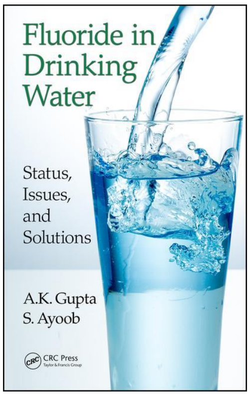

Fluoride in Drinking Water
Status, Issues, and Solutions

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Fluoride in the Environment and Its Toxicological Effects

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Fluoride in the Environment and Its Toxicological Effects

6.1 Introduction

Fluorine is the most electronegative and the most reactive element present in the periodic table. It is always found in the nature with the combination of some other elements because of its reactivity. Fluoride is a naturally occurring, widely distributed element, and it is found in varying amounts in minerals, rocks, gases from volcanoes, and so forth. Anthropogenic sources such as coal-fired power plants; aluminum smelters; phosphate fertilizer plants; glass, brick, and tile works; and plastics factories are also responsible for the increase in the level of the fluorine in the atmosphere.[1,2] As stated in previous chapters, human beings are benefited when the fluoride uptake is of an appropriate quantity. If the fluoride uptake is lower than the minimum amount or more than the upper limit, it can adversely affect human health. Studies have shown that apart from human beings, plants, and animals also experience toxicological issues when they are exposed to fluoride. Drinking water serves as the major source of fluoride in humans; however, other environmental sources also contribute to it.[2]

6.2 Sources of Environmental Exposure

Fluorine is present in the environment mostly as fluorides. Fluoride is released into the environment either naturally or through human activities. The natural processes that are responsible for fluoride intrusion into the environment may include weathering and dissolution of minerals, volcanic eruption, and contribution of marine aerosols.[3] Fluoride is also released into the environment by manifold human activities, for example, coal combustion; processing of water and waste from various industrial processes, including steel manufacture; aluminum, copper, and nickel production;

phosphate ore processing; phosphate fertilizer production and use; glass, brick, and ceramic manufacturing; glue and adhesive production; and so forth. Among these, industrial sources such as phosphate ore production and use, and aluminum manufacture are the major anthropogenic sources of fluoride.[4,5] Controlled addition of fluoride to a public water supply, food items, dental products, and pharmaceutical products also contribute to the release of fluoride into the environment through anthropogenic sources.[6] A number of fluoride compounds that are mostly used for industrial and commercial purposes are also potential sources of fluoride in the environment. In this direction, some important fluoride compounds are listed as follows:[2,4]

- Hydrogen fluoride is predominantly used in the production of aluminum and chlorofluorocarbons (CFCs). It is used in electronic industries, cleaning glass, brick and tiles work, tanning leather, and in commercial rust removers and pickling operation in stainless steel. It has wide application in separating uranium isotopes or as a catalyst in the petroleum industry.
- Calcium fluoride has multiple uses in the fiber glass, ceramic, welding rod, glass, and fluorescent lamps industry. It is used in blending with burned lime and dolomite in the steel industry, and it is also a fluxing agent for aluminum metallurgy.
- Sodium fluoride has wide use in fluoridation of drinking water. It is used as a preservative in glues and wood, and as an insecticide. It is also used as a flux in steel and aluminum production, as well as in glass and enamel production.
- Sulfur hexafluoride is used as a gaseous dielectric medium in the electrical industry for high-voltage circuit breakers, switch gear, various electronic components, and so forth. It has some application in the production of magnesium and aluminum.
- Fluorosilicic acid and sodium hexafluorosilicate are used for the fluoridation of drinking-water supplies.

6.3 Environmental Transport, Distribution, and Transformation

In the atmosphere, fluorides exist in gaseous or particulate form. Gaseous fluorides can be either transported over long distances by the effect of wind or atmospheric turbulence or absorbed by the atmospheric water (rain, clouds, fog, snow), forming an aerosol or a fog of aqueous hydrofluoric acid. They can be removed from the atmosphere via wet deposition. Fluoride present in the particulate form can be removed from the atmosphere and deposited on land or surface water by wet and dry deposition.[7] Most of the fluoride compounds are not expected to remain in the troposphere for long periods or to migrate to the stratosphere. However, sulfur hexafluoride can reside in the atmosphere for a period ranging from 500 years to several thousand years.[2] Several factors influence the process of the transport, and transformation of fluoride in water. Some of the important factors are pH, water hardness, and the presence of ion-exchange materials such as clays. Fluorides usually combine with aluminum during their transportation and transformation process through water cycle. In soils, the transport and transformation of fluoride are influenced by pH and the formation of complexes, predominantly those with aluminum and calcium. When the soil is slightly acidic (pH 5.5–6.5), fluoride may be adsorbed more strongly by the soil particles. Fluorides strongly bond with the soil and are not easily leached from it. Terrestrial plants may accumulate fluorides from the atmosphere through the opening of stomata and from the soil via roots. Some aquatic plants and animals can bioaccumulate the soluble fluorides from water. The quantity of fluoride uptake depends on the route of exposure, how fluoride is absorbed by the body and how quickly it is consumed and excreted.

6.4 Environmental Levels and Human Exposure

The level of fluoride in surface water such as rivers, lakes, and so forth depends on its location and distance from the emission source. Fluoride concentration in the range between 0.01 and 0.3 mg/L is found in surface water,[2] whereas sea water contains more fluoride than fresh water and it ranges between 1.2 and 1.5 mg/L.[2] Fluoride concentration in groundwater is very high in areas where the natural rocks and soil are rich in fluoride. Inorganic fluoride concentration is very high in the regions where there is geothermal or volcanic activity. Anthropogenic discharges are also one of the major sources that increase the concentration of fluoride in the environment.

The fate and transport of gaseous and particulate fluorides in the environment occurring from natural and anthropogenic sources depend on various atmospheric conditions. The transportation, distribution, transformation, and deposition of airborne fluorides are governed by meteorological conditions, particulate size, chemical reactivity, and emission strength of the source. Fluorides that are released as gaseous and particulate matter are generally deposited in the vicinity of an emission source, whereas some particulates may react with other atmospheric constituents. It has been found that the fluoride concentrations in the ambient air in areas that do not have any nearby emission sources[2] are generally less than 0.1 μg/m^3. However, even in the areas that have nearby emission sources, the concentration of levels of airborne fluoride[2] usually do not exceed 2–3 μg/m^3.

Fluoride is present in various concentrations in different types of soils. The fluoride concentrations in the areas without natural phosphate and fluoride deposits range from 20 to 1000 μg/g, whereas the concentration may increase to several thousand micrograms per gram for the soil that is enriched with natural deposits of fluoride.[2] Many foodstuffs contain very small amounts of fluoride; however, very high amounts of fluoride are reported in fish and tea leaves. The exposure of individuals to fluorides varies considerably. It depends on the level of fluoride in drinking water or dietary intake, the use of fluoridated dental/pharmaceutical products and, in some cases, the levels of fluoride in indoor air. The inhalation of airborne fluoride generally contributes a minor stake in the total fluoride (TF) intake. Infants who are fed with formula receive 50–100 times more fluoride than infants who are fed exclusively breast milk. In the case of young children, the ingestion of toothpaste containing fluoride contributes a significant amount to their TF intake. The intake of fluoride in adults is mainly through foodstuffs and drinking water. Generally, 2 mg/day of fluoride finds its way into the body of children and adolescents.[2] Although adults may have a higher absolute daily intake of fluoride in terms of milligrams, the daily fluoride intake of children, expressed on a milligram-per-kilogram body weight basis, may exceed that of adults.[2] Occupational individuals working in industries such as aluminum, fertilizer, iron, oil refining, semiconductor, phosphate, ore, and steel are more susceptible to get exposed to fluoride via inhalation or dermal contact. Recent studies[2] reported that the concentration of fluoride in the pot rooms generated from aluminum smelters is found to be in the order of 1 mg/m^3.

