Hydrogeochemistry of Aquatic Ecosystems

Edited by

Sughosh Madhav • Virendra Bahadur Singh
Manoj Kumar • Sandeep Singh

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Preface

Hydrogeochemistry has always been a subject to solve the relationships between groundwater, surface water, and aquatic systems' chemical characteristics and their relationship with the area's geology. The phenomenon of hydrogeochemical variations depends on various geochemical processes, like weathering, evaporation, and dissolution, and diverse anthropogenic activities that control the aquatic systems' hydrogeochemistry. Almost all aquatic systems are affected by human interventions, causing several problems. Further climate change also impacts the hydrogeochemistry of different ecosystems. It is, therefore, vital to understand the current status of the aquatic systems to manage and mitigate the impacts. This book covers current issues related to hydrogeochemistry of natural aquatic systems, including river, glaciers, lake, and sub-surface ecosystems, processes involved, and human beings' interference. This book tries to address all the major impending problems related to hydrogeochemistry of surface and sub-surface water with a certain degree of solutions to manage and conserve water resources. The various chapters will help to understand the processes and factors controlling the hydrogeochemistry of water resources. The book discusses multiple hydrogeochemical techniques like nutrient geochemistry, solute acquisition processes, water–sediment interactions, enrichment of geogenic elements like arsenic, fluoride, and uranium, anthropogenic addition, and biogeochemical cycling of metals, CO_2 consumption rate in the surface water bodies, sand mining in rivers, and hydrogeochemical modeling. The other highlights of the book are carbon dynamics and its sequestration in surface water bodies, soil–water interactions, and sediment loading in aquatic ecosystems. The book encompasses knowledge on isotopic studies, microbial control in hydrogeochemistry along nutrient dynamics of the polar ice sheet and glaciers. The work contained in the book covers holistic and in-depth knowledge of the hydrogeochemistry of different aquatic ecosystems.

The chapters in the book address the impending problems with a certain degree of solutions to manage and conserve water resources. This book contains both practical and theoretical aspects of the hydrogeochemistry of aquatic systems. It will be helpful for undergraduate and graduate university students or researchers and teachers, environmental engineers, and scientists working in water resource management, environmental studies, and social issues. It will also be helpful for researchers and stakeholders from all the sectors of industries and governmental agencies who are directly or indirectly associated with water resource research and management.

We tried a humble attempt to reflect upon the various aspects of aquatic hydrogeochemistry, hoping that it would be a significant addition to the already available literature. The contributors to the book having different backgrounds provide a holistic approach to the topic imbibing diverse practices and perspectives. We express our sincere gratitude to all the contributors and publishers for producing a remarkable and meaningful edited volume on an important issue.

1

Fluoride in Groundwater: Distribution, Sources, Processes, Analysis, and Treatment Techniques: A Review

Bedour Al Sabti, Dhanu Radha Samayamanthula, Fatemah M. Dashti, and Chidambaram Sabarathinam

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1.1 Introduction

Fluoride (F^-) belongs to the halogen family and is a constituent in minerals such as fluorite, fluorspar, apatite, biotite, cryolite, and muscovite (Bretzler and Johnson 2015; Dehbandi et al. 2017), apart from its availabilities in plants, soil, and groundwater. Groundwater is one of the most important sources of drinking water and one of the fundamental human rights around the globe is an access to safe drinking. Contamination and unsustainable drinking water sources could affect human health, resulting in the transmission of diseases (WHO 2018). Fluoride is one of the ions which may lead to groundwater contamination if present in high concentrations. Although high F^- in groundwater is a major concern that is still being debatable around the globe, fluoride is essential for the growth of the dental and skeletal frame of the body. Fluoride concentration in groundwater differs from one region to another based on aquifer material, geology, weathering rate, aquifer depth, contact time, pH, rainfall, and temperature (Brunt et al. 2004; Onipe et al. 2020). The geochemical process governs fluoride mobility through leaching from soil and rocks to the groundwater. Studies suggest that exposure to high fluoride imparts a vulnerable effect on the mental ability of children. The IQ levels of children exposed to higher F^- are lower than unaffected children (Choi et al. 2012; Das and Mondal 2016). The thyroid gland is susceptible to F^-, which causes an increase in thyroid-stimulating hormone (TSH) leading to a drop in Triiodothyronine (T3) and Thyroxine (T4) levels, thereby resulting in hypothyroidism (McLaren 1976; Shashi 1988; Kumar et al. 2019). Fluorosis results from a high concentration of fluoride in drinking water and depends on other sources such as dietary habits that enhance the incidence of fluorosis (Brindha and Elango 2011; Srivastava and Flora 2020). Several countries, such as West Indies, India, Poland, China, Spain, Africa, and Italy, have been reported with high fluoride concentrations (Huang et al. 2017). The geochemical data for Cameroon, Algeria, Ghana, United Kingdom, Siri Lanka, Argentina, Canada, Tanzania, Kuwait, South Africa (Silom), India (Telangana), and Brazil were

