of 16 major cities of four provinces, and they found fluoride concentration beyond the permissible limit (Tahir and Rasheed 2012). Study conducted by Naseem et al. (2010) in Sindh area of

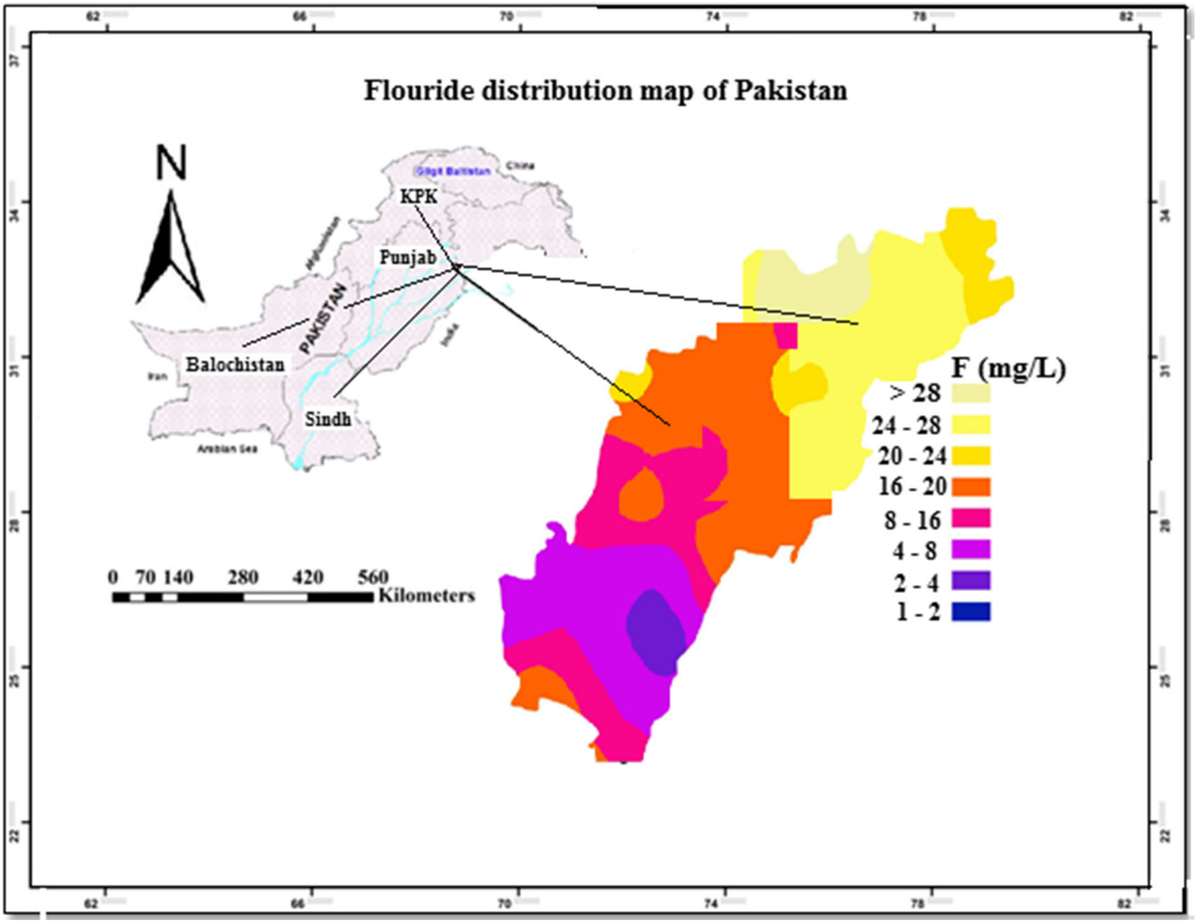

Fig. 3 Spatial distribution of fluoride in groundwater of Pakistan published in the literature (Reproduced with permission from Rasool et al. 2015; Arain et al. 2009; Azizullah et al. 2011; Baig et al. 2009, 2011; Brahman et al. 2013; Farooqi et al. 2012a; b; Haque et al. 2008; Iqbal et al. 2001; Malana and Khosa 2011; Muhammad et al. 2010; Nickson et al. 2005; Rafique et al. 2015; Rahman et al. 2011)