6.4.1 Fluoride from Dental Products

It has been established that different dental and pharmaceutical products that are used by people in their daily life for oral hygiene contain fluoride. These include toothpastes (1.0–1.5 g/kg fluoride), gels (0.25–24.0 g/kg fluoride), fluoride tablets (0.25–1.00 mg fluoride/tablet) and so forth.[6] Fluorides in the form of sodium fluoride (NaF), sodium monofluorophosphate (Na_2FPO_3) and tin fluoride (SnF_2), or in the form of different amines can be added to toothpastes. Dental products such as toothpaste and tooth powder may also contribute to the TF intake. In pharmaceutical products, fluoride can be added in the form of NaF or Na_2FPO_3. The intake of fluoride through dental products varies from person to person on the basis of their practice and exercise of cleaning teeth. Generally, small children are more susceptible to ingestion of toothpaste while cleaning their teeth. Studies on toothpaste suggest that during cleaning of the teeth, most children ingest approximately 20% of the toothpaste. It has been found that ingesting the toothpastes containing fluoride may result in a contribution of about 0.50–0.75 mg of fluoride per child per day.[7–9] Some of the researchers conducted studies to determine the fluoride concentration in dental products. Kumar and Yadav (2014) estimated the fluoride concentration in toothpastes and tooth powder available in the market of Rampur district, Uttar Pradesh, India.[10] The water-soluble fluorides in the toothpastes were found to vary from 20 to 1100 mg/kg and those in tooth powders ranged from 9.11 to 22.11 mg/kg.[10] Yadav et al. (2007) collected 15 samples of toothpaste and determined the fluoride concentration present in them.[11] It was found that one gram of toothpaste contributes approximately 53.5–338.5 μg of fluoride to the human body with a mean value of 183.78 μg.[11]

6.4.2 Fluoride from Food and Beverage

Fluorides may find their way into the human body through diet. Generally, food contains low levels of fluoride, though a trace amount of fluoride may be present in all foodstuffs. However, fluoride may be present in higher amounts in the food grown in areas where soils contain higher amounts of fluorides or where phosphate fertilizers are used for agricultural purposes. Tea and some seafood are reported to have very high levels of fluoride. A summary of various studies in which the levels of fluoride in foods have been assessed is presented in Table 6.1.

The concentration of fluoride in food items mainly depends on the nature of soil and the quality of water used for irrigation; thus, it varies from place to place. Several studies were conducted in the past to determine the intake of fluoride through the food items. Most of the studies suggested that the concentration of the fluoride in the raw food items is the function of the fluoride content in the water that is used for irrigation. Some of the studies related to the fluoride concentration in Indian food items with reference to the Indian context are interesting.

Rao and Mahajan (1990) conducted a survey in 41 villages of Anantapur district, Andhra Pradesh, India, to determine the fluoride concentration in 98 different food items.[33] In this area, a fluoride concentration up to 4.5 mg/kg was reported in irrigation water and this fluoride finds its way into most of the food items that are grown in this area. It was estimated that 32 locally grown food items generally had a fluoride concentration ranging from 0.2 to 11.0 mg/kg. The TF intake from both food and drinking water was found to be in the range of 2.2–7.3 mg/d (0.05–0.32 mg/d/kg body weight): Food contributes a large fraction to TF intake, ranging from 1.3 to 3.4 mg/d.[33] Gautam et al. (2010) estimated the concentration of fluoride in the food items collected from Nawa tehsil in Nagaur district of Rajasthan.[34] The fluoride content in water was found to be in the range of 0.92–14.62 mg/L. Leafy vegetables grown in fluoride endemic areas were found to be the most susceptible to fluoride and they contained fluoride in the range of 8.08–25.70 mg/kg. Fluoride concentrations in cereal crops were also high (ranging from 1.88 to 18.98 mg/g).[34] Bhargava and Bhardwaj (2009) conducted a study in 10 endemic villages of north-east Rajasthan to determine the fluoride levels in different local food items.[35] Food items such as vegetables, cereals, fodder, and milk were collected from the fluoride endemic villages and analyzed for fluoride content. It was reported

TABLE 6.1

Fluoride Concentration in Different Foodstuffs

Type of Food	Test Insights	Fluoride Concentration (mg/kg)[a]	Study Area	References
Milk and milk products	30 samples of milk and milk products	0.23–1.36	Connersville and the Richmond community, Indiana (USA)	Jackson et al.[12]
	42 different types and brands of milk	0.007–0.068	Houston, Texas, USA	Liu et al.[13]
	66 cow milk samples	0.043–0.147	Dindigul district, Tamil Nadu, India	Amalraj and Pius[14]
	Pasteurized milk supplied to households	0.143–0.157	United kingdom (non-fluoridated area)	Duff[15]
	Untreated milk samples	0.162–0.173	United kingdom (where the farm water supply was fluoridated at 1 mg/L level)	Duff[15]
	68 samples of market milk	0.007–0.086	Canada	Dabeka and McKenzie[16]
	Chocolate-flavored milk for infant	0.05–1.27	Bauru municipality, Brazil	Buzalaf et al.[17]
	Soy beverages for infant	0.09–0.29	Bauru municipality, Brazil	Buzalaf et al.[17]
Meat and poultry	Mechanically separated chicken and turkey	0.08–8.63	Corvallis, Oregon, USA	Fein and Cerklewski[18]
	9 kinds of deboned poultry meat	0.3–2.7	Poland	Jedra et al.[19]
	55 samples of meat and poultry	0.03–1.41	Connersville and the Richmond community, Indiana (USA)	Jackson et al.[12]
	25 ready to eat samples of meats and chicken for infant	0.01–8.38	Iowa City, Iowa	Heilman et al.[20]
Fish	Range of fluoride levels in skeletal bone of saltwater fish	45–1207	–	Camargo[21]

(*Continued*)

TABLE 6.1 (***Continued***)