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collected from the literature to understand the geochemistry of F^- (Table 1.1). Some of the published data for selected countries does not contain the complete analysis results. Based on the available ions in the analytical data, they were used for statistical analysis using Statistical Package for Social Sciences (SPSS) software. The same analytical data were used

Table 1.1 Lithology and analytes considered from the literature studies of various countries but clay minerals like Vermiculite have also reported to be a source of F^- in groundwater due to the process of Fluoride ion.

Country	Lithology type	Analytes	Reference
Algeria	Sedimenatary (sand and gravel, limestone, clay, and shale)	pH, EC, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, F^-	Messaitfa (2007)
Argentina	Thick sedimentary rock and volcanoclastic mineral	pH, EC, temperature, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} F^-, NO_3^-, Si, Fe^{2+}, Al^{3+}, Be^{2+}, U, B	Ganyaglo et al. (2019); Jayawardana et al. (2012); Edmunds and Smedley (2013)
Brazil	Sedimentary	pH, EC, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, F^-	Rockett et al. (2013)
Canada	—	pH, EC, temperature, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} F^-, NO_3^-, Si, Fe^{2+}, Al^{3+}, Be^{2+}, U, B	Ganyaglo et al. (2019); Jayawardana et al. (2012); Edmunds and Smedley (2013)
Central Africa (Cameroon)	Crystalline basement (granite)/ Tertiary sedimentary rocks	pH, EC, temperature, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, F^-, NO_3^-	Fantong et al. (2009)
Ghana	Precambrian crystalline and igneous rocks (granite)	pH, EC, TDS, temperature, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-},HCO_3^-,CO_3^{2-} F^-,NO_3^-	Sunkari an Abu (2019)
India (Telangana)	Igneous rock (granite)		Narsimha and Sudarshan (2017)
Kuwait	Sedimentary siliciclastic and carbonates	pH, EC, TDS, temperature, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} F^-, NO_3^-, B, $NH4^+$, PO_4^{3-}, SiO_2, Fe^{2+}, Al^{3+}, Ba^{2+}, Li^+, Mn^{2+}, Mo, Ni^{2+}, Zn^{2+}	Al-Senafy et al. (2011)
South Africa (Silom)	—	pH, EC, TDS, temperature, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} F^-, NO_3^-, PO_4^{3-}	Onipe et al. (2021)
Sri Lanka	High-grade metamorphic rock	pH, EC, temperature, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} F^-, NO_3^-, Si, Fe^{2+}, Al^{3+}, Be^{2+}, U, B	Ganyaglo et al. (2019); Jayawardana et al. (2012); Edmunds and Smedley (2013)
Tanzania	Volcanic rock and metamorphic		
United Kingdom	—		

for different plots developed from the output results of WATEQ4F and AQUACHEM. The objective of this review is to emphasize the global distribution, sources, analysis, and treatment strategies for excessive fluoride levels in groundwater. Also, the review presents geochemical plots, statistical techniques, thermodynamic and modeling approaches to determine processes governing the fluoride release and distribution in groundwater.

