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REVIEW

Fluoride in the environment: sources, distribution and defluoridation

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Abstract Fluoride is one of the most widespread groundwater pollutant. More than 200 million people, from 25 nations, are suffering from fluorosis. This review presents an overview of fluoride distribution in groundwaters, and defluoridation techniques. Adsorption is the most common technique; however, the efficiency, sorbate disposal and continuous supply of efficient sorbates are still problematic. Membrane processes are quite efficient but not economical for developing communities. This article therefore highlights the importance of further research on efficient and cost-effective defluoridation for the rural developing communities not only to be used for household filtration units but also for use in community water supply schemes.

Keywords Fluorosis · Groundwater · Adsorption · Ion exchange · Coagulation · Co-precipitation

Introduction

Fluorine is the most electronegative and reactive element in the periodic table, occurring primarily as the fluoride ion (F^-) in the natural environment. Fluoride mobilization in the natural conditions is the cause of most environmental fluoride problems. However, in some special cases, such as the recent incident happened (October 2012) in the Republic of South Korea with the hydrofluoric gas leakage in an industrial accident may also provide fluoride into the environment in heavy loadings. Fluorine, the element of fluoride, associates with many mineral deposits containing fluoride-bearing minerals, and weathering, dissolution and other pedogenic processes can release fluoride into groundwater. Even though fluoride is considered as an essential element for human health, especially for the strengthening of tooth enamel, excessive doses can be harmful. While fluoride is present in air, water and food, the most common way it enters the food chain is via drinking water (Fawell et al. 2006).

Fluoride-rich drinking water is a widespread problem which can be seen all over the world. Fluorosis is endemic in at least 25 countries around the world, and is most prevalent in India, China, and parts of Africa. It is not known how many people are currently afflicted with the disease, but conservative estimates are in the tens of millions of people (WHO 2004). According to the WHO, at concentrations above 1.5 mg/L, fluoride is considered as dangerous to human health. Excessive fluoride can lead to dental and skeletal fluorosis, a disease that can cause mottling of the teeth and calcification of ligaments (Fig. 1) (Fawell et al. 2006; Kowalski 1999). Long-term ingestion of fluoride-rich drinking water may show the way to crippling bone deformities, cancer (Kowalski 1999; Yiamouyiannis 1993), decreased cognitive ability, lower intelligence quotient and developmental issues in children (Li et al. 1994). The populations in tropical belt are having close contacts with their surrounding environment, and thereby, the geochemical anomalies play a role in the people's health (Dissanayake and Chandrajith 2009). One argument is that the fluoride toxicity increases with the

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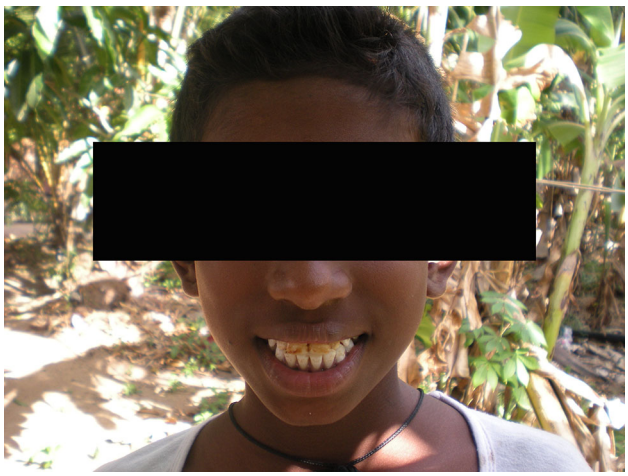

Fig. 1 Dental fluorosis-affected child in Anuradhapura, Sri Lanka

amount of drinking water consumed especially in the humid tropics; thus, the maximum permissible fluoride concentration in drinking water has to be lowered from the existing WHO limit (Dissanayake 2005; WHO 1996, 2004).

The presence of fluoride in water does not impart any color, odor or taste. Hence, it acts as an invisible poison such as arsenic in groundwater. Unless otherwise tested, one cannot reveal the high concentrations of fluoride in their waters. This review therefore focuses on the sources, distribution and treatment methods of fluoride available in the literature. Furthermore, we discuss the problems of the processes involved in the removal methods which have been proposed as well as future perspectives of fluoride research. This mini review is an abridged version of our book chapter published in the book Environmental for a Sustainable World (Vithanage and Bhattacharya 2014).

Different sources of fluoride in the environment

The possible sources of fluoride in the environment are schematically shown in Fig. 2. The largest fluoride reserve is considered as the natural input from the rocks and minerals containing fluoride in there composition.

Rocks and minerals

Fluoride is one of the most abundant trace elements in the Earth's crust, with an average concentration of 625 mg/kg in different rock types (Edmunds and Smedley 2005; Tavener and Clark 2006). The largest fluoride reserve is the rocks containing fluorine-rich minerals (WHO 1984). The highest fluoride levels are associated with syenites, granites, quartz monzonites, granodiorites, felsic and biotite gneisses, and alkaline volcanics (Apambire et al. 1997a; Chae et al. 2006, 2007; Dissanayake 1991; Handa 1975; Hyndman 1985; Jones et al. 1977; Moore 2004; Nanyaro et al. 1984; Ozsvath 2006; Robinson and Kapo 2003; Rosi et al. 2003; Stormer and Carmichael 1970; Taylor and Fallick 1997). In Coimbatore district in Tamil Nadu, rocks are found to contain 180–2600 mg/kg F (Table 1).

Among all fluoride-rich minerals, fluorite (CaF_2), fluoroapatite ($Ca_5(PO_4)_3F$), micas, amphiboles, cryolite (Na_3AlF_6), villiaumite (NaF) and topaz ($Al_2(SiO_4)F_2$) are considered as the most abundant minerals which occur in most rocks and sediments (Apambire et al. 1997a; Chae et al. 2007; Cronin et al. 2000; Edmunds and Smedley 2005; Handa 1975; Hem 1985; Saxena and Ahmed 2003). The granitic rocks containing fluoride minerals such as amphibolites, pegmatites, hornblende, muscovite and biotite micas supply fluoride to soils and groundwater by weathering and soil-forming processes. Among the few laboratory model studies, it has been observed that granites, acid volcanic rocks, basic dikes and hornblende in gneisses contribute to fluoride-rich soils and waters in the surrounding (Saxena and Ahmed 2001).

Fluoride dissolution into the environment

Wall rock interaction is believed to be the foremost process on fluoride release to groundwater (Abdelgawad et al. 2009; Handa 1975; Saxena and Ahmed 2003). High-F groundwaters are common in the dry parts of the world. The reason behind is that the fluoride originates mainly from hydroxypositions in biotite and hornblende and is concentrated through evapotranspiration in soil and groundwater exhibiting residual alkalinity. Such waters are common in areas with generally alkaline soils. Along the flow paths of the water from hill tops to valley bottoms, calcite, dolomite and fluorite seem to precipitate, in that order (Jacks et al. 2005).

The high-fluoride groundwater typically has high pH value, high HCO_3^- content and high Na^+ content (Guo et al. 2007; Handa 1975; Jacks et al. 1993, 2005). Guo et al. (2007) indicated that the fluoride concentration is positively correlated with HCO_3^- and Na^+ contents. Alkaline conditions, moderate specific conductivity and their ratios play a significant role in F dissolution from rocks (Saxena and Ahmed 2001, 2003). For the dissolution of fluorite in groundwater with high HCO_3^- contents, the reaction is as follows:

$$CaF_2 + 2HCO_3^- \Leftrightarrow CaCO_3 + 2F^- + H_2O + CO_2 \quad (1)$$

Moreover, groundwaters with high HCO_3^- and Na^+ content are usually alkaline and have relative high OH^- content, so the OH^- can replace the exchangeable F^- of

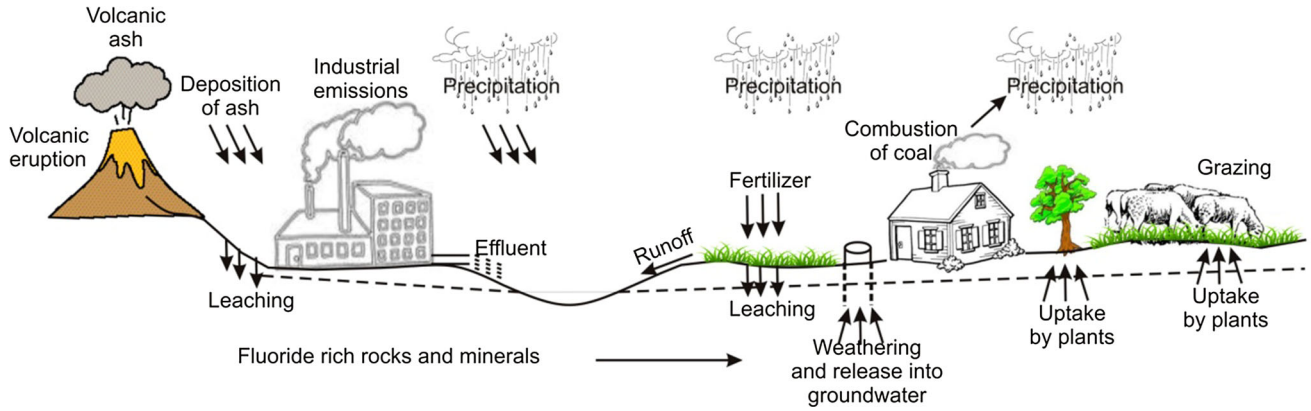

Fig. 2 A schematic diagram showing the fluoride-existing sources in the environment