Fluoride Concentration in Different Foodstuffs

Type of Food	Test Insights	Fluoride Concentration (mg/kg)[a]	Study Area	References
	Range of fluoride levels in muscle of saltwater fish.	1.3–26	–	Camargo[21]
	Different variety of fishes samples included in the Valencian Community Total Diet Study	2.10–11.10	Spain	Rocha et al.[22]
	3 different species of fish (The fluoride concentration in the water samples from where fishes were caught were in the range of 0.035–0.051 mg/L)	2.35–274.29	Alappuzha district, Kerala, India	Thomas and James[23]
Baked goods and cereals	129 samples of uncooked grain products	0.07–1.36	Connersville and the Richmond community, Indiana (USA)	Jackson et al.[12]
	528 staple food grain samples	1.16–4.94	Dindigul district, Tamil Nadu, India	Amalraj and Pius[14]
	66 cooked rice samples	0.34–0.73	Dindigul district, Tamil Nadu, India	Amalraj and Pius[14]
	Rice samples included in the Valencian Community Total Diet Study	2.20	Spain	Rocha et al.[22]
	9 ready to eat samples of cereals for infant	0.01–0.31	Iowa City, Iowa	Heilman et al.[20]
	Cereals for infant	0.20–7.84	Bauru municipality, Brazil	Buzalaf et al.[17]
	Biscuits for infant	0.34–13.68	Bauru municipality, Brazil	Buzalaf et al.[17]

(*Continued*)

TABLE 6.1 (***Continued***)

Fluoride Concentration in Different Foodstuffs

Type of Food	Test Insights	Fluoride Concentration (mg/kg)[a]	Study Area	References
Vegetables	65 samples of vegetables	0.38–5.37	Warsaw market, Poland	Sawilska-Rautenstrauch et al.[24]
	660 green leafy vegetable samples	0.58–7.68	Dindigul district, Tamil Nadu, India	Amalraj and Pius[14]
	Samples of various vegetable included in the Valencian Community Total Diet Study	0.74–4.76	Spain	Rocha et al.[22]
	48 ready to eat samples of vegetables for infant	0.01–0.42	Iowa City, Iowa	Heilman et al.[20]
	78 samples of uncooked vegetables	0.003–1.930	Connersville and the Richmond community, Indiana (USA)	Jackson et al.[12]
Fruits and fruit juices	Different fruit juice samples	0.07–0.53	Davangere city, India	Thippeswamy et al.[25]
	105 juice samples	0.67	Mexico City, Mexico	Jimenez-Farfan et al.[26]
	88 ready to eat samples of fruits and desserts for infant	0.01–0.49	Iowa City, Iowa	Heilman et al.[20]
	26 samples of fruits	0.01–0.84	Connersville and the Richmond community, Indiana (USA)	Jackson et al.[12]
Fats and oils	14 samples of fats and oils	0.05–0.62	Connersville and the Richmond community, Indiana (USA)	Jackson et al.[12]
Sugars and candies	15 samples of sugar and sweets	0.07–0.60	Connersville and the Richmond community, Indiana (USA)	Jackson et al.[12]
Beverages	32 samples of beverages	0.04–0.93	Connersville and the Richmond community, Indiana (USA)	Jackson et al.[12]

(*Continued*)

TABLE 6.1 (*Continued*)

Fluoride Concentration in Different Foodstuffs

Type of Food	Test Insights	Fluoride Concentration (mg/kg)[a]	Study Area	References
	12 different carbonated soft drinks	0.19–0.42	Davangere city, India.	Thippeswamy et al.[25]
	57 carbonated drinks	0.43	Mexico City, Mexico	Jimenez-Farfan et al.[26]
	332 soft drinks samples	0.02–1.28	Iowa, USA	Heilman et al.[27]
Tea	6 different kind of tea	1.97–8.64	Taiwan	Lung et al.[28]
	Different types of tea products	170–878	China	Wong et al.[29]
Bottled drinking water	10 different types of bottled drinking water	0.06–1.05	Davangere city, India	Thippeswamy et al.[25]
	20 types of bottled waters	0.21	Mexico City, Mexico	Jimenez-Farfan et al.[26]
	10 types of bottled waters recommended for use by infants and young children	0.08–0.30	Poland	Opydo-szymaczek and Opydo[30]
	15 randomly selected commercial brands (12 local brands + 3 imported brands) of bottled water	0.5–0.83	Riyadh, Saudi Arabia.	Aldrees and Al-Manea[31]
	29 commercially available brands of bottled waters	0.19–1.07	Algeria	Bengharez et al.[32]

[a] For liquid items, concentrations are in mg/L.

that the fluoride concentrations in vegetables and cereals varied, respectively, from 3.91 to 29.15 mg/kg and 0.45 to 5.98 mg/kg. Fluoride content in milk samples was found to be in the range of 0.37–6.85 mg/L. Results suggested that along with drinking water, food items, and milk also contribute to the TF intake.[35] Raghavachari et al. (2008) conducted a study on the fluoride concentration present in the food items available at Palamau district of Jharkhand, where food is grown with irrigation water that has a fluoride concentration 0.10–12.30 mg/L.[36] The fluoride content of cereals and pulses ranges from 1.5 to 1.78 mg/kg and from 1.46 to 2.28 mg/kg, respectively. The concentration of fluoride in vegetables is very low (0.14–0.23 mg/kg) compared with that of cereals and pulses. Fluoride intake through food items alone was found to be between 0.97 and 1.23 mg/capita/day.[36] Ramteke et al. (2007) performed a study on the fluoride concentration in commonly used food items such as rice, corn, wheat, and lentils (dal) in Dhar and Jhabua districts of Madhya Pradesh.[37] It was found that the fluoride concentrations in rice, corn, wheat, and lentils (dal) were in the ranges of 0.51–5.52, 10.2–40, 0.75–9.02, and 1.1–13.42 mg/kg, respectively. The TF consumption was in the range of 10.7–21.21 mg/capita/person. The maximum consumption of fluoride was 21.21 mg/day in the age group of 31–45 years.[37] Yadav et al. (2012) investigated fluoride concentration in one crop (wheat) and two vegetables (potato and tomato) that were collected from seven villages of Dausa district in Rajasthan, India.[38] The fluoride concentration in groundwater samples obtained from hand pumps and open wells of these seven villages was found to vary from 5.1 to 14.7 mg/L. The fluoride accumulation in crop (wheat) ranged from 3.24 to 14.3 mg/kg, and the fluoride content in vegetables ranged from 1.10 to 4.60 mg/kg.[38]