1.2 Permissible Limits of Fluoride in Drinking Water

According to the WHO (2006), the maximum permitted level of F^-in drinking water is 1.5 mg/L. While the USPHS (1987) established a range of allowable F^- concentration in drinking water for regions based on their climatic conditions, because the amount of water consumed and, the amount of F^- ingested is primarily influenced by the air temperature. The rise in air temperature decreases the concentration of F^-. The maximum permissible level in tropical climates with temperatures above 26 °C is 1.4 mg/L. In light of the Indian subcontinent's environmental and socioeconomic situation, the F^- desirable limit is established at 0.6–1.2 mg/L, and the highest allowed level in the absence of any other source is set at 1.5 mg/L for drinking water (ISI 1995). The limit was set based on the daily consumption rate of water, about 2 L/day for an adult body mass, and contains about 0.2–0.5 mg fluorine as a standard diet (WHO 1994). A range of environmental, social, cultural, economic, and other circumstances affecting possible exposure, as well as the default assumptions used to create the guideline values, will need to be taken into account when creating national drinking-water standards based on these guideline values. In addition, the environmental-based variation depends on the region, as regional diets and ambient temperature control the permissible limit (Apambire et al. 1997). Furthermore, in a country with a constant warm environment and piped water as the main drinking-water source, authorities may choose a lower health-based fluoride target than this guideline value as water consumption is predicted to be higher (Guidelines for drinking-water quality 2021). Drinking water from groundwater may be beneficial or harmful depending on the concentration level of fluoride. In recent years, countries have been developing drinking standards to decrease waterborne diseases and improve safe water resources management (Ali et al. 2019). As the concentration of F^- in drinking water is different for each country, and the amount of water consumed by a person also varies concerning the climate and availability, so each region has its own standard (Figure 1.1). Drinking high fluoride groundwater is the primary reason for endemic fluorosis in the countries such as China (Guo et al. 2007). Higher F^- concentration in groundwater, i.e. exceeding the permissible limit of WHO, is observed in countries like Japan, Cameroon, China, Turkey, India, Sri Lanka, Iran, Pakistan, Brazil, and Canada. Fluorosis, on the other hand, is caused by a high quantity of fluoride in drinking water and is exacerbated by other factors such as dietary choices (Brindha and Elango 2011).

Fluoride concentrations above the permissible limit are harmful to human health, such as dental fluorosis, crippling skeletal fluorosis, and skin lesions (Rasool et al. 2017), and it also depends on the amount of intake, duration of exposure, and gastrointestinal traces. The absorbed fluoride from the food sources in the digestive system is about 30–40% (Kumar et al. 2019).

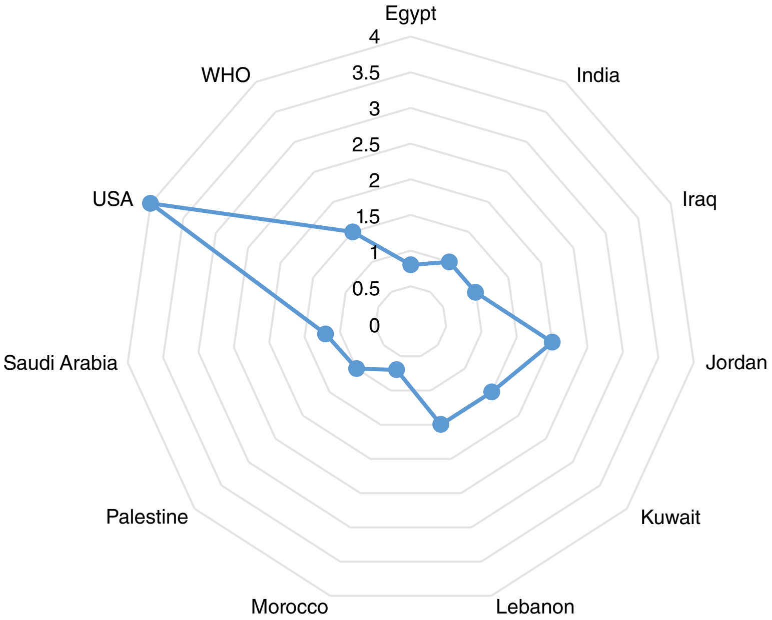

Figure 1.1 A radar chart representing the maximum fluoride concentration standard for each country as specified. Data *Source:* Guo et al. (2007), Jagtap et al. (2012), Abu-Zeid and El-Hatow (2007), and KEPA (2017).

1.3 Concentration of High Fluoride Around the Globe

Data for groundwater samples signifying maximum value fluoride concentration were collected from literature studies to represent the highest value of F^- distribution in a world map (Figure 1.2). The map represents a total of 46 regions with F^- concentration above the allowable limits, reaching up to 160 mg/L. One of the highest F^- concentration values that was found with a total of 160mg/L, found to be reported in California, North America (McMahon et al. 2020). The high fluoride concentration as it is shown on the map mostly represents the igneous and metamorphic rock formations predominantly around the tropical region. However, elevated fluoride concentration may result from various sources affecting the groundwater to be discussed in the following section.