Table 1 Fluorine in fresh rocks, weathered material and soils from Coimbatore district in Tamil Nadu, India (Modified from Jacks et al. 2005)

Sample/site	Fraction	Weight (%)	F concentration (mg/kg)	Fluoride in groundwater (mg/L)	Fluoride in calcrete (mg/kg)
Gneiss/Nallur	Light	74	1520	5.9	800–900
	Dark	26	5700		
	Fresh rock		2500		
	Weathered		1880		
	Soil (<2 mm)		2000		
Gneiss/Ponnandakavundanur	Light	70	1270	4.0	510–1300
	Dark	30	5400		
Gneiss/Kodavadi	Light	65	195	5.2	1600–2500
	Dark	38	2700		
	Fresh rock	1070			
	Weathered	900			
	Soil (<2 mm)	690			
Granite/Karunagarapuri	Light	95	360	1.5	
	Dark	5	2100		
Vedasandur	Fresh rock	380			1080
	Weathered	360			
	Soil (<2 mm)	470			

fluoride-bearing minerals, increasing the F^- content in groundwater. The reactions are basically as follows:

Muscovite:

$$KAl_2[AlSi_3O_{10}]F_2 + 2OH^- \Leftrightarrow KAl_2[AlSi_3O_{10}]OH_2 + 2F^- \quad (2)$$

Biotite:

$$KMg_3[AlSi_3O_{10}]F_2 + 2OH^- \Leftrightarrow KMg_3[AlSi_3O_{10}]OH_2 + 2F^- \quad (3)$$

Evaporation is another important factor resulting in the occurrence of high-fluoride groundwater. Calcium ions precipitate out as $CaCO_3$, due to high evaporation resulting in reducing Ca^{2+} concentration of the groundwater, and consequently, the solubility control of CaF_2 on fluoride enrichment in the aqueous phase becomes weaker. This has been described in detail by Handa (1975). Also, secondary mineral deposition has shown a great potential to act as sinks for fluoride and with their quick dissolution release fluoride based on the pH of the media (Jacks et al. 1993, 2005).

Fluoride mobility in soils and groundwater

Although the fluorine content of most rocks ranges from 100 to 1,300 mg/kg (Faure 1991), soil concentrations typically vary between 20 and 500 mg/kg (Edmunds and Smedley 2005). In some cases, higher concentrations have

been reported in soils affected by anthropogenic inputs, such as phosphate fertilizers (Kabata-Pendias and Pendias 2001), sewage sludge (Rea 1979) and industrial pollution (Cronin et al. 2000).

Fluoride is commonly found in soils ranging from 200 to 300 mg/kg (WHO 2002), however, strong association of fluoride with the soil components does not readily released from soil (Ayoob and Gupta 2006 and references therein). The chemical speciation, soil chemistry and climate are the factors influencing the fluoride release from soils. Below pH 6, in acidic soils, fluoride forms complexes with Fe and Al in the soil, and the adsorption is significantly high in low pHs (below pH 4.0) and decreases above pH 6.5 (WHO 2002). Alkalinization of soils by application of fertilizers under irrigation may increase the fluoride release from soils to the groundwater. Study conducted in China has reported values up to 2860 mg/kg of fluoride in soils (Zhu et al. 2007).

Other sources

Several studies conducted in India have reported different sources of fluoride for soil and groundwater other than weathering.

Other common sources of fluoride in soil and groundwater are the following (Datta et al. 1996):

1. Hydrogeothermal sources
2. Volcanic ash
3. Wet and dry depositions of gaseous (e.g., HF, SiF_4), particulate fluoride (e.g., $A1F_3$, $NaAlF_6$, CaF_2) emissions from steel, aluminum, glass, phosphate fertilizer, brick and tile industries, soil dust and crustal material. Burning of coal and fly ash deposition (Pickering 1985; Skjelkvåle 1994).
4. Phosphate fertilizers, fumigants, rodenticide, insecticides and herbicides containing fluoride as impurity or constituent (Poovaiah 1988; Ware 1975), e.g., cryolite, barium fluorosilicate, sodium silicofluoride, sulfuryl fluoride and trifluralin.

It has been found that the hydrothermal vein deposits and rocks that crystallize from highly evolved magmas contain fluorite, fluorapatite, and fluoride-enriched micas and/or amphiboles (Dolejš and Baker 2004; Hyndman 1985; Stormer and Carmichael 1970; Taylor and Fallick 1997).

The natural atmospheric sources of fluorine in precipitation include marine aerosols, volcanic gas emissions and air-borne soil dust (De Angelis and Legrand 1994; Saether et al. 1995; Tavener and Clark 2006). Volcanic eruptions are common in Iceland, and fluorosis poisoning in livestock and humans was identified long ago in 1978 from the Laki eruption (Brindha and Elango 2011). The fluoride content in ash from Hekla eruption in 2010 was 23–35 mg/kg (Matvaelastofnun 2010). Volcanic ash is readily soluble, and thus, the risk of fluoride contamination in groundwater is very high. These volcanic sources have also been found to cause fluoride contamination in groundwater of Kenya (Gaciri and Davies 1993). The industrial aerosols from brickworks, aluminum smelters, iron and steel production, fossil fuel burning, ceramic industries and phosphate fertilizer plants are the primary anthropogenic sources of fluorine (Bonvicini et al. 2006; Cronin et al. 2000; Feng et al. 2003; Fuge 1977; Tavener and Clark 2006; Walna et al. 2007). Both gaseous (e.g., HF, SiF_4, F_2, and H_2SiF_4) and particulate forms (e.g., CaF_2, NaF, and Na_2SiF_6) of fluoride is being released by the industrial sources. It has been reported that the rainfall contaminated by such industrial emissions may contain fluoride concentrations exceeding 1 mg/L (Feng et al. 2003; Neal 1989; Saether and Andreassen 1989; Walna et al. 2007), and these concentrations can persist up to 2 km from the source (Mirlean and Roisenberg 2007).

Global distribution of fluoride in aqueous environment

Fluoride content in drinking water varies around the world depending on the geographical location. Fluoride contamination is widely reported in groundwater in different parts of the world especially from the humid tropics. These areas include Africa, China, South Asia and Middle East (Ayoob and Gupta 2006). It is estimated that more than 200 million people worldwide rely on drinking water with fluoride concentrations that exceed the present WHO guideline of 1.5 mg/L (WHO 2004). In Mexico, it has been estimated that about more than 5 million people are affected by fluoride in groundwater (Ayoob and Gupta 2006 and references therein). Dangerous levels of fluoride that are increasingly found in groundwater in south and southeastern Asia are of growing concern, along with infectious or other toxic substances (WHO 2000). A detailed description on the concentration of fluoride in groundwater and its sources in various regions of the world based on literature (Ayoob and Gupta 2006; Brindha and Elango 2011) are given in Table 2.

Asian setting

The big picture: India

Of the 85 million tons of fluoride deposits on the earth's crust, 12 million tons are found in India (Teotia and Teotia 1994). Hence, fluoride contamination is widespread, intensive and alarming in India. About 50 % of the groundwater in Delhi exceeds the maximum permissible limit for fluoride in drinking water (Datta et al. 1996). Jacks et al. (2005) observed that high fluoride in groundwater in many