Table 3 Natural and anthropogenic sources of fluoride in groundwater

Sources of arsenic	
Natural sources	Anthropogenic sources
Fluoride-bearing minerals	Mining activity, household waste, industrial activities
Hydrothermal mineral deposits	Agricultural chemicals like algaecides, desiccants used in mechanical cotton harvesting and in herbicides
Fluorite (CaF2), sellaite (MgF2), fluorapatite (Ca5(PO4)3F), cryolite (Na3AlF6), villiaumite (NaF) and topaz (Al2(SiO4)F2)	Fluoride trioxide may be found in pesticides and defoliants and as a contaminant of moonshine whiskey
	Glass manufacturing industries, brick industries, coal industries, electronic industry

NagarParker discovered granite rocks containing an average fluoride concentration of 1939 mg/kg, while fluoride in kaolin deposits between 468 and 1722 mg/kg and secondary deposits have 270 mg/kg. (Farooqi et al. 2007b) reported that in Pakistan more than 2 million people are being affected by high fluoride. The highest fluoride contents have been observed from Khalanwala, east Punjab, where the maximum

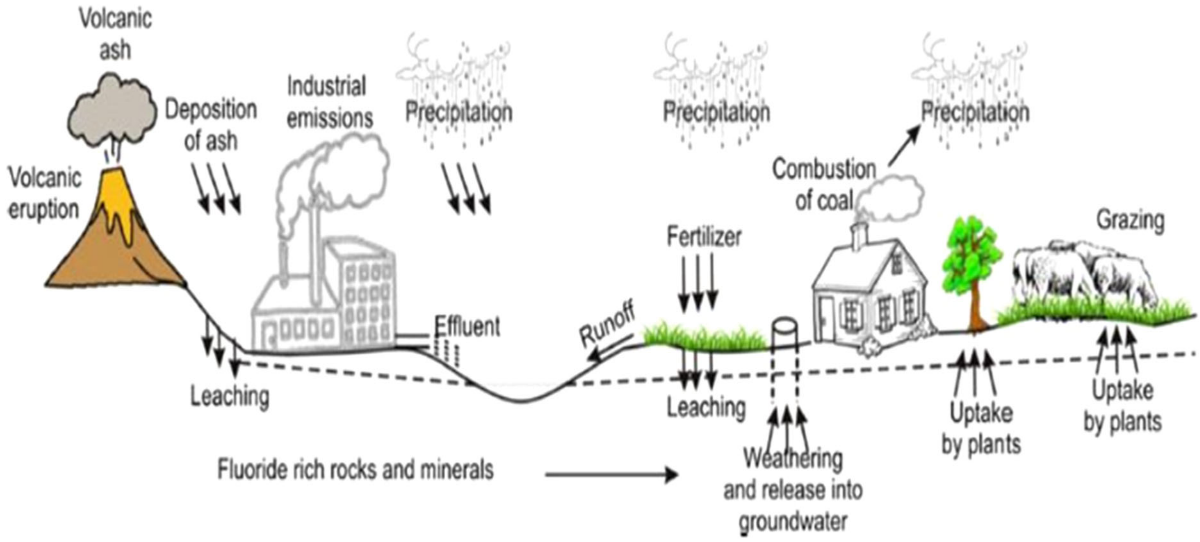

Fig. 4 Existing sources of fluoride (Reproduced with permission from Vithanage and Bhattacharya 2015)

concentration recorded as high as 21.1 mg/L. The major sources mainly comprise of phosphate fertilizer, containing leachable fluoride (52–25 mg/kg) and coal-containing fluoride (5–20 mg/kg) was noticed to pollute water with fluoride. Fluoride contamination of groundwater has also been reported in Union Council Gander, district Nowshera, Khyber Pakhtunkhwa. The analysis of water samples ($n = 49$) for fluoride shown that 17 samples exhibit higher concentration above the permissible limits (F > 1.5 mg/L) recommended by World Health Organization.

The study area is covered with lacustrine, deltaic, fluvial, alluvial, flood plain and loess which caused a high amount of fluoride content in groundwater source (Shah and Danishwar 2003). Higher-fluoride concentration up to 6.3 mg/L has been observed in groundwater of Karachi city from the industrial zone site, while the sample from tap water shown the fluoride concentration in the range between 0.60 and 3.64 mg/L. The high-fluoride content in the samples collected from industrial zone was due to the input of glass, tiles and ceramic industries (Fig. 4) which use fluoride in the manufacturing process (Siddique et al. 2006).