1.4 Sources of Fluoride in Groundwater

Fluoride in groundwater occurs in variable concentrations and <1.0 mg/L is generally reported in natural waters (Hem 1985). Anion exchanges, solubility of minerals, temperature, pH, nature of the aquifers, matrix, and availability of complexing ion, residence time, and chemical composition of the groundwater are the main governing factors affecting the concentration of F^- (Apambire et al. 1997). The presence of F^- in groundwater is mostly caused by natural or geogenic contamination (Manikandan et al. 2014). Chemical

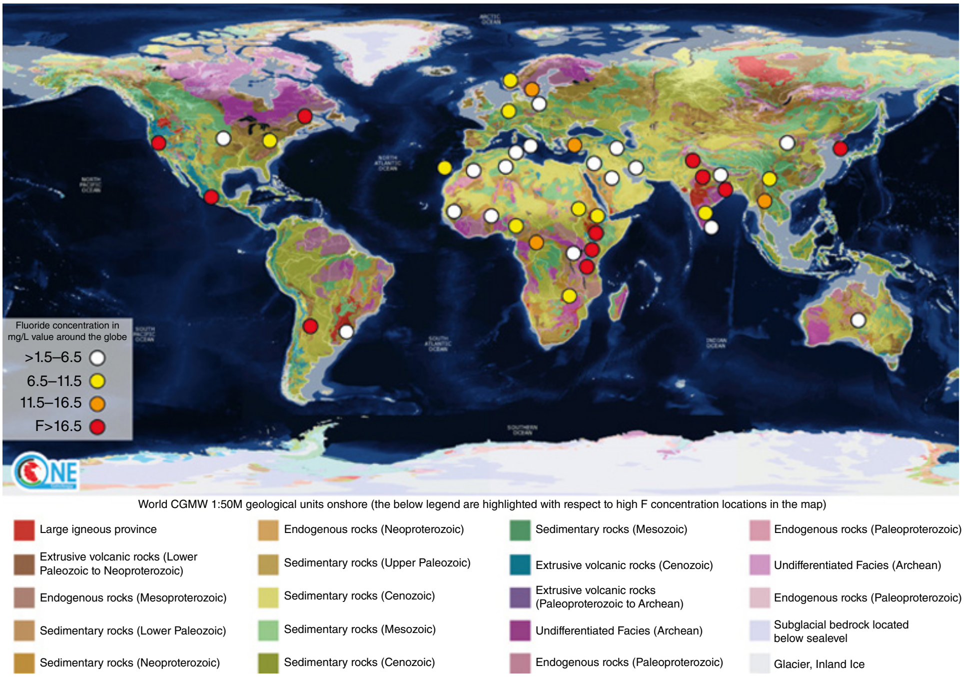

Figure 1.2 Global map represents the maximum fluoride values concentration which is above the standard limits in different regions. The lithology legend highlights only the areas of high fluoride concentration in groundwater. Source: Reproduced with the permission of the OneGeology. All rights reserved.

weathering, atmospheric dust from continental sources, industrial pollutants, and magmatic emissions are also potential sources of F^{-} (Gizaw 1996). In other words, F^{-} reaches groundwater due to input from natural or anthropogenic sources or both. Fluorides can be transported to groundwater via water–rock interaction by different fluoride-bearing minerals (Narsimha and Sudarshan 2017). This interaction is used to examine the geogenic input of fluoride in groundwater aquifers from various forms of fluoride minerals.