Table 2 Fluoride levels reported in different countries

Country	Location	Water source	Fluoride concentration or range (mg/L)	References
Ghana	Upper regions	Shallow and deep groundwater	0.11–4.6	Apambire et al. (1997b)
Ghana	Nathenje and Lilongwe	Shallow and deep groundwater	0.5–7.02	Msonda et al. (2007)
Pakistan	Naranji	Shallow groundwater	1.08–1.38	Tahir Shah and Danishwar (2003)
Pakistan	Faisalabad	Groundwater	0.38–1.15	Kausar et al. (2003)
Pakistan	Kalalanwala	Shallow groundwater	2.47–21.1	Farooqi et al. (2007b)
Pakistan	Lahore	Shallow and deep groundwater	ND–8.46	Naeem et al. (2007)
Pakistan	Sialkot	Shallow groundwater	0.41–0.99	Ullah et al. (2009)
Pakistan	Nagar Parkar	Groundwater	1.13–7.85	Naseem et al. (2010)
Canada	Gaspe, Quebec	Shallow, intermediate and deep groundwater	0.05–10.9	Boyle and Chagnon (1995)
India	Nalgonda	Shallow groundwater	0.1–8.8	Brindha et al. (2011)
India	Majhiaon	Shallow and deep groundwater	–	Avishek et al. (2010)
	Guntur, Andhra Pradesh	Shallow groundwater	0.6–2.5	Rao (2009)
	Anantapur, Andhra Pradesh	Shallow groundwater	0.56–5.8	Rao and Devadas (2003)
	Hyderabad, Andhra Pradesh	Shallow and intermediate groundwater	0.38–4.0	Sreedevi et al. (2006)
	Ranga Reddy, Andhra Pradesh	Groundwater	0.4–4.8	Sujatha (2003)
	Karbi Anglong, Assam	Groundwater	0.4–20.6	Chakraborti et al. (2000)
	Bihar	Shallow groundwater	0.1–2.5	Ray et al. (2000)
	Delhi	Groundwater	0.2–32.5	Raju et al. (2009)
	Gujarat	Groundwater	0.1–40	Raju et al. (2009) and reference therein
	Bellary, Karnataka	Groundwater and surface water	0.33–7.8	Wodeyar and Sreenivasan (1996)
	Karnataka	Shallow groundwater	1–7.4	Latha et al. (1999)
	Palghat, Kerala	Shallow, intermediate and deep groundwater	0.2–5.75	Shaji et al. (2007)
	Chandidongri, Madhya Pradesh	Shallow groundwater	1.5–4.0	Chatterjee and Mohabey (1998)
	Shivpuri, Madhya Pradesh	Groundwater	0.2–6.4	Ayoob and Gupta (2006)
	Orissa	Groundwater	0.1–10.1	Kundu et al. (2001)
	Churu/Dungarpur, Rajasthan	Groundwater	0.1–14	Muralidharan et al. (2002), Choubisa (2001)
	Kacnheepurum, Tamil Nadu	Shallow–deep groundwater	1–3.24	Dar et al. (2011)
	Tamil Nadu	Shallow–deep groundwater	0.5–4.0	Handa (1975); Raju et al. (2009) and references therein
	Varanasi, Uttar Pradesh	Groundwater	0.2–2.1	Raju et al. (2009) and references therein
	Agra, Uttar Pradesh	Shallow–deep groundwater	0.1–17.5	Gupta et al. (1999)
	Mathura, Uttar Pradesh	Shallow–deep groundwater	0.6–2.5	Misra et al. (2006)
	Sonbhadra, Uttar Pradesh	Shallow–deep groundwater	0.48–6.7	Raju et al. (2009)
	Cambay, North Gujarat	Deep groundwater	0–10	Gupta et al. (2005)
Sri Lanka	Dry Zone	Shallow–deep groundwater	0.02–5.30	Chandrajith et al. (2011)
	Udawalawe	Shallow groundwater	0.09–5.9	Van der Hoek et al. (2003)
Manitoba	Lake Saint Martin	Groundwater	0–15.1	Desbarats (2009)
Camaroon	Mayo Tsanaga	Shallow groundwater	0.19–15.2	Fantong et al. (2010)
Yemen	Hidhran and Alburayhi Basin and Taiz City	Groundwater	1.08–10	Al-Amry (2009)
Ethiopia		Shallow–deep groundwater	0–204	Ayenew et al. (2008)
Iran	Posht-e-Kooh-e-Dashtestan	Shallow groundwater	0.7–6.6	Battaleb-Looie and Moore (2010)

Table 2 continued

Country	Location	Water source	Fluoride concentration or range (mg/L)	References
	Maku area	Groundwater	0.46–5.96	Moghaddam and Fijani (2008b)
South Korea		Thermal groundwater	0–40.8	Chae et al. (2007)
	Gimcheon	Deep groundwater	0.04–2.15	Kim et al. (2011)
China	Yung–Chen Basin	Shallow–deep groundwater	0–3.3	Currell et al. (2011)
	Zhuiger Basin, Kuitun area	Groundwater	0–21.5	(Wang et al. 1997)
	Taiyuan Basin	Groundwater	0.4–3.32	Guo et al. (2007)
	Taiyuan Basin	Shallow groundwater	0.4–2.4	Li et al. (2011)
Turkey		Groundwater	0.51–33.0	Oruc (2008)
Germany	Muenster Region	Groundwater	0.01–8.8	Queste et al. (2001)
Mexico	San Luis Potosi Basin	Groundwater	0–3.7	Carrillo-Rivera et al. (2002)
	Hermosillo city, Sonara	Shallow groundwater	0–7.59	Valenzuela-Vásquez et al. (2006)

parts of India was due to evapotranspiration of groundwater with residual alkalinity. Fluoride content was higher in deeper aquifers of Maharashtra (Madhnure et al. 2007) which was due to long residence time than shallow groundwater. The rocks in southern India are rich with fluoride which forms the major reason for fluoride contamination in groundwater. It is a well-established fact that groundwater in Nalgonda district, Andhra Pradesh, has high fluoride due to the inherent fluoride-rich granitic rocks with 325–3200 mg/kg. The mean fluoride content in Hyderabad granites is 910 mg/kg (Ramamohana Rao et al. 1993). In Kurmapalli watershed, rocks are enriched in fluoride from 460 to 1706 mg/kg (Mondal et al. 2009). Co-precipitation and/or adsorption of fluoride by calcrete deposits in Wailapalli watershed had resulted in high fluoride in groundwater (Reddy et al. 2010).

Considerably higher concentrations, around 0.1–0.3 mg/L, have been reported from two sites in Uttar Pradesh (Satsangi et al. 1998) and Madhya Pradesh in India (Das et al. 1981; Singh et al. 2001). The reason behind this was predicted as the deposition of soil dust. Jain et al. (2000) found wet deposition of crustal material in Haryana south of New Delhi. About 0.05–0.22 mg/L fluoride concentrations have been reported by Chandrawanshi and Patel (1999) from eastern Madhya Pradesh comprising 13 sites, and this area is close to an industrial Al plant. Recently published measurements of dry deposition near Agra, Satsangi et al. (2002) indicate even larger amounts of F derived by atmospheric deposition. Thus, as several authors claim that the atmospheric deposition is largely from a crustal source.

East Asia

Excessive fluoride in drinking water has been reported from many different parts of China (Guo et al. 2007; Zhu et al. 2007). In Taiyuan Basin of China, interaction between recharge area and fluoride-containing minerals was the sources for high fluoride, whereas in discharge area, evaporation and mixing of karst water contributed to high fluoride (Guo et al. 2007). In Yuncheng Basin of China, a salty lake water intrusion has been reported as the source of high concentrations of fluoride in groundwater (Gao et al. 2007).

Groundwater studies on fluoride in South Korea show that the concentration of fluoride depends on the residence time (Kim and Jeong 2005) due to geogenic source of fluoride (Chae et al. 2007; Kim et al. 2011). People living in Ikeno district of Japan were exposed to drinking water containing 7.8 mg/L fluoride for 12 years (Ish and Suckling 1991). Ash from the volcanic explosion of Sakurajima volcano, Japan, was found to contain average fluoride concentration of 788.1 mg/kg (Nogami et al. 2006). Oversaturation of fluoride in groundwater in Mizunami area, Japan, is due to weathering and alteration of granitic rocks (Abdelgawad et al. 2009).

South Asia

Fertilizer containing leachable fluoride ranging from 53 to 255 mg/kg and coal containing fluoride ranging from 5 to 20 mg/kg were reported to pollute groundwater with high fluoride in east Punjab, Pakistan, by Farooqi et al. (2007a) where 2 million people are at risk of being exposed to high fluoride. The granitic rocks with average fluoride concentration of 1939 mg/kg in Nagar Parkar area, Pakistan, contain fluoride in kaolin deposits between 468 and 1722 mg/kg and secondary kaolin deposits have 270 mg/kg which are the source of fluoride up to 7.85 mg/L in groundwater in this area (Naseem et al. 2010).

Studies on fluoride in groundwater in Sri Lanka carried out by Dissanayake (1991) and Young et al. (2011) show

that the condition has not changed even after about two decades with fluoride above 4 mg/L in groundwater. It was found that high-fluoride areas lie within low plains. It may be due to the fact that contact time with the geological material was longer in the plains, and there exists slow groundwater movement compared to highlands (Dharmagunawardhane and Disanayake 1993).

Rest of the Asia

The public drinking water supply system in Isparta, Turkey, which draws water from lakes and springs discharged from volcanic rocks, Golcuk pyroclastic and Miocene clastic rocks contained fluoride between 0.39 and 5.62 mg/L. Moghaddam and Fijani (2008a) found that groundwater occurring almost everywhere in basaltic rocks in northwestern Iran contain fluoride beyond the suitable range. High concentrations of fluoride up to 2.3 mg/L have been found in groundwater in Algeria (Messaïtfa 2008). It has been estimated that about 70 % of the fluoride intake for the people of this region is through groundwater used for drinking. Apart from these, dates and tea contribute to 10 and 20 % of fluoride intake, respectively. Thus, the daily intake of fluoride ingested by an adult exceeds the threshold limit of 0.05–0.07 mg of fluoride/kg/day (Burt 1992).

European setting

The concentration of fluoride in spring and stream waters was used to determine the occurrences of fluorite in Osor district, Spain (Schwartz and Friedrich 1973). In Poland, fluoride concentration of 1.38 mg/L was detected around a phosphate industry waste disposal site (Czarnowski et al. 1996). The fluoride concentrations of about 7 mg/L occur naturally in western Estonia which is due to Silurian-Ordovician aquifer system (Indermitte et al. 2009). Alumina production plants had increased the fluoride concentration in nearby soils (0.3–9.2 mg/L) in Greece (Haidouti 1991).

African setting

An example from around the world with volcanic activity leading to high-fluoride concentration in the waters is Tanzania and the area surrounding the East African Rift system. Many of the lakes in this area have fluoride concentrations reaching up to 1640 and 2800 mg/L (IPCS 2002). Fluoride contents in some rivers (12–26 mg/L), springs (15–63 mg/L) and alkaline ponds and lakes (60–690 mg/L) were found to be very high in Tanzania (Nanyaro et al. 1984). Gaciri and Davies (1993) noticed that in natural waters of Kenya, fluoride concentration was greater in lake water than groundwater and springs which was greater than river water. Evaporation would have been a major cause to increase the concentration of fluoride in lakes of this region.