6.4.3 Fluoride in Soil

Fluorine concentration in soil generally varies between 150 and 400 mg/L. Soils that are derived from rocks with a high fluorine content or that are affected by anthropogenic sources contain a very high concentration (1000 g/kg) of fluorine.[39] Fluoride mobility in soil is highly dependent on the sorption capacity of the soil and varies with pH, types of sorbents, and soil salinity.[40] This is because the fluoride concentration in the soil differs from place to place. Jha (2012) studied the distribution of the fluoride in the soils of Indo-Gangetic plains.[41] The fluoride distribution in soil profiles and surface soil (0–15 cm) samples were analyzed. Results demonstrated that the TF in the profiles varied from 248 to 786 mg/kg. The $CaCl_2$ extractable soluble fluoride (FCa) was found to be in the range of 1.68–99.1 mgF/kg soil. While in surface soils, the TF and FCa ranged from 118 to 436 mg/kg and from 1.01 to 5.05 mg/kg, respectively.[41] Mishra et al. (2009) conducted an experiment to measure the effect of fluoride emission from an aluminum smelter located at Hirakud in western Orissa on the environment.[42] The study was carried out in a radius of 5 km from the plant. It was found that the concentration of fluoride in soil varied from 88.30 to 191.20 mg/L.[42] Jha et al. (2008) estimated the fluoride concentration in the soil in the vicinity of a brick field in the suburb of Lucknow, India.[43] It was observed that the water-soluble fluoride in the surface soil varied from 0.59 to 2.74 mg/L, and the $CaCl_2$ extractable fluoride ranged from 0.69 to 3.18 mg/L. The mean TF concentration in surface soil varied from 322 to 456 mg/kg.[43] Chaudhary et al. (2009) determined the fluoride concentration in the soil samples from 60 village sites in the Indira Gandhi, Bhakra, and Ganga canal catchment areas of north-west Rajasthan, India.[44] Results suggested that the mean water-extractable soil fluoride concentrations varied from 0.50 to 3.00 mg/L. It was concluded that the heavy use of diammonium phosphate (DAP) fertilizer is a possible source of elevated fluoride in the soil of that area.[44] Anbuvel et al. (2014) studied the accumulation of fluoride in the soil of eight villages near the bank of Thovalai Channel in Kanyakumari district, Tamilnadu.[45] The result showed that the fluoride content of the soil varied from 1.0 to 3.2 mg/L. Since this area is free from industrial activity, the heavy use of phosphate fertilizers over long periods may be the reason for the increased concentrations of fluoride in the soil.[45]

6.4.4 Fluoride in Tobacco and Pan Masala

In India, a large number of people are addicted to tobacco and pan masala. While calculating the TF intake, generally these items are not taken into consideration. Generally, tobacco and pan masala are not swallowed, only some fraction of them is ingested during their consumption, which ultimately becomes available to the body for absorption along with sublingually absorbed fluoride. Therefore, these items should be considered while calculating the TF intake by a human body. The exposure of fluoride through pan masala and tobacco differs from person to person depending on their consumption habits. Yadav et al. (2007) estimated the fluoride content in tobacco and pan masala that are available in the local market of Delhi.[46] They investigated 8 samples of tobacco and 15 samples of pan masala (7 without tobacco and 8 with tobacco). It was found that the fluoride content varied from 28.0 to 113.0 mg/kg for tobacco. In the case of pan masala without tobacco, the fluoride content varied between 23.5 and 185.0 mg/kg, whereas for pan masala with tobacco, it was between 16.5 and 306.5 mg/kg. Fluoride ingestion would be different depending on the intake habits of various people.[46] Kumar and Yadav (2014) estimated the levels of fluoride content in pan masala, chewing tobacco, and betel nuts in the rural and urban areas of Rampur district, Uttar Pradesh, India.[47] Water soluble fluoride content ranged from 23.50 to 42.50 mg/kg in pan masala. In case of chewing tobacco, water-soluble fluoride ranged from 18.10 to 40.00 mg/kg. Water-soluble fluoride in supari (betel nut) was found to be in the range of 8.8–76.50 mg/kg. The intake of two to four sachets of pan masala and chewing tobacco by a person would yield between 0.18 and 1.20 mg and between 0.40 and 1.20 mg of fluoride per day, in addition to the fluoride ingested from food and liquids.[47]

6.4.5 Fluoride from Occupational Exposure

Fluoride is a common pollutant in the industrial workspace. Workers in many heavy industries such as aluminum, fertilizer, iron, oil refining, semiconductor, and steel may be routinely exposed to high levels of fluoride. Fluoride is also used in the welding process; therefore, welders are also commonly exposed to airborne fluorides. As per current U.S. regulations, industries can have fluorides up to 2.5 mg/m^3 in the workspace air, which produces a fluoride intake of 16.8 mg/day for an 8-h working day. A long-term air-monitoring study[48] demonstrated that the fluorine concentration in the air all around the workplace of a small-scale enamel enterprise was in the range of 0.1–3.7 mg/m^3. In the United States, the fluoride concentration in the aluminum production industries for exposed workers was reported to be 1.25 mg/m^3. The average concentration of particulate fluorides was measured as 1.024 mg/m^3, whereas gaseous fluoride (HF) had a mean level[49] of 0.22 mg/m^3. In Sweden, the average TF exposure of the workers in an aluminum plant was calculated as 0.91 mg/m^3, of which 34% (approximately 0.31 mg/m^3) was gaseous fluoride.[50] Electronic industry workers in Japan, where hydrogen fluoride is used for glass etching of TV picture tubes and as a silicon cleaner for semiconductors, are exposed to a daily average concentration of up to 5 mg/L of air hydrogen fluoride.[51] It was reported[52] that the workers in the pot room of an aluminum smelter in British Columbia, Canada, were exposed to an average total airborne fluoride concentration of approximately 0.48 mg/m^3. In Netherlands, the concentrations of fluoride range in the workroom air of welding machine shops and shipyards were reported[2] to be 30–16,500 μg/m^3. From 1981 to 1983, the National Institute for Occupational Safety and Health (NIOSH) conducted the National Occupational Exposure Survey (NOES), which collected data on the effect of occupational exposure of chemical, physical, and biological agents on the workers. The NOES estimated that about 182,589 workers were affected by inhalation of hydrogen fluoride.[53]

As pointed out earlier, large numbers of workers are getting exposed to toxic chemicals while working in industrial areas. Workers in many heavy industries such as aluminum, fertilizer, iron, oil refining, semiconductor, and steel may be routinely exposed to high levels of fluoride. Arshad and Shanavas (2013) studied the effect of fluoride exposure on workers in the fertilizer industry and the wood industry in Mangalore city, India.[54] They investigated the fluoride concentration in the serum and urine of the 34 workers from the fertilizer industry and the 55 workers from the wood industry. Urinary fluoride and serum fluoride levels are valid biomarkers for estimating the levels of occupational exposure to fluoride. The fluoride concentrations in the serum and the urine of the workers employed in the fertilizer industry were 0.077 ± 0.027 and 3.85 ± 1.66 mg/L, respectively. The workers in the wood industry had fluoride concentrations of 0.037 ± 0.009 and 0.97±0.37 mg/L in their serum and urine, respectively. The study concluded that the phosphate fertilizer workers in India are at a high risk of exposure to excessive amounts of fluoride.[54] Sharma et al. (1991) conducted a study to investigate the effect of fluoride in a factory manufacturing inorganic fluoride compounds.[55] The preshift and postshift urinary fluoride levels of workers were estimated. The preshift urinary fluoride levels ranged from 0.5 to 4.54 mg/L and the postshift levels ranged from 0.5 to 13.00 mg/L. The preshift and postshift urinary fluoride concentration depends on the nature of work and the category of workers in each department.[55] Susheela et al. (2013) performed a study on the effect of fluoride exposure on the workers in one of the largest primary aluminum-producing industries located in the north-eastern part of the state of Uttar Pradesh, India.[56] It was observed that smelter workers had a significantly higher fluoride concentration in their urine and serum than non-smelter workers; in addition, the nail fluoride content was higher in smelter workers than in nonsmelter workers. These studies clearly demonstrate that industrial emission of fluoride is a major source of fluoride exposure.[56]

6.4.6 TF Exposure

As discussed in Sections 6.4.1 through 6.4.5, the TF exposure is influenced by different sources and several factors. The factors that affect the fluoride concentration in foodstuffs include fluoride emission sources in the local area, amount of fertilizers and pesticides applied in agricultural activities, and use of fluoridated water in the preparation of food and so forth.[57] The fluoride concentration in the ambient air is influenced by several factors such as nature and type of the industrial sources in the area, the distance from the fluoride sources, the prevailing meteorological conditions and the geological features of the area defined by its topography.[58] The fluoride concentration in water depends on many factors such as the local geological features and proximity to emission sources, mineral constitution of the aquifers, seepage from nearby saline formations, low recharge and dilution rates in the aquifers, peculiarities of the local soil or rock formations, and so forth.[59] However, many scientific studies suggest that the total daily fluoride exposure in a temperate climate when no fluoride is added to the drinking water is approximately equal to 0.6 mg/adult/day; whereas it is around 2 mg/adult/day in a fluoridated area.[60] A range of estimated fluoride intakes as a consequence of exposure to a number of different sources is given in Table 6.2.