1.4.1 Natural Sources

The parent rock serves as the primary source of fluoride in groundwater. Thus, various geochemical studies have been performed on various aspects of fluoride in groundwater. Some rock types showed a higher fluoride concentration than others with groundwater, such as volcanic zones with geothermal sources, sedimentary basins, and crystalline basement aquifers (Edmunds and Smedley 2005). An average F^{-} concentration of 715 mg/kg is observed in igneous rocks globally (Gizaw 1996). These rocks are likely to be formed in volcanic areas with magmas enriched with fluoride concentration, and the sodium plagioclase is most likely to form soft groundwater that allows higher fluoride production when reaching equilibrium (Ozsvath 2006). Fluorine can be present in different igneous rock-forming minerals such as mica, apatite, amphiboles, pegmatite, and certain types of clay (Ayoob and Gupta 2006). The predominant minerals are depicted in Table 1.2, but clay minerals like Villiaumite have also reported to be a source of F^{-} in groundwater due to the process of ion exchange (Handa 1975; Pickering 1985; Wenzel and Blum 1992; Bardsen et al. 1996; Subba Rao and Devadas 2003). Fluoride concentrations, on the other hand, are frequently related to water–rock interaction to a certain degree because fluoride is mostly from lithology (Manikandan et al. 2014). The hydrogeochemical studies in groundwater had reported several mechanisms of F^{-} release based upon the composition of the aquifer matrix, the physio chemical conditions, and the rock–water interaction. They have also inferred that the residence time in the aquifer and temperature also play a major role in release of F^{-} from the rock matrix to groundwater. Some researchers have studied the

Table 1.2 Classification of fluoride minerals in different rock types with their chemical composition.

S.No.	Mineral	Rocks	Chemical composition
1	Fluorite	CaF_2 Pegmatite, Metamorphosed, Limestone	CaF_2
2	Fluorspar	Pegmatite Pneumatolitic, Deposits	$CaF_2.3Ca_3(PO_4)_2$
3	Tremolite Actinolite	Clay	$Ca_2(MgFe^{2+})_5(Si_8O_{22})(OHF)_2$
4	Rock Phosphate	Limestone, Fossils	$NaCa_2(MgFe^{2+})_4(AlFe^{3+})(SiAl)_8O_{22}(OHF)_2$
5	Lepidolite	Gabbros, Dolerites	$K_2(Li, Al)_5(Si_6Al_2)O_{20}(OHF)_4$

Source: Adapted from Yadav and Khan (2010).

relationship between water–rock interaction and F^- concentration in various aquifers having different geologic settings (Saxena and Ahmed 2003; Gaciri and Ad Davis 1993; Edmunds and Smedley 1996; Nordstrom et al. 1989; Nordstrom and Jenne 1977). Groundwater development and management have encountered a serious issue due to the prevalence of F^- when harvesting or recharging structure areas located in granitic terrain. Fluorite is one of the minerals responsible for the presence of fluorine in nature, and it acts as an accessory mineral in granitic rocks (Ayoob and Gupta 2006). Deeper wells in granitic and gneissic aquifers often have higher fluoride contents. Fluorite (CaF_2) present in the granitic formation is a dominant source of F^- (Deshmukh et al. 1995). It is to be noted that the rate of dissolution and stability of the mineral in freshwater is relatively low (Nordstrom and Jenne 1977). Hence, few studies have indicated that biotite mica is present as an accessory mineral in the granitic formation, to be the prime source of F^- in hosted groundwater for their favorable F^-, $(OH)^-$ exchange (Saxena and Ahmed 2001). A pattern that has been documented in several inferences on groundwater collected from granitic regions (Yun et al. 1998a; White et al. 1963). The studies on samples from deep groundwater have indicated that the dissolution of F^- minerals in the rock matrix was governed by the depth of well, residence time, and temperature (Saxena and Ahmed 2003; Nordstrom et al. 1989). Higher residence time is generally found in massive hard rock aquifers and lesser in porous sedimentary formations. This is also an important fact that higher F^- in groundwater is more prevalent in hard rock aquifers. Fluoride can mix with clay by displacing the hydroxide from its surface in acidic water. F^- is adsorbed on the clay surface but desorbed from solid phases in alkaline water. The evaporation process can also cause fluoride enrichment in groundwater; however, the evaporation process is usually characterized by the preponderance of Cl^- ion in groundwater (Manikandan et al. 2014). Because of its granitic-type composition (alkaline), augen gneiss has the largest potential for higher groundwater fluoride. The augen gneiss is metamorphosed granite that contains fluoride-bearing minerals like biotite, hornblende, and distinctive Na-feldspar mega crystals that serve as a secondary source of sodium for fluoride enrichment (Addison et al. 2020). One of the important fluoride-bearing minerals is muscovite, with fluorine in its hydroxyl groups and crystal lattices that can act as fluoride substitutes due to their similar ionic charges. Among the micas apart from muscovite, biotite is also reported to have exchangeable F^- of octahedral sheet at the hydroxyl sites (Chidambaram et al. 2007). The lithological influences of F^- in groundwater were investigated by Singaraja et al. (2013), where the study stated that elevated F^- concentrations in groundwater were due to charnockite, hornblende biotite gneiss marine alluvium, and by flood plain alluvium. Higher concentration of F^- in hydrological systems also depends on the rate of recharge and the transport of the ion along with the groundwater flow. There is also a probability of reduction of F^- along the flow direction either due to mineral precipitation or removal by adsorption or by ion exchange process. The studies on the thermodynamic properties and the relative F^- enrichment in groundwater in the different geochemical environments are still scanty.