Fluoride distribution in America

High-fluoride concentrations in groundwater are reported from USA in the industrial facility wells in Pennsylvania having 3.2 and 6.5 mg/L, deep aquifers of Western US with 5–15 mg/L and Southern California Lakeland having 3.6–5.3 mg/L (Cohen and Conrad 1998). The prevalence of fluorosis in different states of the USA such as Arizona, Arkansas, California, Colorado, Idaho, Illinois, Iowa, Kansas, Minnesota, Nevada, New Mexico, North Carolina, North Dakota, Oklahoma, Oregon, South Carolina, South Dakota, Texas, Utah and Virginia is found. In Mexico, 5 million people (about 6 % of the population) are affected by fluoride in groundwater. Throughout Canada, there are a number of communities whose sources of drinking water contain elevated levels of fluoride (as high as 4.3 mg/L) from natural sources. However, in most of the cases, the fluoride contamination reported by Canada and USA are due to industrial emissions (Rose and Marier 1977). Some parts of Argentina consist of groundwaters with fluoride levels about 5 mg/L (Kruse and Ainchil 2003).

Defluoridation

Many defluoridation techniques already exist, but there is still no one method that has been found effective, safe and cheap enough to implement widely. The defluoridation techniques can be broadly classified into four categories, namely coagulation and precipitation, adsorption and/or ion exchange, electrochemical and membrane techniques. An in-depth analysis through the annals of defluoridation research reveals that very few proven sustainable solutions have been developed so far (Ayoob et al. 2008b; Jagtap et al. 2012). Furthermore, the coagulation and adsorption/ion-exchange processes are still the most widely used fluoride removal techniques practiced in endemic areas of the developing world. Many countries like India and Tanzania use both the domestic and community-based defluoridation techniques in different levels. Of late, a paradigm shift has occurred in the perception of people in India and Sri Lanka, toward community-based water supply treatment systems, using activated alumina like sorbents and electrocoagulation, respectively. However, some of these defluoridation systems are not affordable to the bulk of population in the fluoride-endemic rural areas. Similarly, other techniques as reverse osmosis, electrodialysis and nanofiltration assure good quality water; however, very high cost and high technical competence is a must, which limits the use of these techniques in the developing community. An overview of the different defluoridation techniques is given in Table 3.

Table 3 An overview of the defluoridation techniques

Defluoridation technique	Household or community level	Removal efficiency (%)	pH	Operator Skills	Relative cost	Strengths	Limitations
Alum (aluminum sulfate)	C	>90 %	Non-specific	Low	Medium–high	Established process	Production of sludge Acidic treated water Residual Al High-dose requirements for higher fluoride concentrations
Lime	C	>90 %	Non-specific	Low	Medium–high	Established process	Production of sludge Alkaline treated water
Alum + Lime (Nalgonda) (Aluminum sulfate-based coagulation–flocculation sedimentation)	C	70–90 %	Non-specific optimum pH 6.5	Low	Medium–high	Low-tech Established process No risk of medium/chemicals unacceptability Construction materials are cheap and widely available Easy to construct, even by the users No regeneration or renewal of medium is required No risk of false treatment due to break point Dosage designed for actual F conc. Independent of unit or plant	Production of sludge High chemical dose, residual sulfate salinity in the treated water High hardness, pH Residual aluminum Removal capacity of medium is not independent of F concentration; water quality may deteriorate due to medium escaping from the treatment container Low percentage removal
Gypsum + fluorite	C		Non-specific	Medium	Low–medium	Simple	Requires trained operators Low efficiency High residual $CaSO_4$
Calcium chloride	C	>90 %	6.5–8	NA		Emerging technology at reliable operating cost No health risk in the case of misuse or over dosage of chemicals as in conventional precipitation techniques	Too short contact times increase the escape of chemicals in the treated water Long contact time may result in precipitation of calcium phosphates in the upper parts of the filter bed
Calcium oxide		30 mg/mg F		NA		Cheapest, established Most commonly used technology	Quantity of sludge production and pH of treated water are high Poor settling characteristics of the precipitate High effluent fluoride concentration
Magnesium oxide	C	86 %	10–11	Low		Established technology Affordable cost	Sludge production High pH of treated water

Table 3 continued

Defluoridation technique	Household or community level	Removal efficiency (%)	pH	Operator Skills	Relative cost	Strengths	Limitations
Contact precipitation (calcium and phosphate compounds and bone charcoal medium)	C	>90 %			Low	No health risk in the case of misuse or over dosage of chemicals High reliability without the need of surveillance of flow or effluent concentration No risk of deterioration of the original water quality Construction materials are cheap and widely available Easy to construct High removal efficiency No regeneration or renewal of medium is required Removal capacity of medium is independent of F concentration No risk of false treatment due to break point, Dosage designed for actual F conc. independent of unit or plant Small-scale point-of-use technique	Needed daily dosage of chemicals, i.e., daily working load
Lanthanum-treated chitosan granules		8.07 mg/g (91.3–97.7 %)		Medium	High	Simple Cleanliness and safe method User's perception	Small quantities of water at household level
Activated carbon	H/C	>90 %	<3	Medium	High		Many interferences Large pH changes Pre and post-treatment
Plant carbon	C	>90 %	7	Medium	Low–medium	Locally deliverable	Requires soaking in potassium hydroxide
Zeolites	H/C	>90 %	Non-specific	Medium	High		Poor capacity
Defluoron 2	C	>90 %	Non-specific	Medium	Medium		Disposal of chemicals used in resin regeneration
Clay	H	60–70 %	Non-specific	Low	Low	Locally deliverable	Regeneration is very difficult Low capacity Slow

Table 3 continued

Defluoridation technique	Household or community level	Removal efficiency (%)	pH	Operator Skills	Relative cost	Strengths	Limitations
Mixed rare earth oxides			6.5	Medium	Medium	Very suitable for use in drinking water treatment Method is simple Potential for selective removal of fluoride Mixture of rare earth elements adsorb fluoride rapidly and effectively	
Activated alumina	C	85–95 % (between 4 and 15 mg/g)	5.5	Low	Medium	Proven effectiveness will treat current F and As Low energy consumption Sludge typically non-hazardous No risk of medium/chemicals unacceptability Construction materials are cheap and widely available Easy to construct High removal efficiency Concurrently remove other anions, such as arsenate	Source water pH adjustment to 6.5 Spent regeneration solution contains high-F (and As) concentrations Chemical and sludge handling needed Efficiency dependent on source water, water quality may deteriorate due to medium escaping from the treatment container High cost-tech method Limited capacity High pH Reduces potential Regeneration result in a reduction of about 5–10 % in material 30–40 % in capacity with increased presence of aluminum (>0.2 mg/L)
Bone	C	NA	>7	Low	Low	Locally available	May give taste Not universally accepted
Bone char/bone charcoal	C	reduced to ≤1 mg/l	>7	Low	Low	Locally available, high capacity Simple and easy to build Construction materials are cheap and widely available Easy to construct High removal efficiency No daily working load	Not universally accepted Capacity reduces drastically after successive Regenerations More expensive than coagulation techniques Limited social acceptance
Electrocoagulation	C	100 %	Non-specific	High	High	Emerging technique Efficiency of EC system is very high	Interference from other anions like sulfate Need for regular replacement of sacrificial electrodes High consumption of Electric power

Table 3 continued

Defluoridation technique	Household or community level	Removal efficiency (%)	pH	Operator Skills	Relative cost	Strengths	Limitations
Electrosorption	C	Highly efficient	Non-specific	High	High	Emerging technique Capacity of adsorbent enhanced by more than 50 % Excellent regeneration potential	High consumption of Electric power
Electrodialysis	C	85–95 %	Non-specific	Medium	Very high	Treat and As and other contaminants Positive public perception Suitable if a high fluoride removal is necessary Excellent technique for simultaneous defluoridation and desalination More economical than RO More resistant to fouling	High water loss High energy consumption High (capital) costs Membrane scaling Not suitable for waters of very low salinity exhibiting a conductivity of <0.5 mS Require high degree of pretreatment Ineffective in removing low molecular mass non-charged compounds Treated water quality is inferior to that of RO
Reverse osmosis	C	85–95 %	Non-specific	Medium	Very high	Treat and As and other contaminants Positive public perception Suitable if a high fluoride removal is necessary Excellent technique for simultaneous defluoridation and desalination Significant removal of virtually all dissolved contaminants, Small foot print Organics and salts are also removed	High water loss High energy consumption High (capital) costs Almost all fluoride is eliminated therefore the treated water may lack the right balance of minerals Pre- (filtration) and post (pH/alkalinity adjustment)-treatment may be needed Chemical handling facilities needed Multiple systems needed to achieve water conservation goals (<5 % water loss), sensitive to polarization phenomenon Chances of biological and mineral fouling
Nanofiltration	C	Highly efficient	Non-specific	High	High	Well accepted Membrane separation process Handles higher water fluxes at lower transmembrane pressures than RO	More sensitive than RO to pH and ionic strength Leaves large concentrations of retentate fraction
Donnan dialysis	C	Highly efficient	Non-specific	Medium	High	Permanent separation between solutions which is not reversed even if the system is closed to the surroundings	Operation requires addition of a so-called driving counter-ion to stripping solution Reduced efficiency in high-saline waters