6.5 Effects of Fluoride on Laboratory Animals and In Vitro Systems

Considerable research was undertaken to determine the effect of fluoride in laboratory animals. Effects on the skeleton, organs, and tissues have been observed in a variety of studies conducted in rats and rabbits. Both short-term and long-term effects of fluoride exposure for low doses and high doses were investigated by a number of researchers. Some of the studies related to fluoride exposure on laboratory animals are listed in Table 6.3.

TABLE 6.2
Fluoride intake from different sources

Sources of Fluoride Exposure	Age Group of Exposure	Estimated Fluoride Intake, mg/day (mg/kg Body Weight per day)a	Test Insights	Study Area	References
Foodstuffs	Children aged 1–4 years	(0.05)	457 whole-day meals	Poland	Jedra et al.[61]
Toothpaste and diet	1- to 3-year old children	(0.130)	Fluoride intake from diet was measured by the duplicate plate method, and fluoride ingested from dentifrice was determined by subtracting the amount of fluoride recovered after brushing from the amount originally placed onto the child's toothbrush. Samples were carried out by analyzing 33 children.	Brazil	de Almedia et al.[62]
Food group (Grain products, Vegetables, Fruits, Milk products, Meat and poultry , Nuts and seeds, Fats and oils, Sugars and sweets, and Beverages)	3–5 years	0.454	Estimated mean daily fluoride ingestion	Connersville community (Indiana, USA) having water fluoride concentration of 0.16±0.01 mg/L	Jackson et al.[12]
	3–5 years	0.535	Estimated mean daily fluoride ingestion	Richmond community (Indiana, USA), an optimally fluoridated area having water fluoride concentration of 0.90±0.05 mg/L	Jackson et al.[12]
Commercial food for Infant	Infants, 3–8 months	(0.023–0.029)	Estimated mean daily fluoride intake of infants from food	Japan	Tomori et al.[63]
Total diet samples, including drinking water and beverages	Slovenian military personnel	(0.010–0.035)	Range of fluoride intake was calculated by assuming the mean weight of Slovenian military personnel as 70 kg. The amount of fluoride was determined in 20 lyophilized total diet samples obtained from the Slovenian Military.	Slovenia	Ponikvar et al.[64] Vaidya et al.[65]

(*Continued*)

TABLE 6.2 (***Continued***)

Fluoride intake from different sources

Sources of Fluoride Exposure	Age Group of Exposure	Estimated Fluoride Intake, mg/day (mg/kg Body Weight per day)[a]	Test Insights	Study Area	References
Food Diet, Liquid included water, milk, ready-made beverages and beverages made at home (diluted powder and concentrated fruit juice, etc., and a beverage of tea leaves and wheat ears with tap water).	2–5 years (Moderate fluoride area)	(0.0252)	Estimated the mean concentration of fluoride from the diet ingested by children of two age groups susceptible to dental fluorosis	Two areas of Japan (Moderate fluoride area having mean water fluoride concentration of 0.555 mg/L and relatively low fluoride area having fluoride concentration in the community water in the range of 0.040–0.131 mg/L)	Nohno et al.[66]
	2–5 years (Relatively low fluoride area)	(0.0126)			
	6–8 years (Moderate fluoride area)	(0.0254)			
	6–8 years (Relatively low fluoride area)	(0.0144)			
Solids food, water and other beverages	2–6 years	(0.017)	Mean fluoride intake from food items	Nonfluoridated area of Brazil	Levy et al.[67]
All drinks (Water, Tea, Milk, Soft drink) All foods (Fruit, Vegetable, Soup and gravy, Rice, Bread)	4-year-old children (First area)	0.413	Dietary fluoride intake in children residing in low, medium and high fluoride areas. (The mean fluoride concentrations in drinking water in the three areas were 0.3, 0.6 and 4.0 mg F/L.)	Iran	Zohouri and Rugg-Gunn.[68]
	4-year-old children (Second area)	0.698			
	4-year-old children (Third area)	3.472			
Food (Enjera, homemade bread, kale stew, potato stew, shiro stew, fish stew), beverage (including tea, coffee), and water (used for drinking and cooking).	Adults (Village A)	10.5	Daily dietary fluoride intake by adults from three rural villages of the Ethiopian Rift Valley (Village A uses water with 1.0 mg/L fluoride, village B uses water with 3.0 mg/L fluoride, and village C uses water with 11.5 mg/L fluoride both for food preparation and for drinking)	Ethiopia	Dessalegne et al.[69]
	Adults (Village B)	16.6			
	Adults (Village C)	35.3			

[a] Data in parentheses are the estimated intakes of fluoride, expressed as mg/kg body weight per day, when presented in the reference cited.

TABLE 6.3

Effect of Fluoride Exposure on Laboratory Animals

Laboratory Animal/In Vitro System	Fluoride Dose and Exposure Time	Affected Organ/System	Toxicological Issues	References
Female Wistar mice	226 mg/L fluoride ion in drinking water from day 15 of pregnancy until day 14 after delivery	Liver	Ingestion of a high amount of fluoride through drinking water may lead to impaired liver function.	Bouaziz et al.[70]
Adult female mice of Swiss Albinos strain	226 mg/L fluoride ion in drinking water from day 15 of pregnancy until day 14 after delivery	Brain	Fluoride intoxication in the early stage of life interfered with brain physiology and induced neurotoxicity in mice.	Bouaziz et al.[71]
Wistar rats	5, 15 or 50 mg/L of fluoride in drinking water over 60 days	Liver and kidney	Exposure fluoride doses (15 and 50 mg/L) caused alterations in the antioxidant system of liver and kidney of rats. However, exposure to 5 mg/L of a fluoride dose causes few changes in the parameters.	Iano et al.[72]
Rats with surgically induced renal deficiency	5, 15 or 50 mg/L of fluoride in drinking water for a period of 6 months	Bones	Fluoridated water of concentrations of 15 and 50 mg/L caused osteomalacia and reduced bone strength in rats, whereas water with a low to moderate fluoride concentration (0 and 5 mg/L) affected neither bone mineralization nor strength in rats.	Turner et al.[73]
Mature female rats	100 and 150 mg/L of fluoride in drinking water for 90 days	Vertebral bone	Fluoridated water causes an increase in bone mass while simultaneously causing a decrease in bone strength/quality, thereby suggesting the negative effect of fluoride on bone quality.	Sogaard et al.[74]