1.4.2 Anthropogenic Sources

Pollution that results from industries such as fabrication of aluminum, fertilizers, and steel has been reported to generate higher F^- through anthropogenic means to the natural environment (Datta et al. 2014). The use of phosphate fertilizer in agricultural operations also results in the probable presence of fluoride in groundwater (Thivya et al. 2015) where phosphate fertilizers generally contain fluorine ranging from 1.3 to 3.0% (Mclaughlin et al. 1996). Apart from the above anthropogenic sources, pesticides, sewage and sludge, groundwater table depletion, and other agricultural practices have also been linked to a rise in F^- concentrations in groundwater (Srinivasamoorthy et al. 2007). F^- may infiltrate streams through adjacent uneven joints, cracks, and through damaged pipelines transporting household, agricultural, and industrial effluents (Datta et al. 2014). Farooqi et al. (2009) study illustrated that familiar source of F^- in the environment including air pollution from coal combustion and phosphate fertilizers, whereas soluble F^- in fertilizers ranged from 60 to 255 mg/kg, with a mean of 175 mg/kg. In contrast, total F^- in coal samples ranged from 5.12 to 20.1 mg/kg, with an average value of 10.2 mg/kg (Farooqi et al. 2009). However, only a small portion of overall fluoride exposure is typically attributed to air (Fawell et al. 2006). Another study by Loganathan et al. (2006) reported that fluoride concentrations in New Zealand agricultural surface soils varied from 212 to 617 μg F^-, which was significantly lower than the fluoride values reported in the literature for sites polluted with fluoride from industrial sources.

1.4.3 Health Effects

The association between human health and fluoride was first explored in the late nineteenth century when chemists discovered varying levels of fluorine in human bones, tissues, and teeth (Kanduti et al., 2016). Fluoride is vital to human health for developing strong bones and teeth, but only in trace amounts ranging between 0.5 and 1 mg/L worldwide (Addison et al. 2020; Ozsvath 2006). However, fluoride is also known to be a very toxic element to human health if it exceeds the average standard limits published by WHO (Narsimha and Sudarshan 2017). Fluoride operates as hydrofluoric acid and is absorbed by humans and animals through their skin, where it travels quickly through the circulatory system and is stored in teeth and bones, according to Hodge and Smith (1977). According to another study, fluorosis is widespread in more than 200 million people globally (Ayoob and Gupta 2006). High fluoride levels can result in severe health issues in both adults and children, including dental fluorosis, bone deformation, and skeletal fluorosis (Narsimha and Sudarshan 2017).

1.4.4 Dental Fluorosis

Dental fluorosis considers as an irreparable toxic condition that affects the human teeth cells as an early-stage sign of having a fluoride increase in the body (Ayoob and Gupta 2006). Any fluoride ingestion in water with a concentration above the standard limits may cause dental fluorosis (Apambire et al. 1997). A case study in India illustrated that out of 258 children in the study area were examined, and 84 of them were diagnosed with dental fluorosis with ages ranging between 3 and 17 years old. The dental signs of the patients were identified from their teeth, such as chalky white color stain, browning of the tooth surface, yellowish stain, deep brown or black discoloration, pitting, and teeth loss (Jha et al. 2009). Opaque white patches on teeth characterize the diagnosis of early-stage dental fluorosis, unlike the advanced stages where the teeth are displayed as pitting on the surface of the teeth and brown to black staining (Figure 1.3) (Apambire et al. 1997). In addition, it was also suggested that calcium fluoroapatite crystals replaced the calcium in the teeth during

Figure 1.3 Effect of dental fluorosis due to high concentration of F^-.

a process known as mineralization. This process happens when the fluoride accumulates and combines with the calcium, and further on, the calcium will be reduced and lost from the teeth (Ayoob and Gupta 2006).