Geological sources of fluoride contamination in groundwater: worldwide scenario

Fluoride cases in drinking water have been reported from different parts of the world (Table 3). Depending on geographical location, fluoride concentration varies around the world (Vithanage and Bhattacharya 2015). (Teotia and Teotia 1994) reported that 85 million tons of 12 million fluoride deposits are found in India. Some regions of India such as Nalgonda district, Andhra Pradesh, composed of granitic rocks with 325–3200 mg/kg which contributed to higher-fluoride content in groundwater of the region. (Jacks et al. 2005) observed that high-fluoride content in different parts of India was due to natural factors mainly evapotranspiration which caused contamination of groundwater with fluoride. In New Delhi, about 50% of the groundwater has found contaminated with fluoride (Datta et al. 1996). A study conducted in different parts of Sri Lanka shows a high concentration of F even more than 4 mg/L in groundwater (Young et al. 2010). Higher concentrations of fluoride have largely been observed in plain areas where due to slow water movement and prolong rocks–water interaction caused elevation of fluoride (Dharmagunawardhane and Dissanayake 1993). In Japan, volcanic explosion may cause groundwater contamination of fluoride through ash. Ash from Sakurajima volcano explosion of Japan reported to contain an average concentration of 788.1 mg/kg fluoride (Nogami et al. 2006). Abdelgawad et al. (2009) noticed that high saturation of groundwater with fluoride in Mizunami area of Japan was due to weathering and alteration of granite rocks. The reported study on Taiyuan basin of China revealed that interaction between fluoride-bearing minerals and groundwater in recharge area contributed high fluoride while in the discharge area mixing of karst water and evaporation caused high fluoride (Gao et al. 2007).

Anthropogenic sources of fluoride contamination in groundwater: worldwide scenario

Cronin et al. (2000) noticed industrial plants such as the manufacture of hydrofluoric acid, aluminum and superphosphate; bricks are the main source polluting the atmosphere with fluorine. In Tamil Nadu, South India (Kumar 2013) observed impact of leather industry on F mobilization. He found that disposal of untreated effluent enriched with TDS, NaCl and sulfide is responsible factors to raise fluoride contents. The high concentration of sodium and TDS favored elevation of fluoride in groundwater. The quality of groundwater in Poland was investigated with respect to fluoride pollutant by Czarnowski et al. (1996) and noted that they were within the limit in most of the places. Though, around 1.38 mg/L of fluoride was observed in the locality of disposal site of a phosphate industry. Around 16.5 million people in China are at risk of fluorosis due to coal combustion and coal bricks (Chaoke et al. 1997). It is established that more than 26 million people suffer from chronic fluorosis due to indoor combustion and brick tea. Another study conducted in 2003 by Anderson and Stevenson (1930) identified coal burning and coal bricks as the major source of gaseous and aerosol fluoride in rural areas of China. A large number of people exposed to fluoride were due to consumption of contaminated food items, i.e., potatoes, chilies and corn. A study on airborne fluoride was carried out by Mirlean and Rosenberg (2007), in rainwater, groundwater and surface soil samples along the gradient of emission of phosphate fertilizer factory in Brazil. They observed fluoride concentration 3 mg/L in the rain and 5 mg/L in groundwater. Also, fluoride accumulated in a superficial horizon of soil from the emission of industry was in quantities comparable to those in the manufactured end products.

Health impacts of fluoride

Fluoride contaminated groundwater in the environment creates a serious public health problem in many parts of the world (Table 4). Around 28 developed and developing countries, including India, China, Pakistan, Sri Lanka, Turkey, Iran, East Africa's Rift Valley, Scandinavia, Algeria, Libya, Iraq, USA, Canada, Thailand, New Zealand and Japan, are fluoride endemic suffering 200 million people in the world (Rafique et al. 2015). Fluoride is an essential micronutrient necessary in low quantity in drinking water for the human body. Ingestion of 1 mg/L of fluoride in drinking water reduces the dental carries and strengthening the apatite matrix tissues (Naseem et al. 2010; Reddy et al. 2010). When concentration of fluoride exceeds the 1.5 mg/L in drinking water, it causes different disorders of teeth and bones at a different degree of concentration which is as follows: skeletal fluorosis and crippling disease afflicted by over-mineralization of joints and bones which occur because of persisting exposure to high fluoride (F^-) exceeding (4–10 mg/L) in drinking water (Phan et al. 2010). Around 2.7 million cases of acute to chronic skeletal fluorosis are reported in China and India (Shemirani et al. 2005; Wade et al. 2009; Phan et al. 2010; McClintock et al. 2012; Tahir and Rasheed 2013; Tsuji et al. 2014). Dental fluorosis takes place when fluoride concentrations exceed 1.5 mg/L. In the initial stage of dental fluorosis, the tooth becomes yellow to brown and then turns into black. In addition to fluorosis (dental and skeletal), fluoride has been known to cause impacts on kidney, muscular system and levels of erythrocyte due to a high level of fluoride in drinking water (Barringer and Reilly 2013; Bashir et al. 2013).