Table 3 continued

Defluoridation technique	Household or community level	Removal efficiency (%)	pH	Operator Skills	Relative cost	Strengths	Limitations
Memstill technology (membrane-based distillation concept)	C		Non-specific	High	Low cost	Low energy consumption Suitable for low-grade energy, solar cells, etc. Simple construction, based on prefabricated modules Lower cost price than existing technology Large-scale production of drinking-water from seawater Co-generation of electricity and water Reprocessing brackish water Production of ultrapure water, boiler supply water, etc. Treatment of waste water	

C is for the community level and H is for household level

Coagulation

In this process of coagulation for defluoridation, the chemical coagulant are placed in the raw water under specific dosages and conditions to form a solid flocculent or flakes that may be easily filtered from the water (Fawell et al. 2006). The precipitated floc removes the dissolved fluoride contaminant by charge neutralization, adsorption and entrapment. Hence, this is a combined process of coagulation and precipitation. This process is also known as the Nalgonda process that was developed for low-income Indian and African households (Fawell et al. 2006). Lime, other calcium salts, alum and magnesium oxides are the cheapest and most commonly used coagulants for this process (Ayoob et al. 2008b). This process will remove fluoride up to 50 % and possibly more depending on the nature and degree of the fluoride content in the water (Fawell et al. 2006). Addition of lime, calcium salts and magnesium oxides allows fluoride to precipitate. However, in the case of lime, the process is mainly co-precipitation. Co-precipitation is the method used in Nalgonda process of fluoride removal.

Adsorption and ion exchange

Because of the limited applications of fluoride treatment techniques, adsorption/ion exchange is the most frequently used (Ayoob et al. 2008a; Jagtap et al. 2012). Alumina, bone charcoal and many clays and soils have been tested and used for defluoridation since 1930s (Ayoob et al. 2008b; Boruff 1934; Harmon and Kalichman 1965; Jagtap et al. 2012; Mohapatra et al. 2009).

Activated alumina, made of aluminum oxide, has a very high surface area to weight ratio allowing it to have many small pores that run through it (Fawell et al. 2006). This process will have a success rate of up to 80 % removal of fluoride with less that 1 mg/L of fluoride content left in the water (Fawell et al. 2006). Similarly, many aluminum-based sorbents have shown better adsorption capacity (Fig. 3); however, activation has shown an increase in surface area and thereby increasing fluoride adsorption (Shimelis et al. 2006). Defluoridation has also been tested using aluminum-based adsorbents together with calcium, iron and manganese oxides and minerals (Vithanage et al. 2012). However, all these have shown different defluoridation capacities depending on dosage of fluoride, adsorbate, temperature, reaction time, etc. In reality, defluoridation using these sorbents can even show rather different results due to the differences in scale, the presence and influence of other ions and differences in other environmental conditions such as pH, EC, hardness, alkalinity, etc.

Electrochemical methods

Electrocoagulation (EC) utilizes an electrolytic process to generate a coagulant in situ by oxidation of an appropriate

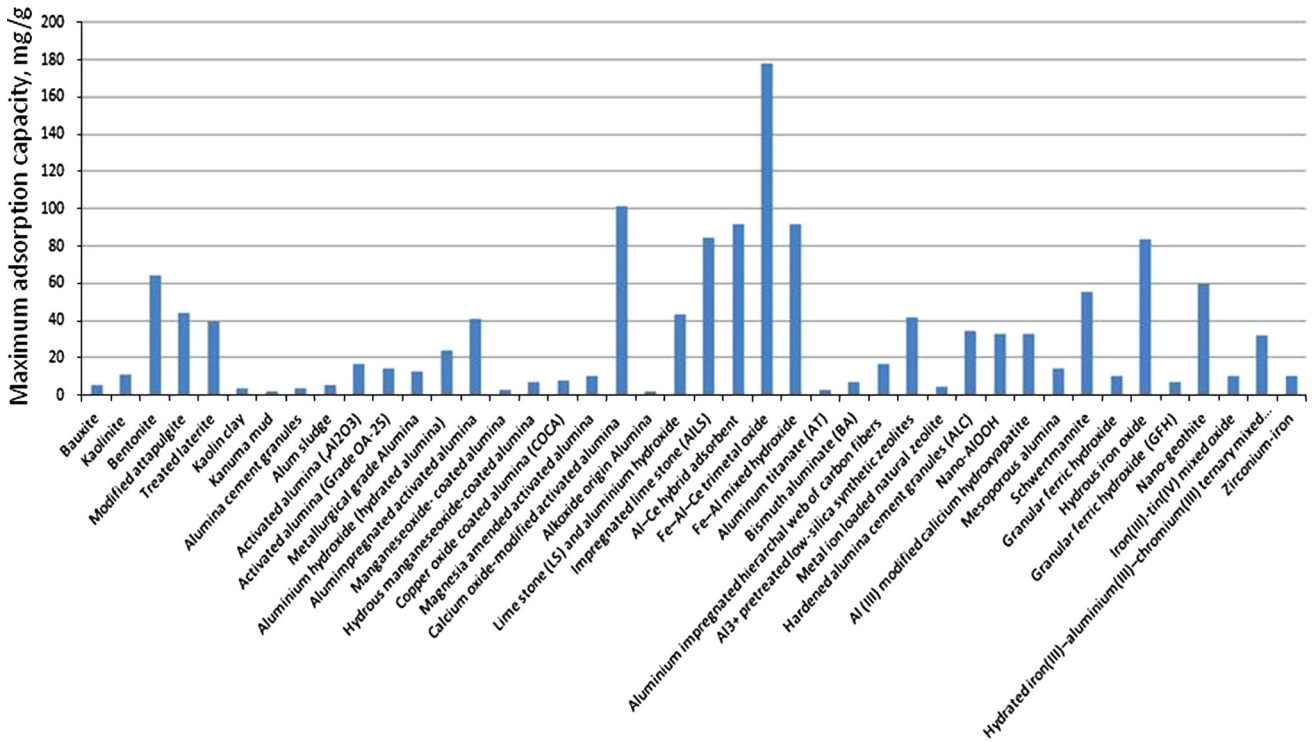

Fig. 3 Maximum adsorption capacities of fluoride sorption into different aluminum- and iron-based materials

anodic material, and the coagulant ions then react with the target pollutant ions, initiating coagulation (Ayoob et al. 2008b). The defluoridation of water by EC using aluminum electrodes was introduced by Ming et al. (1983). With the electric current passing through the aluminum electrodes, an anodic reaction releases Al(III) ions, which then react with hydroxide ions produced at the cathode and with fluoride ions in solution. This method has been successfully applied by a group of scientists and engineers (Padmasiri et al. 2012) in the rural villages in Sri Lanka where people are suffering from chronic kidney disease of unknown etiology (CKDu) to provide drinking water with less fluoride and hardness.

Membrane process

The most significant processes in water treatment for membrane processes include reverse osmosis, ultrafiltration, micro-filtration and nanofiltration (Fawell et al. 2006). These processes are now recently being applied to the treatment of drinking water. Membrane operations generally utilize artificial membranes to separate the mixtures and capture the undesired material. This process is successful in fluoride removal from drinking water up to 80 % or more, leaving the water with a fluoride content of <1 mg/L (Chubar et al. 2005; Fawell et al. 2006; Ruixia et al. 2002). Similarly, Schneiter and Middlebrooks (1983) have reported 59–67 % removal of fluoride using a reverse osmosis (RO) unit, employing spiral wound cellulose acetate membranes, after adjusting the pH from 8.2 to 6.4. Successful implementation of a pilot scale RO plant was reported in Lakeland, southern California (Cohen and Conrad 1998).

Nanofiltration (NF) was used in commercial level in Finland with a capacity of 380–600 m^3/day which was intended for the removal of fluoride and aluminum from groundwater (Kettunen and Keskitalo 2000). Selective defluoridation was observed for the first time using an NF membrane that has mass transfer properties very similar to RO membranes (Pontie et al. 2003). Electrodialysis (ED) is also used as an excellent technique for simultaneous defluoridation and desalination of brackish water (Adhikary et al. 1989). Fluoride removal by Donnan Dialysis (DD) was investigated by many researchers (Dieye et al. 1998; Garmes et al. 2002; Hichour et al. 1999a, b).

Problems and perspectives

Many defluoridation techniques have been examined since the 1930s, when the danger of excess fluoride in drinking water was first identified (Boruff 1934). More than 70 years since the problem was recognized, however, the attempts to develop a method of defluoridation that can be

sustained under differing social, financial, environmental and technical constraints have not been successful (Brunt et al. 2004). Although coagulation methods are generally effective and are in use commonly in defluoridation, the major limitation is that the process is unsuccessful in bringing fluoride to desired concentration levels. Ion exchange and/or adsorption are widely accepted technologies utilized on a full-scale basis; however, the regeneration and disposal of the material have made the process quite questionable. Though a number of adsorbents with very high potential have had been developed, only activated alumina and bone char were reported successful at the implementation level (Ayoob et al. 2008b). For many methods, the most critical factor in the sorption process is pH as it dictates the entire process chemistry of defluoridation. Membrane methods are relatively expensive to install and operate and prone to fouling, scaling or membrane degradation as well as these need skillful operational capability which will be a limitation for the developing world where the excessive fluoride problem is mostly reported. Similarly, the electrochemical techniques are with high cost factor, during both installation and maintenance. Especially for developing countries, the high cost of technology, cost of power supply, expensive chemicals, operational and maintenance costs, regeneration cost and use of sophisticated accessories act as major constraints for implementation. In the developing world, people always are in contact with the immediate environment, and they prefer to use drinking water directly from the source or tap. Such household filter systems do not succeed due to this reason. Most of the techniques are not achieving the social acceptance and the implementation fails. Very limited studies have been carried out on bioremediation of fluoride (Evans-Tokaryk 2011; Ramanaiah 2010). It may be important to focus on the bioremediation potential for the defluoridation. Although defluoridation research has made significant advancement, still no sustainable solution to this salient crisis exists. Hence, still there is need for a best available technology for defluoridation of drinking water.