1.4.5 Skeletal Fluorosis

The consumption of water with F^- concentration greater than the permissible limit that ranges between 4.0 and 8.0 mg/L and higher (Apambire et al. 1997), will lead to severe and long-term damage to the human skeleton, a disease known as skeletal fluorosis (Ayoob and Gupta 2006). The lowest limit that has been noticed, which causes skeletal fluorosis, is 3.0 mg/L (Manikandan et al. 2014). Moreover, higher the duration and amount of fluoride entering the human body, the higher the severity of the disease (Ayoob and Gupta 2006). The symptoms shown on people with a possibility of having skeletal fluorosis vary in severity, with excess fluoride concentration consumption by Sutter from muscle and joint pain or mild rheumatic pain. In addition, to severe pain in the cervical spine region, stiffness and rigidity in joints, and crippling; skeletal fluorosis can occur once the fluoride concentration in drinking water exceeds 10 mg/L (Apambire et al. 1997; WHO 1970). Likewise, skeletal fluorosis can also be witnessed in the X-ray by increasing the bone density in adults (Mohammadi et al. 2017). Fluoride can disrupt the equilibrium of bone mineral metabolism by affecting the accretion and desorption of bone tissue (Ayoob and Gupta 2006). A study by Mohammadi (2017) analyzed two categories one with high fluoride concentration above the standard limit was diagnosed in a total of 445 people, and the other one containing low fluoride concentration below the standard limit was observed in a total of 470 people. The first area with high F^- showed that 21.1% of the people have skeletal fluorosis, only 3% from the second area suffered from skeletal fluorosis. The rates of the fluoride concentration in this study ranged from 0.22 to 10.33 mg/L (Mohammadi et al. 2017).

1.5 Hazard Index

The Hazard Index or Hazard Quotient (HQ) is the ratio of a single drug exposure level (dose or concentration) during a defined time period to the Rf_D computed for the same substance over the same time period. HQ, ratio greater than one indicates that the chemical

Table 1.3 Calculated and standard values of the parameters needed for the HQ calculation. The mean value of F^- from Kuwait's groundwater samples.

Variable	Description	Value (Women)	Value (Men)
C (mg/L)	Mean F concentration in groundwater	1.98	1.98
IR (L/day)	Daily water intake rate	2	2
EF (days/year)	Exposure frequency	365	365
ED (Year)	Exposure duration	76.4	74.6
Lt	Lifetime expectancy	75.4	75.4
BW (kg)	Average body weight	78.3	88.1
AT (Lt × 365)	Averaging time of exposure	27 521	27 521
EDI	Estimated daily intake of F^- from groundwater	0.05	0.04
RfD (mg/kg)	Oral toxicity reference	0.06	0.06
HQ	Hazard index	0.85	0.74

Source: Data from Worldbank – Kuwait Data (2021).

concentration is enough to induce persistent noncarcinogenic effects. In this review, samples of Kuwait (Table 1.3) are considered to check the effect of high concentration of fluoride using the following equation:

$$\mathrm{HQ} = \frac{\mathrm{EDI}}{\mathrm{RfD}} \tag{1.1}$$

This value is according to the USEPA's Integrated Risk Information System (USEPA 2014).

The estimated daily intake (EDI) of F from groundwater is used to calculate the F exposure dosage. The EDI values were calculated using Eq. 1.9 from the US Environmental Protection Agency. EDI can be determined using the following equation:

$$\mathrm{EDI} = \mathrm{C} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{EDBW} \times \mathrm{AT} \tag{1.2}$$

The optimum level of oral intake was assessed to depend on the baby weight and annual mean maximum temperature (Galagan et al. 1957)

$$\mathrm{F}(\mathrm{mg/L}) = 0.34/\mathrm{E} \tag{1.3}$$

E is the estimated average daily water intake for children <10 years old.

$$\text{Optimal fluoride intake}(\mathrm{mg/L}) = \frac{0.022}{(0.0104 + 0.000724) * \mathrm{AMMT}^{\circ}\mathrm{C}} \tag{1.4}$$

AMMT is for a period of five years but due to malnutrition the amount of water intake is more and then the equation is modified (Ramadan and Hilmi 2014) as

$$= \frac{(0.022 * 0.56)}{(0.0104 + 0.000724) * \mathrm{AMMT}^{\circ}\mathrm{C}} \tag{1.5}$$