(Continued)

TABLE 6.3 (*Continued*)

Effect of Fluoride Exposure on Laboratory Animals

Laboratory Animal/In Vitro System	Fluoride Dose and Exposure Time	Affected Organ/ System	Toxicological Issues	References
Rats	25 mg/L of fluoride/rat/day for 8 and 16 weeks	Tissue	Drinking of water containing high fluoride may result in tissue damage and other secondary complications.	Shanthakumari et al.[75]
Male Long–Evans rats	0.33 and 0.95 mg/L of fluorine ion in drinking water for 52 weeks	Nervous system	Chronic administration of fluorine in the form of AlF_3 and NaF in the drinking water of rats caused distinct morphological alterations in the brain, including effects on neurons and cerebrovasculature, and may cause injury to the brain.	Varner et al.[76]
Rabbits	Drinking water with fluoride concentrations of 50 and 100 mg/L for 5 months	Blood	Excessive ingestion of fat and fluoride can cause an oxidative stress reaction and increase serum lipid levels either separately or synergistically, which leads to hypercholesterolemia in the experimental rabbits.	Sun et al.[77]
Male Kunming mice	Drinking water with fluoride concentrations of 11, 22, and 45 mg/L and food with 8.40 mg/kg for 180 days	Nervous system	Chronic exposure of fluoride may impair the long-term recognition memory of male mice, enhance the excitement of mice, and upregulate VAMP-2 mRNA expression, all of which are involved in object recognition memory of the nervous system.	Han et al.[78]
Male albino rats	2 mg of sodium fluoride in 1 ml of distilled water per 100 g body weight per day for 29 days	Reproductive system	Fluoride exposure may cause an adverse effect on the reproductive system.	Ghosh et al.[79]

6.6 Effect of Fluoride on Aquatic Organisms

Industrial applications such as phosphate processing, aluminum smelting, steel manufacturing, and glasses frosting are capable of producing an effluent with a high concentration of fluoride. These high fluoride effluents may find their way to the nearby water bodies, thereby causing damage to the aquatic animals and plants. Several researchers gathered information on the effect of fluoride on aquatic organisms. Mishra and Mohapatra (1998) performed a study to measure the fluoride concentration in bones and to monitor the haematological characteristics (RBC, haemoglobin, haematocrit, mean corpuscular haemoglobin, and mean corpuscular volume) in amphibians, *Bufo melanostictus*, collected from fluoride-contaminated and -uncontaminated areas of the Hirakud Smelter Plant, Hirakud, India.[80] The average haemoglobin content, total RBC count and haematocrit in blood samples were significantly reduced, whereas the mean corpuscular concentration and volume were found to significantly increase with respect to the toads at an uncontaminated site. The average fluoride concentration in bones was 2736 mg/kg at the contaminated site, which was 11 times greater than the fluoride concentration in bones of toads from the contaminated areas (241 mg/kg).[80] Hemens and Warwick (1972) performed experiments to determine the short-term and long-term effects of fluoride on fish and prawns in an estuary in Zululand, South Africa.[81] No toxic effects of fluoride were noticed on the species of fish and prawns during their exposure to fluoride up to 100 mg/L for 96 h (short-term exposure). The brown mussel *Pernaperna* showed evidence of toxic effects after the fifth day of fluoride exposure at a concentration of 7.2 mg/L. Long-term (72 days) exposure of fluoride at a concentration of 52 mg/L was performed in recirculated outdoor laboratory estuary models without providing external food and with 20% salinity. Results of long-term exposure showed physical deterioration and an increase in mortality in the mullet *Mugil cephalus* and the crab *Tylodiplax blephariskios*. The reproductive processes of the shrimp *Palaemon pacificus* were found to be adversely affected due to the long-term exposure of fluoride.[81] Johnstone et al. (1982) conducted an experiment to determine the effect of exposure of cryolite recovery sludge (CRS, an aluminum smelter waste dumped at sea) filtrate, which also contains fluoride on salmon fish.[82] The effects of exposure of salmon on CRS filtrate (for up to 1 h) were monitored. It was observed that Atlantic salmon exposed to aluminum smelter waste (including fluoride) experienced an increase in oxygen consumption and ventilation rates and a decrease in heart rate.[82] Shi et al. (2009) carried out an experiment to determine the accumulation of fluoride ion in juvenile sturgeon fish.[83] In a growth trial of 90 days, fishes were exposed to concentrations of 4, 10, 25 and 62.5 mg/L of F (added as NaF), along with a control group. Results indicated that there was a significant inhibition of growth for groups exposed to high fluoride concentrations (10, 25 and 62.5 mg/L) compared with the control group. Shi et al. also observed that exposure of fluoride to a concentration of 25 mg/L or more may cause alterations in the fishes' respiration and violent erratic movements.[83]

6.7 Effect of Fluoride on Plants

Fluoride can enter into plants mainly through two pathways: aerial deposition of gaseous fluoride through stomatal diffusion and passive diffusion through soil and water into the plant roots. Fluoride in the form of gas enters into the stomata of the leaf by diffusion. Initially, it accumulates in the stomata from where it moves toward the tip and the margin, causing injury to the leaf. The injury symptoms are produced only when a critical level of fluoride is attained.[84] Fluoride as particulate falls on the leaf from the polluted atmosphere and gets deposited on the surface of the leaf. Subsequently, these deposited fluorides on the surface penetrate into the leaf and destroy it.[85] The symptoms observed in plants due to the exposure to hydrogen fluoride depend on a number of factors such as the concentration of HF, time of exposure, type and age of plant, temperature, type of light and intensity, composition and rate of circulation of air. When exposed to high concentrations of HF gas for sufficient time under controlled environmental conditions, the plants that are sensitive to the HF may produce one or more of the following effects: slight paling of normal green pigment at the tips or margins of the leaf that may spread to other portions of the leaf; a pale green area at the margins that may gradually turn into a light buff color and finally, a reddish brown. All these stated effects of fluoride influence the photosynthesis and respiration process of plants. The exact mechanism of injury to plants by fluorides is unknown. It has been postulated that they interfere with the functioning of certain enzymes such as enolase.[86] Fluoride can enter into the plant system through the soil; it may also be deposited into the soil from several anthropogenic sources from where it gets accumulated in the plant through roots. The accumulation of fluoride from the soil is generally very small, and there is a limited relationship between concentrations in plants and the total content in soils.[87] Plants absorb fluoride from the soil by their roots, and this gets transported to the transpiratory organs of the plant (mainly the leaves) via xylematic flow. This transported fluoride from the soil can accumulate in the leaves where it can cause adverse effects such as tip burning and even plant death by affecting the photosynthesis and transpiration process.[88,89] A lot of research was undertaken to determine the effect of fluoride on different types of plants and tree species.

Kessabi et al. (1984) performed a study to determine the effect of fluorine emission from the factories processing natural phosphate on plants and animals of south Safi zone (Morocco).[90] These factories were 10 km south of Safi.