References

Abdelgawad AM, Watanabe K, Takeuchi S, Mizuno T (2009) The origin of fluoride-rich groundwater in Mizunami area, Japan—Mineralogy and geochemistry implications. Eng Geol 108:76–85

Adhikary SK, Tipnis UK, Harkare WP, Govindan KP (1989) Defluoridation during desalination of brackish water by electrodialysis. Desalination 71:301–312

Al-Amry AS (2009) Hydrogeochemistry and origin of fluoride in groundwater of Hidhran and Alburayhi Basin, northwest Taiz City, Yemen. Delta J Sci 33:10–20

Apambire WB, Boyle DR, Michel FA (1997a) Geochemistry, genesis, and health implications of fluoriferous groundwater in the upper regions of Ghana. Environ Geol 33:13–24

Apambire WB, Boyle DR, Michel FA (1997b) Geochemistry, genesis, and health implications of fluoriferous groundwaters in the upper regions of Ghana. Environ Geol 33:13–24

Avishek K, Pathak G, Nathawat M, Jha U, Kumari N (2010) Water quality assessment of Majhiaon block of Garwa district in Jharkhand with special focus on fluoride analysis. Environ Monit Assess 167:617–623

Ayenew T, Demlie M, Wohnlich S (2008) Hydrogeological framework and occurrence of groundwater in the Ethiopian aquifers. J Afr Earth Sci 52:97–113

Ayoob S, Gupta AK (2006) Fluoride in drinking water: a review on the status and stress effects. Crit Rev Environ Sci Technol 36:433–487

Ayoob S, Gupta AK, Bhat VT (2008a) A conceptual overview on sustainable technologies for the defluoridation of drinking water. Crit Rev Environ Sci Technol 38:401–470

Ayoob S, Gupta AK, Bhakat PB, Bhat VT (2008b) Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules. Chem Eng J 140:6–14

Battaleb-Looie S, Moore F (2010) A study of fluoride groundwater occurrence in Posht-e-Kooh-e-Dashtestan, South of Iran. World Appl Sci J 8:1317–1321

Bonvicini G, Fregni A, Palmonari C (2006) Fluorine compounds from industrial sources: the case of ceramic industries. In: Tressaud A (ed) Fluorine and the environment: atmospheric chemistry, emissions, and lithosphere. Elsevier, Amsterdam, pp 225–249

Boruff CS (1934) Removal of fluorides from drinking waters. Ind Eng Chem 26:69–71

Boyle DR, Chagnon M (1995) An incidence of skeletal fluorosis associated with groundwaters of the maritime carboniferous basin, Gaspé region, Quebec, Canada. Environ Geochem Health 17:5–12

Brindha K, Elango L (2011) Fluoride in groundwater: causes, implications and mitigation measures. In: Monroy SD (ed) Fluoride properties, applications and environmental management. pp 111–136. https://www.novapublishers.com/catalog/product_info.php?products_id=15895

Brindha K, Rajesh R, Murugan R, Elango L (2011) Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. Environ Monit Assess 172:481–492

Brunt R, Vasak L, Griffioen J (2004) Fluoride in groundwater: probability of occurrence of excessive concentration on global scale. IGRAC, Utrecht, Netherlands

Burt BA (1992) The changing patterns of systemic fluoride intake. J Dent Res 71:1228–1237

Carrillo-Rivera JJ, Cardona A, Edmunds WM (2002) Use of abstraction regime and knowledge of hydrogeological conditions to control high-fluoride concentration in abstracted groundwater: San Luis Potosí basin, Mexico. J Hydrol 261:24–47

Chae G-T, Yun S-T, Kim K, Mayer B (2006) Hydrogeochemistry of sodium-bicarbonate type bedrock groundwater in the Pocheon spa area, South Korea: water–rock interaction and hydrologic mixing. J Hydrol 321:326–343

Chae G-T, Yun S-T, Mayer B, Kim K-H, Kim S-Y, Kwon J-S, Kim K, Koh Y-K (2007) Fluorine geochemistry in bedrock groundwater of South Korea. Sci Total Environ 385:272–283

Chakraborti D, Chanda CR, Samanta G, Chowdhury UK, Mukherjee SC, Pal AB, Sharma B, Mahanta KJ, Ahmed HA, Sing B (2000) Fluorosis in Assam India. Curr Sci 78:1421–1423

Chandrajith R, Dissanayake CB, Ariyarathna T, Herath HMJMK, Padmasiri JP (2011) Dose-dependent Na and Ca in fluoride-rich

drinking water: another major cause of chronic renal failure in tropical arid regions. Sci Total Environ 409:671–675
Chandrawanshi CK, Patel KS (1999) Fluoride deposition in central India. Environ Monit Assess 55:251–265
Chatterjee MK, Mohabey NK (1998) Potential fluorosis problems around Chandidongri, Madhya Pradesh, India. Environ Geochem Health 20:1–4
Choubisa SL (2001) Endemic fluorosis in Southern Rajasthan, India. Fluoride 34:61–70
Chubar NI, Samanidou VF, Kouts VS, Gallios GG, Kanibolotsky VA, Strelko VV, Zhuravlev IZ (2005) Adsorption of fluoride, chloride, bromide, and bromate ions on a novel ion exchanger. J Colloid Interface Sci 291:67–74
Cohen D, Conrad HM (1998) 65,000 GPD fluoride removal membrane system in Lakeland, California, USA. Desalination 117:19–35
Cronin SJ, Manoharan V, Hedley MJ, Loganathan P (2000) Fluoride: a review of its fate, bioavailability, and risks of fluorosis in grazed-pasture systems in New Zealand. N Z J Agric Res 43:295–321
Currell M, Cartwright I, Raveggi M, Han D (2011) Controls on elevated fluoride and arsenic concentrations in groundwater from the Yuncheng Basin, China. Appl Geochem 26:540–552
Czarnowski W, Wrześniowska K, Krechniak J (1996) Fluoride in drinking water and human urine in Northern and Central Poland. Sci Total Environ 191:177–184
Dar MA, Sankar K, DarImran A (2011) Fluorine contamination in groundwater: a major challenge. Environ Monit Assess 173:955–968
Das DK, Burman GK, Kidwai AL (1981) Chemical composition of monsoon rainwater over Bhopal, Madhya Pradesh during 1977 and 1978. Mausam 32:221–228
Datta PS, Deb DL, Tyagi SK (1996) Stable isotope (18O) investigations on the processes controlling fluoride contamination of groundwater. J Contam Hydrol 24:85–96
De Angelis M, Legrand M (1994) Origins and variations of fluoride in Greenland precipitation. J Geophys Res 99:1157–1172
Desbarats A (2009) On elevated fluoride and boron concentrations in groundwaters associated with the Lake Saint-Martin impact structure, Manitoba. Appl Geochem 24:915–927
Dharmagunawardhane HA, Disanayake CB (1993) Fluoride problems in Sri Lanka. Environ Manage Health 4:9–16
Dieye A, Larchet C, Auclair B, Mar-Diop C (1998) Elimination des fluorures par la dialyse ionique croisée. Eur Polym J 34:67–75
Dissanayake CB (1991) The fluoride problem in the groundwater of Sri Lanka-environmental management and health. Int J Environ Stud 38:137–156
Dissanayake CB (2005) Water quality in the dry zone of Sri Lanka: some interesting health aspects. J Natl Sci Found Sri Lanka 33:161–168
Dissanayake CB, Chandrajith R (2009) Introduction to medical geology: focus on tropical environment. Springer, Heidelberg
Dolejš D, Baker D (2004) Thermodynamic analysis of the system Na_2O–K_2O–CaO–Al_2O_3–SiO_2–H_2O–F_2O-1: stability of fluorine-bearing minerals in felsic igneous suites. Contrib Mineral Petrol 146:762–778
Edmunds WM, Smedley PL (2005) Fluoride in natural waters. In: Selinus O (ed) Essentials of medical geology. Elsevier Academic Press, London, pp 301–329
Evans-Tokaryk K (2011) Biogeochemical Defluoridation. Department of Geology, University of Toronto, Toronto
Fantong W, Satake H, Ayonghe S, Suh E, Adelana S, Fantong E, Banseka H, Gwanfogbe C, Woincham L, Uehara Y, Zhang J (2010) Geochemical provenance and spatial distribution of fluoride in groundwater of Mayo Tsanaga River Basin, Far North Region, Cameroon: implications for incidence of fluorosis and optimal consumption dose. Environ Geochem Health 32:147–163
Farooqi A, Masuda H, Firdous N (2007a) Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources. Environ Pollut 145:839–849
Farooqi A, Masuda H, Kusakabe M, Naseem M, Firdous N (2007b) Distribution of highly arsenic and fluoride contaminated groundwater from east Punjab, Pakistan, and the controlling role of anthropogenic pollutants in the natural hydrological cycle. Geochem J 41:213–234
Faure G (1991) Principles and applications of inorganic geochemistry. Macmillan Publ. Co., New York, NY, p 626
Fawell J, Bailey K, Chilton J, Dahi E, Fewtrell L, Magara Y (2006) Fluoride in drinking-water. IWA Publishing, London
Feng YW, Ogura N, Feng ZW, Zhang F, Shimizu H (2003) The concentrations and sources of fluoride in atmospheric depositions in Beijing, China. Water Air Soil Pollut 145:95–107
Fuge R (1977) On the behaviour of fluorine and chlorine during magmatic differentiation. Contrib Mineral Petrol 61: 245–249
Gaciri SJ, Davies TC (1993) The occurrence and geochemistry of fluoride in some natural waters of Kenya. J Hydrol 143:395–412
Gao X, Wang Y, Li Y, Guo Q (2007) Enrichment of fluoride in groundwater under the impact of saline water intrusion at the salt lake area of Yuncheng basin, northern China. Environ Geol 53:795–803
Garmes H, Persin F, Sandeaux J, Pourcelly G, Mountadar M (2002) Defluoridation of groundwater by a hybrid process combining adsorption and Donnan dialysis. Desalination 145:287–291
Guo Q, Wang Y, Ma T, Ma R (2007) Geochemical processes controlling the elevated fluoride concentrations in groundwaters of the Taiyuan Basin, Northern China. J Geochem Explor 93:1–12
Gupta MK, Singh V, Rajwanshi P, Agarwal M, Rai K, Srivastava S, Shrivastav R, Dass S (1999) Groundwater quality assessment of Tehsil Kheragarh, Agra (India) with special reference to fluoride. Environ Monit Assess 59:275–285
Gupta SK, Deshpande RD, Agarwal M, Raval BR (2005) Origin of high fluoride in groundwater in the North Gujarat-Cambay region, India. Hydrogeol J 13:596–605
Haidouti C (1991) Fluoride distribution in soils in the vicinity of a point emission source in Greece. Geoderma 49:129–138
Handa BK (1975) Geochemistry and genesis of fluoride-containing ground waters in India. Ground Water 13:275–281
Harmon JA, Kalichman SC (1965) Defluoridation of drinking water in Southern California. J Am Water W Assoc 57:245–251
Hem JD (1985) The study and interpretation of the chemical characteristics of natural water. U.S Geological Survey Water-Supply, New York
Hichour M, Persin F, Sandeaux J, Gavach C (1999a) Fluoride removal from waters by Donnan dialysis. Sep Purif Technol 18:1–11
Hichour M, Persin F, Molénat J, Sandeaux J, Gavach C (1999b) Fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes. Desalination 122:53–62
Hyndman DW (1985) Petrology of igneous rocks, 2nd edn. McGraw-Hill Inc, New York
Indermitte E, Saava A, Karro E (2009) Exposure to high fluoride drinking water and risk of dental fluorosis in Estonia. Int J Environ Res Public Health 6:710–721
IPCS (2002) Fluorides. Environmental Health Criteria 227, UNEP, ILO and WHO, Geneva
Ish T, Suckling G (1991) The severity of dental fluorosis in children exposed to water with a high fluoride content for various periods of time. J Dent Res 70:952–956