Another study was conducted by Wade et al. (2009) in Mongolia which announced that approximately 12,600 peoples have a risk of heart disease due to increasing concentraion of fluoride in well water. In Cambodia, about 98.6% population at risk of non-cancer health effects and 33.7% highly threatened toward cancer by consumption of fluoride contaminated water (Phan et al. 2010). In Bangladesh, hyperkeratosis and hyper-pigmentation are mostly common symptoms of disease in local residents that lead to cancer (Nguyen et al. 2009). In Pakistan, study was conducted by Kazi et al. (2009); their finding showed that 61–73% people residing on the bank of Manchar Lake suffered from the chronic fluoride toxicity melanosis and keratosis was found common disease. Another study was conducted in Bobak village near Manchar Lake; according to study, there is about 30–40% resident of the study area suffering

Table 4 Chronic Effects of fluoride on human health in groundwater

System	Effects on health
Cardiovascular system	Effects on thinking of blood vessels, increased the risk of heart attack, hypertension, Cardiac arrhythmias, decreased in blood circulation that cause gangrene of extremities
Dermal	Thickening of skin, the hyper-pigmentation, size decrease in small arteries that cause numbness known as Reynaud's disease, basal cell cancer and squamous
Gastrointestinal	The effects on abdominal pain, nausea and heartburn, dental fluorosis
Hepatic	Effects that cause abnormal cell growth known as neoplasia, and cirrhosis
Hematological	Decreased white blood cell count known as leukopenia and anemia
Neurological	Effects on memory loss, coma, brain malfunction, the hallucinations, seizures and neuropathy
Pulmonary	Dental carries, dental fluorosis, long time cough and restrictive lungs
Renal	Skeletal fluorosis, crippling fluorosis, dehydration and the cortical necrosis
Respiratory	Effects on tracheal bronchitis that cause shortness of breath, rhinitis, pharyngitis, perforation of the nasal septum and laryngitis
Reproductive	Highly effects on the congenital malformations of fetus, low bright weight, still birth and increase the risk of spontaneous abortions

from the skin lesions diseases, dental disease, backbone pain and rough skin which may cause due to consumption of fluoride contaminated water (Arain et al. 2009). The recent study was reported in Tehsil Mailsi, according to this study there are about 40–50% people suffering from lung cancer, hepatitis, dental problem, blood pressure diseases cause due to consumption of polluted drinking water through fluoride (Rasool et al. 2015).

Mitigation technologies for removing fluoride from water

Numerous alternative water supply technologies have been identified and tested in different areas of Pakistan and worldwide to reduce the concentration of fluoride in water. Various technologies of fluoride removal usually based on six principles are as follows: adsorption, membrane tools, filtration and oxidation and biological oxidation. Mostly, simple and cost-effective method reverse osmosis (Viswanathan and Meenakshi 2009) and ion exchange (Meenakshi and Viswanathan 2007) have been used for removal of fluoride from drinking water. However, in some developing countries, commonly Nalgonda technique has been used for water defluoridation (Waghmare et al. 2015). In this method, probably lime, alum and bleaching powder have been added in polluted water for rapid mixing, sedimentation, filtration and flocculation. The impenetrable sediment of aluminum hydroxide flocks along with fluoride precipitation, whereas bleaching powder performance as a disinfectant. Nevertheless, in the treated water residual aluminum high concentration (2–7 mg/L), which was greater than WHO standard (0.2 mg/L; Maheshwari 2006; Ayoob et al. 2008), is the highest disadvantage of this process. Similarly, natural materials which are found easily in large quantity are being examined for fluoride contaminated water (Biswas et al. 2010). Usually, a simple method has been carried out for the removal of fluoride with help of low-quality coal (Borah and Dey 2009).

In basic to accomplish agent of fluoride removal with low-cost, bentonite clay was amended chemically by $MgCl_2$ (Thakre et al. 2010). Most cost-effective and economical method is agricultural waste used for removal of fluoride and its easy availability. Calcium chloride and aluminum chloride were used to treat corn cobs powder for defluoridaion of water (Parmar et al. 2006). Removal of fluoride using Al/Ca cobs showed excellent results (Parmar et al. 2006). Similarly, some other agricultural materials include shell fibers, coconut shell and rice husk in order to remove pollutants that are fluoride (Mohan et al. 2008). Coconut shell of carbon provides the good adsorbent. Similarly, palm seed coat charcoal utilizing fluoride adsorbent to expel fluoride from water (Sivabalan et al. 2003).