Results revealed that the concentrations of fluoride were 4–10 times higher in contaminated plants than in noncontaminated plants. In a certain study area, the effect of fluoride pollution is so high and noticeable that grain crops and vegetables are no longer grown there. In some areas, 30% of the grain corps showed burn signs at the tips of leaves and their yield was reduced. In trees, many fruits either fail or are necrosed. But even in the most contaminated zones, the grasses were unaffected.[90] Zouari et al. (2014) carried out a pot experiment to investigate the uptake, accumulation, and toxicity effects of fluoride in olive trees that were grown in a soil spiked with inorganic fluoride in the form of sodium fluoride.[91] NaF was applied through irrigating water in six different groups of olive with six different concentrations (0, 20, 40, 60, 80 and 100 mM NaF). Symptoms due to fluoride toxicity such as leaf necrosis and leaf drop appeared only in highly spiked soils (80 and 100 mM NaF). It was also reported that a significant reduction of biomass took place in roots, shoots, and leaves of olive plants that are exposed to 60, 80 and 100 mM NaF in comparison to the control plants. But the biomass reduction was not significant for both 20 and 40 mM NaF treated soil.[91] Singh and Verma (2013) performed an experiment to examine the influence of fluoride-contaminated irrigation water having a concentration of fluoride from 100 to 500 mg/L on poplar seedlings (*Populus deltoides* L. clone-S_7C_{15}).[92] Results indicated that the exposure of the poplar seedlings to 100, 200 and 500 mg/L of fluoride in the irrigation water for six weeks decreases the physiological characteristics (growth, leaf expansion, photosynthetic CO_2 assimilation, stomatal conductance, chlorophyll fluorescence yield, and plant biomass). Intervein chlorosis and leaf-margin necrosis followed by leaf curl were observed even in the younger leaves after the exposure of the seedling to irrigation water containing 500 mg/L of fluoride for six weeks. It was also observed that continuous and prolonged exposure of fluoride-contaminated water results in falling of the leaves.[92]

6.8 Effect of Fluoride on Animals

Excessive fluoride injections can affect animals. The impact of fluoride depends on a number of factors such as dosage or amount of intake, rate of intake, period of administration, and the presence of interfering substances. Fluoride effects on animals also depend on the physical parameters of the animal, such as age, state of health, and sensitivity. Young animals are generally more susceptible to harmful effects of fluoride than older ones. Healthy animals have more resistance to the harmful effects of fluoride than sick or inadequately nourished animals.[86] The intake of fluoride in an excessive quantity than required by the animal body can either induce acute toxicosis or cause chronic intoxication depending on the concentration of fluoride and the time of exposure of the animals. The symptom that arises in the animals when they inhale large quantities of fluoride (several grams) in a very short interval of time (few minutes or hours) is termed *acute symptom*. The symptoms that usually arise due to acute toxicosis are an immediate decrease in appetite, high fluoride content in animals' blood and urine, rapid loss of weight, reduced milk production, weakness, excessive salivation, perspiration, dyspnea, and weakened pulse.[93] Animals grazing on fluoride-affected plants may develop fluorosis, characterized by damage to the musculoskeletal system, including difficulty in mastication, softening of the teeth, painful gait, and lameness. Fluorosis occurs in animals grazing in fields near brickworks, aluminum smelters, and phosphate fertilizer factories.

6.9 Guidelines Values and Standards

The WHO guidelines on fluoride in drinking water stipulate that less than 1 mg/L may give rise to dental fluorosis in some children, and much higher concentrations (>1.5 mg/L) may eventually result in skeletal damage in both children and adults. So, in order to prevent dental caries, a large number of communities supply water with a fluoride concentration that is equal to approximately 1.0 mg/L. The 1971 International Standards recommended control limits for fluorides in drinking water for various ranges of the annual average of maximum daily air temperatures. This limit ranges from 0.6 to 0.8 mg/L for a temperature range of 26.3–32.6°C and from 0.9 to 1.7 mg/L for a temperature range of 10–12°C. In the first edition of the *Guidelines for Drinking Water Quality*, published in 1984, a guideline value of 1.5 mg/L was recommended by the WHO for fluoride, as mottling of teeth has been reported very occasionally at higher levels. It was also noted that this guideline value is not fixed and local application must take consideration of local climatic conditions, diet, and water consumption. The 1993 WHO Guidelines concluded that there was no sufficient evidence to suggest that the guideline value of 1.5 mg/L set in 1984 needed to be revised. In some countries, particularly parts of India, Africa, and China, drinking water can contain very high concentrations of naturally occurring fluoride (in excess of the WHO guideline value of 1.5 mg/L). So, it was felt that the guideline value may be difficult to achieve in some circumstances with the treatment technology available. In 1994, the WHO recommended that the optimal concentration of fluoride should be in the range of 0.5–1.0 mg/L and should vary according to climatic conditions, volume of water intake, and intake of fluoride from other sources. Fluoride effects are best predicted by the dose (mg fluoride/kg of body weight/day), the duration of exposure, and other factors such as age. The U.S. National Academy of Sciences Institute of Medicine has recommended an adequate intake of fluoride from all sources as 0.05 mg F/kg body weight/day. This amount exhibits a reduction in the occurrence of dental caries in maximum cases without inducing unwanted side effects, including moderate dental fluorosis.[2,6,94]

6.10 Summary

- Natural processes such as weathering and dissolution of minerals, volcanic eruptions, and marine aerosols are responsible for fluoride release into the environment. Volcanoes are the main natural persistent source of fluorine.
- The transportation, distribution, transformation, and deposition of airborne fluoride are governed by meteorological conditions, particulate size, chemical reactivity, and emission strength of the source.
- The daily fluoride intake of children, expressed in a milligram-per-kilogram body weight basis, may exceed that of adults. It has been found that ingestion of the toothpastes containing fluoride may contribute to 0.50–0.75 mg fluoride per child per day.
- The concentration of the fluoride in the raw food items is the function of fluoride content in the irrigation water.
- Workers in many heavy industries such as aluminum, fertilizer, iron, oil refining, semiconductor, and steel get routinely exposed to high levels of fluoride.
- Urinary fluoride and serum fluoride levels are valid biomarkers for estimating the levels of fluoride due to occupational exposure of fluoride.
- Industrial emission of fluoride is a major source of fluoride exposure.
- Studies on toxicological impacts of fluoride on animals suggest impaired liver function, changes in brain physiology, induced neurotoxicity, alterations in the antioxidant system of liver and kidney, reproductive systems, reduced level of bone quality, tissue damages, morphological alterations and injury to brain, oxidative stress reaction, and so forth.
- Fluoride exposures influence the photosynthesis and respiration process of plants.
- Fluorosis occurs in animals grazing in fields near brickworks, aluminum smelters, and phosphate fertilizer factories.