Jacks G, Rajagopalan K, Alveteg T, Jönsson M (1993) Genesis of high-F groundwaters, southern India. Appl Geochem 8:241–244
Jacks G, Bhattacharya P, Chaudhary V, Singh KP (2005) Controls on the genesis of some high-fluoride groundwaters in India. Appl Geochem 20:221–228
Jagtap S, Yenkie MK, Labhsetwar N, Rayalu S (2012) Fluoride in drinking water and defluoridation of water. Chem Rev 112:2454–2466
Jain M, Kulshrestha UC, Sarkar AK, Parashar DC (2000) Influence of crustal aerosols on wet deposition at urban and rural sites in India. Atmos Environ 34:5129–5137
Jones BF, Eugster HP, Rettig SL (1977) Hydrochemistry of the Lake Magadi Basin, Kenya. Geochim Cosmochim Acta 41:53–72
Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants, 3rd edn. CRC Press, Boca Raton, FL
Kausar R, Ahmad S, Rehman KL, Ahmad R (2003) Fluoride Status of underground water of Faisalabad city area. Int J Agric Biol 5:536–539
Kettunen R, Keskitalo P (2000) Combination of membrane technology and limestone filtration to control drinking water quality. Desalination 131:271–283
Kim K, Jeong GY (2005) Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula. Chemosphere 58:1399–1408
Kim Y, Kim J-Y, Kim K (2011) Geochemical characteristics of fluoride in groundwater of Gimcheon, Korea: lithogenic and agricultural origins. Environ Earth Sci 63:1139–1148
Kowalski F (1999) Fluoridation. J AWWA 91:4
Kruse EK, Ainchil JA (2003) Fluoride variations in groundwater of an area in Buenos Aires Province, Argentina. Environ Geol 44:86–89
Kundu N, Panigrahi MK, Tripathy S, Munshi S, Powell MA, Hart BR (2001) Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh district of Orissa, India. Environ Geol 41:451–460
Latha SS, Ambika SR, Prasad SJ (1999) Fluoride contamination status of groundwater in Karnataka. Curr Sci 76:730–734
Li XS, Zhi JL, Gao RO (1994) Effect of fluoride exposure on intelligence in children. Fluoride 28:189–192
Li X, Hou X, Zhou Z, Liu L (2011) Geochemical provenance and spatial distribution of fluoride in groundwater of Taiyuan basin, China. Environ Earth Sci 62:1635–1642
Madhnure P, Sirsikar DY, Tiwari AN, Ranjan B, Malpe DB (2007) Occurrence of fluoride in the groundwaters Pandharkawada area, Yawatmal district, Maharastra, India. Curr Sci 92:675–679
Matvaelastofnun (2010) Volcanic activity in Iceland. Possible effects on food safety, animal health and animal welfare, MAST-Icelandic Food and Veterinary Authority. http://www.mast.is/Uploads/document/leidbeiningar/Enska/volcaniceruptioninfoodsafetyanimalhealth.pdf
Messaïtfa A (2008) Fluoride contents in groundwaters and the main consumed foods (dates and tea) in Southern Algeria region. Environ Geol 55:377–383
Ming L, Yi SR, Hua ZJ, Lei BYW, Ping L, Fuwa KC (1983) Elimination of excess fluoride in potable water with coacervation by electrolysis using aluminium anode. Fluoride 20:54–63
Mirlean N, Roisenberg A (2007) Fluoride distribution in the environment along the gradient of a phosphate-fertilizer production emission (southern Brazil). Environ Geochem Health 29:179–187
Misra AK, Mishra A, Premraj (2006) Escalation of groundwater fluoride in the Ganga alluvial plain of India. Fluoride 39:35–38
Moghaddam AA, Fijani E (2008a) Distribution of fluoride in groundwater of Maku area, northwest of Iran. Environ Geol 56:281–287
Moghaddam AA, Fijani E (2008b) Distribution of fluoride in groundwater of Maku area, northwest of Iran. Environ Geol 56:281–287
Mohapatra M, Anand S, Mishra BK, Giles DE, Singh P (2009) Review of fluoride removal from drinking water. J Environ Manage 91:67–77
Mondal NC, Prasad RK, Saxena VK, Singh Y, Singh VS (2009) Appraisal of highly fluoride zones in groundwater of Kurmapalli watershed, Nalgonda district, Andhra Pradesh (India). Environ Earth Sci 59:63–73
Moore RB (2004) Quality of water in the fractured-bedrock aquifer of New Hampshire. U.S. Geological Survey Scientific Investigations Report 2004–5093, p 30
Msonda KWM, Masamba WRL, Fabiano E (2007) A study of fluoride groundwater occurrence in Nathenje, Lilongwe, Malawi. Phys Chem Earth Parts A/B/C 32:1178–1184
Muralidharan D, Nair AP, Muralidharan D, Sathyanarayana U (2002) Fluoride in shallow aquifers in Rajgarh Tehsil of Churu District, Rajasthan: an arid environment. Curr Sci 83:699–702
Naeem M, Khan K, Rehman S, Iqbal J (2007) Environmental assessment of ground water quality of Lahore Area, Punjab, Pakistan. J Appl Sci 7:41–46
Nanyaro JT, Aswathanarayana U, Mungure JS (1984) A geochemical model for the abnormal fluoride concentrations in waters in parts of Northern Tanzania. J Afr Earth Sci 2:129–140
Naseem S, Rafique T, Bashir E, Bhanger MI, Laghari A, Usmani TH (2010) Lithological influences on occurrence of high-fluoride groundwater in Nagar Parkar area, Thar Desert, Pakistan. Chemosphere 78:1313–1321
Neal C (1989) Fluorine variations in welsh streams and soil waters. Sci Total Environ 80:213–223
Nogami K, Iguchi M, Ishihara K, Hirabayashi J, Miki D (2006) Behavior of fluorine and chlorine in volcanic ash of Sakurajima volcano, Japan in the sequence of its eruptive activity. Earth Planet Space 58:595–600
Oruc N (2008) Occurrence and problems of high fluoride waters in Turkey: an overview. Environ Geochem Health 30:315–323
Ozsvath D (2006) Fluoride concentrations in a crystalline bedrock aquifer Marathon County, Wisconsin. Environ Geol 50:132–138
Padmasiri JP, Jayawardhene WM, Dissanayake CB (2012) Water quality improvements in the dry zone areas in Sri Lanka. In: Ileperuma OA, Priyantha N, Navaratne A, Yatigammana SK, Weragoda SK (eds) Symposium proceedings, international symposium on water quality and human health: challenges ahead. PGIS, Peradeniya
Pickering WF (1985) The mobility of soluble fluoride in soils. Environ Pollut Ser B Chem Phys 9:281–308
Pontie M, Buisson H, Diawara CK, Essis-Tome H (2003) Studies of halide ions mass transfer in nanofiltration: application to selective defluorination of brackish drinking water. Desalination 157:127–134
Poovaiah BW (1988) Calcium and senescence. In: Nooden L, Leopold AC (eds) Senescence and aging in plants. Academic Press, New York, pp 369–389
Queste A, Lacombe M, Hellmeier W, Hillermann F, Bortulussi B, Kaup M, Ott K, Mathys, W (2001) High concentrations of fluoride and boron in drinking water wells in the muenster region-results of a preliminary investigation. Int J Hyg Environ Heal 203:221–224
Raju JN, Dey S, Das K (2009) Fluoride contamination in groundwaters of Sonbhadra District, Uttar Pradesh, India. Curr Sci 96:979–985
Ramamohana Rao NV, Rao N, Rao KSP, Schuiling RD (1993) Fluorine distribution in waters of Nalgonda District, Andhra Pradesh, India. Environ Geol 21:84–89