Many fluoride treatment tools need pH modification for good performance, which openly affects fluoride in freshwater (Bissen and Frimmel 2003). Mostly, chemical oxidation, the fluoride oxidative procedure, could be catalyzed via some types of bacteria which were useful in drinking water (Jain and Singh 2012). This process would be realistic normally to reduce aquifer situation holding manganese and iron (Jain and Singh 2012). The productivity of fluoride elimination is indomitable over fluoride and iron portion as well as early iron concentration. In definite suitcases, ferric coagulant was auxiliary for effective fluoride removal, and then, this process has liberated the range of pH 5.5–8.5 (Bibi et al. 2015; Violante and Pigna 2009). Many lesions also labeled fluoride sorption on chemical oxidation and manganese oxides (Tournassat et al. 2002).

Hug et al. (2001) introduced a simple method for fluoride removal which was solar oxidation through locally accessible resources at neutral pH, without using any additional chemicals, but in Bangladesh drinking water pH adjustment that provides the issue of fluoride during removal process (Ahmed et al. 2004). Phytoremediation study was convoyed to estimate the fluoride uptake potential of two Cyperaceous species such as Eleocharismacrostachya and Schoenoplectusamericanus, composed nearby Chihuahua State, Mexico (Bundschuh et al. 2010). As well as invented both species were capable of living at the high arsenic level and should be used for rhizofiltraion via plant bear 97% of the arsenic with no clear effect on plant growth. Bundschuh et al. (2010) discovered dried macroalgae (Spyrogiraspp) for fluoride removal from acid mine drainage and successfully remove fluoride up to 80 to 90% with four days consumed. Marine plant species, like Ranunculus peltatus spp. Saniculifolius, Ranunculus trichohyllus, and leaves of Juncus effuses and Azollacaroliniana, had very high latent for fluoride phytofiltration, although they were confirmed for fabricated natural water bodies and wetlands treatment (Parmar and Singh 2015).

Three chemical precipitation processes were used for removing fluoride from drinking water which includes lime softening, the gravity of coagulation filtration and microfiltration (Chwirka et al. 2000; Sancha 2006). Lime softening was used to remove the hardness from water, for enhancing lime addition to increase pH level above 10.5 to remove fluoride, which was not cost-effective or economical. Coagulation depends on microfiltration with modification of granular media filtration, to remove fluoride (Thirunavukkarasu et al. 2003). Most probably, adsorption media used for removing fluoride from water included activated alumina, iron-coated sand, granular ferric hydroxide, filters and some other mixed adsorbent. Mostly used adsorption media for removal of fluoride included activated alumina, granular ferric hydroxide, iron-coated sand, filters and other mixed adsorbents (Thirunavukkarasu et al. 2003). The precipitation and coagulation processes with iron (III), used for removal of the fluoride (Tressaud 2006), alumina invigorated (Ghorai and Pant 2005) and calcium (Yin et al. 2015a, b), usually have been studied worldwide.

Conclusion and recommendations

Summarily, based on the discussion, it is safe to say that fluoridated water contributes to various health issues. Globally, the strong similarities between the sediments type and groundwater geochemical conditions associated with high F^{-} concentration in Pakistan and other semiarid regions, such as Argentina, China, Bangladesh, and Mexico, indicate that certain groundwater chemistry (Na-rich, bicarbonate-rich, high pH) favors the augmentation of F^{-} in groundwater oxidizing condition. The current review reveals the latest state of the skill on an understanding of various interdisciplinary faces of the problem of fluoride in the environmental land, mechanisms of mobilization in groundwater, biogeochemical relations and the measure for remediation. In numerous parts of the world, biogeochemical processes have resulted in the dissolution of naturally occurring fluoride into groundwater. We have reviewed in different parts of the world, the problem of fluoride contamination charted by broad viewpoint in epidemiology and toxicity mechanism of fluoride in humans as well as animals. In order to apprehend the fluoride threat, several remediation methods based on modern, conventional and hybrid technologies for fluoride removal in many parts of the world have been carefully reviewed. Fluoride toxicity affects millions of people in the world but amazingly still remains a neglected public health concern. Administrative, financial and logistic supports may be essential to reduce fluorosis. Further, extensive research should be taken to address the understanding of the occurrence, origin and distribution pattern of fluoride. The government should monitor industrial and agricultural activities leading to fluoride pollution. The Government of Pakistan should provide drinking water alternatives to these areas in recognition of the potential health risks associated with fluoride. In future, this present study is very helpful with regard to diverse fluoride mitigation measures in use at both regional and national level and for better understanding, categorization of hydrological controls and mobilization of fluoride in groundwater and surface water.

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Compliance with ethical standards

Conflict of interest The authors have no conflict of interest.

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