Ramanaiah SV (2010) Bioremediation of fluoride by biosorption. Verlag, VDM
Rao N (2009) Fluoride in groundwater, Varaha River Basin, Visakhapatnam District, Andhra Pradesh, India. Environ Monit Assess 152:47–60
Rao NS, Devadas DJ (2003) Fluoride incidence in groundwater in an area of Peninsular India. Environ Geol 45:243–251
Ray D, Ravindar Rao R, Bhoi AV, Biswas AK, Ganguly AK, Sanyal PB (2000) Physico-chemical quality of drinking water in Rohtas district of Bihar. Environ Monit Assess 61:387–398
Rea RE (1979) A rapid method for the determination of fluoride in sewage sludges. Water Pollut Control (Maidstone) 78:139–142
Reddy A, Reddy D, Rao P, Prasad K (2010) Hydrogeochemical characterization of fluoride rich groundwater of Wailpalli watershed, Nalgonda District, Andhra Pradesh, India. Environ Monit Assess 171:561–577
Robinson GR, Kapo KE (2003) Generalized lithology and lithogeochemical character of near-surface bedrock in the New England Region. U.S. Geological Survey, New York
Rose D, Marier JR (1977) Environmental fluoride NRC Associate Committee on Scientific Criteria for Environmental Quality. National Research Council of Canada, Ontario
Rosi M, Papale P, Lupi L, Stoppato M (2003) Volcanoes: a firefly guide. Firefly Books Ltd., Buffalo, New York, p 335
Ruixia L, Jinlong G, Hongxiao T (2002) Adsorption of fluoride, phosphate, and arsenate ions on a new type pf ion exchange fiber. J Colloid Interface Sci 248:268–274
Saether OM, Andreassen BT (1989) Fluoride in precipitation in Southern Norway: amounts and sources. Report 89/106. Geological Survey of Norway, Norway
Saether OM, Andreassen BT, Semb A (1995) Amounts and sources of fluoride in precipitation over southern Norway. Atmos Environ 29:1785–1793
Satsangi GS, Lakhani A, Khare P, Singh SP, Kumari KM, Srivastava SS (1998) Composition of rain water at a semi-arid rural site in India: inter-relation of acid base components. Atmos Environ 32:3783–3793
Satsangi GS, Lakhani A, Khare P, Singh SP, Kumari KM, Srivastava SS (2002) Measurements of major ion concentration in settled coarse particles and aerosols at a semiarid rural site in India. Environ Int 28:1–7
Saxena VS, Ahmed SA (2001) Dissolution of fluoride in groundwater: a water-rock interaction study. Environ Geol 40:1084–1087
Saxena VS, Ahmed S (2003) Inferring the chemical parameters for the dissolution of fluoride in groundwater. Environ Geol 43:731–736
Schneiter RW, Middlebrooks EJ (1983) Arsenic and fluoride removal from groundwater by reverse osmosis. Environ Int 9:289–291
Schwartz MO, Friedrich GH (1973) Secondary dispersion patterns of fluoride in the osor area, Province of Gerona, Spain. J Geochem Explor 2:103–114
Shaji E, Bindu VE, Thambi DS (2007) High fluoride in groundwater of Palghat district, Kerala. Curr Sci 92:240–245
Shimelis B, Zewge F, Chandravanshi BS (2006) Removal of excess fluoride from water by aluminum hydroxide. Bull Chem Soc Ethiop 20:17–34
Singh SP, Khare P, Satsangi GS, Lakhani A, Kumari SS, Srivastava SS (2001) Rainwater composition at a regional representative site of a semi-arid region of India. Water Air Soil Pollut 127:93–108
Skjelkvåle BL (1994) Factors influencing fluoride concentrations in Norwegian lakes. Water Air Soil Pollut 77:151–167
Sreedevi P, Ahmed S, Made B, Ledoux E, Gandolfi J (2006) Association of hydrogeological factors in temporal variations of fluoride concentration in a crystalline aquifer in India. Environ Geol 50:1–11
Stormer JC, Carmichael ISE (1970) Villiaumite and the occurrence of fluoride minerals in igneous rocks. Am Mineral 55:126–134
Sujatha D (2003) Fluoride levels in the groundwater of the south-eastern part of Ranga Reddy district, Andhra Pradesh, India. Environ Geol 44:587–591
Tahir Shah M, Danishwar S (2003) Potential fluoride contamination in the drinking water of Naranji Area, Northwest Frontier Province, Pakistan. Environ Geochem Health 25:475–481
Tavener SJ, Clark JH (2006) Fluorine: friend or foe? A green chemist's perspective. In: Tressaud A (ed) Fluorine and the environment: agrochemicals, archaeology, green chemistry and water. Elsevier, Amsterdam
Taylor RP, Fallick AE (1997) The evolution of fluorine-rich felsic magmas: source dichotomy, magmatic convergence and the origins of topaz granite. Terra Nova 9:105–108
Teotia SPS, Teotia M (1994) Dental caries: a disorder of high fluoride and low dietary calcium interactions (30 years of personal research). Fluoride 27:59–66
Ullah R, Malik RN, Qadir A (2009) Assessment of groundwater contamination in an industrial city, Sialkot, Pakistan. Afr J Environ Sci Technol 3:429–446
Valenzuela-Vásquez L, Ramírez-Hernández J, Reyes-López J, Sol-Uribe A, Lázaro-Mancilla O (2006) The origin of fluoride in groundwater supply to Hermosillo City, Sonora, México. Environ Geol 51:17–27
Van Der Hoek W, Ekanayake L, Rajasooriyar L, Karunaratne R (2003) Source of drinking water and other risk factors for dental fluorosis in Sri Lanka. Int J Environ Health Res 13:285–293
Vithanage M, Bhattacharya P (2014) Fluoride in drinking water. In: Lichtfouse E, Schwarzbauer J, Robert D (eds) CO_2 sequestration, biofuels and depollution, Environmental chemistry for a sustainable world. Springer
Vithanage M, Jayarathna L, Rajapaksha AU, Dissanayake CB, Bootharaju MS, Pradeep T (2012) Modeling sorption of fluoride on to iron rich laterite. Colloids Surf Physicochem Eng Asp 398:69–75
Walna B, Kurzyca I, Siepak J (2007) Variations in fluoride level in precipitation in a region of human impact. Water Air Soil Pollut Focus 7:33–40
Wang GQ, Huang YZ, Xiao BY, Qian XC, Yao H, Hu Y, Gu YL, Zhang C, Liu KT (1997) Toxicity from water containing arsenic and fluoride in Xinjiang. Fluoride 30:81–84
Ware GW (1975) Pesticides, an auto-tutorial approach. W.H. Freeman and Co., San Francisco
WHO (1984) Fluorine and fluorides, environmental health criteria. World Health Organization, Geneva
WHO (1996) Trace elements in human nutrition and health. World health Organization, Geneva
WHO (2000) Fluorides. In: Air quality guideline for Europe, 2nd edn. World Health Organization, Regional Office for Europe, Copenhagen
WHO (2002) Fluorides, environmental health criteria number. World Health Organization, Geneva
WHO (2004) Guidelines for drinking-water quality. Recommendations, vol 1. World Health Organization, Geneva
Wodeyar BK, Sreenivasan G (1996) The occurrence and movement of ground water Bellary District, Karnataka: a preliminary study. Curr Sci 70:71–74
Young S, Pitawala A, Ishiga H (2011) Factors controlling fluoride contents of groundwater in north-central and northwestern Sri Lanka. Environ Earth Sci 63:1333–1342
Yiamouyiannis JA (1993) Fluoridation and cancer. The biology and epidemiology of bone and oral cancer related to fluoridation. Fluoride 26:83–96
Zhu J, Zhao H, Ni J (2007) Fluoride distribution in electrocoagulation defluoridation process. Sep Purif Technol 56:184–191