References

1. Ayoob, S. and Gupta, A.K. (2006). Fluoride in drinking water: A review on the status and stress effects. *Crit. Rev. Environ. Sci. Technol.*, 36, 433–487.
2. WHO. (2002). Environmental Health Criteria 227, Fluorides. Geneva, Switzerland: World Health Organization.
3. Barnard, W.R. and Nordstrom, D.K. (1982). Fluoride in precipitation-II. Implications for the geochemical cycling of fluorine. *Atmos. Environ.*, 16, 105–111.
4. ATSDR. (2003). Report on Toxicological Profile For Fluorides, Hydrogen Fluoride and Fluorine. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry.
5. Cape, J.N., Fowler, D. and Davison, A. (2003). Ecological effects of sulfur dioxide, fluorides, and minor air pollutants: Recent trends and research needs. *Environ. Int.*, 29, 201–211.
6. WHO. (2006). In: Farewell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L. and Magara, Y. (Eds.) Fluoride in Drinking-Water. World Health Organization. London-Seattle: IWA Publishing.
7. Slooff, W., Eevens, H.C., James, J.A. and Rose, J.R.M. (1989). Integrated Criteria Document Fluoride. The Netherlands: National Institute of Public Health and Environment Pollution, Bilthover (Report No. 758474010).
8. Murray J.J. [Ed.] (1986). Appropriate Use of Fluorides for Human Health. Geneva, Switzerland: World Health Organization.
9. Bralić, M., Buljac, M., Prkić, A., Buzuk, M. and Brinić, S. (2015). Determination fluoride in products for oral hygiene using flow-injection (FIA) and continuous analysis (CA) with home-made FISE. *Int. J. Electrochem. Sci.*, 10, 2253–2264.
10. Kumar, R. and Yadav, S.S. (2014). Fluoride content in pan masala, chewing tobacco, betel nuts (supari), toothpaste and tooth-powder items used and consumed in rural and urban parts of Rampur district, Uttar Pradesh, India. *J. Sci. Technol. Manag.*, 2, 38–47.
11. Yadav, A.K., Kaushik, C.P., Haritash, A.K., Singh, B., Raghuvanshi, S.P. and Kansal, A. (2007). Determination of exposure and probable ingestion of fluoride through tea, toothpaste, tobacco and pan masala. *J. Hazard. Mater.*, 142, 77–80.
12. Jackson, R.D., Brizendine, E.J., Kelly, S.A., Hinesley, R., Stookey, G.K. and Dunipace, A.J. (2002). The fluoride content of foods and beverages from negligibly and optimally fluoridated communities. *Community Dent. Oral Epidemiol.*, 30, 382–91.
13. Liu, C., Wyborny, L.E. and Chan, J.T (1995). Fluoride content of dairy milk from supermarket: A possible contributing factor to dental fluorosis. *Int. Soc. Fluoride Res.*, 28, 10–16.
14. Amalraj, A. and Pius, A. (2013). Health risk from fluoride exposure of a population in selected areas of Tamil Nadu South India. *Food Sci. Hum. Wellness*, 2, 75–86.
15. Duff, E.J. (1981). Total and ionic fluoride in milk. *Caries Res.*, 15, 406–408.
16. Dabeka, R.W. and McKenzie, A.D. (1987). Lead, cadmium, and fluoride levels in market milk and infant formulas in Canada. *J. Assoc. Off. Anal. Chem.*, 70, 754–757.

17. Buzalaf, M.A., de Almeida, B.S., Cardoso, V.E., Olympio, K.P. and Furlani, T. de A. (2004). Total and acid-soluble fluoride content of infant cereals, beverages and biscuits from Brazil. *Food Addit. Contam.*, 21, 210–5.
18. Fein, N.J. and Cerklewski, F.L. (2001). Fluoride content of foods made with mechanically separated chicken. *J. Agric. Food Chem.*, 49, 4284–4286.
19. Jedra, M., Urbanek-Karłowska, B., Fonberg-Broczek, M., Sawilska-Rautenstrauch, D. and Badowski, P. (2001). Bioavailable fluoride in poultry deboned meat and meat products. *Rocz. Panstw. Zakl. Hig.*, 52, 225–230.
20. Heilman, J.R., Kiritsy, M.G., Levy, S.M. and Wefel, J.S. (1997). Fluoride concentrations of infant foods. *J. Am. Dent. Assoc.*, 128, 857–863.
21. Camargo, J. (2003). Fluoride toxicity to aquatic organisms: A review. *Chemosphere*, 50, 251–264.
22. Rocha, R.A., Rojas, D., Ruiz, A., Devesa, V. and Ve, D. (2013). Quantification of Fluoride in Food by Microwave Acid Digestion and Fluoride Ion-Selective Electrode. *J. Agric. Food Chem.*, 16, 10708–10713.
23. Thomas, A. and James, R. (2013). Accumulation of Fluoride in *Etroplus Suratensis, Oreochromis Mossambicus and Anabas Testudineus* Caught from the Surface Fresh Water Sources in Alappuzha town, Kerala, India. *Int. J. Innov. Res. Sci. Eng. Technol.*, 2, 2756–2761.
24. Sawilska-Rautenstrauch, D., Jedra, M., Fonberg-Broczek, M., Badowski, P. and Urbanek-Karłowska, B. (1998). Fluorine in vegetables and potatoes from the market in Warsaw. *Rocz. Panstw. Zakl. Hig.*, 49, 341–346.
25. Thippeswamy, H.M., Kumar, N., Anand, S.R., Prashant, G.M. and Chandu, G.N. (2010). Fluoride content in bottled drinking waters, carbonated soft drinks and fruit juices in Davangere city, India. *Indian J. Dent. Res.*, 21, 528–530.
26. Jimenez-Farfan, M.D., Hernandez-Guerrero, J.C., Loyola-Rodriguez, J.P. and Ledesma-Montes, C. (2004). Fluoride content in bottled waters, juices and carbonated soft drinks in Mexico City, Mexico. *Int. J. Paediatr. Dent.*,14, 260–266.
27. Heilman, J.R., Kiritsy, M.C., Levy, S.M. and Wefel, J.S. (1999). Assessing fluoride levels of carbonated soft drinks. *J. Am. Dent. Assoc.*, 130, 1593–1599.
28. Lung, S.C., Cheng, H.W. and Fu, C.B. (2007). Potential exposure and risk of fluoride intakes from tea drinks produced in Taiwan. *J. Expo. Sci. Environ. Epidemiol.*, 18, 158–166.
29. Wong, M., Fung, K. and Carr, H. (2003). Aluminium and fluoride contents of tea, with emphasis on brick tea and their health implications. *Toxicol. Lett.*, 137, 111–120.
30. Opydo-szymaczek, J. and Opydo, J. (2009). Fluoride content of bottled waters recommended for infants and children in Poland. *Res. Rep. Fluoride*, 42, 233–236.
31. Aldrees, A.M. and Al-Manea, S.M. (2010). Fluoride content of bottled drinking waters available in Riyadh, Saudi Arabia. *Saudi Dent. J.*, 22, 189–93.
32. Bengharez, Z., Farch, S., Bendahmane, M., Merine, H. and Benyahia, M. (2012). Evaluation of fluoride bottled water and its incidence in fluoride endemic and non endemic areas. *e-SPEN. J.*, 7, e41–e45.
33. Rao, K.V. and Mahajan, C.L. (1990). Fluoride content of some common South Indian foods and their contribution to fluorosis. *J. Sci. Food. Agric.*, 51, 215–219.
34. Gautam, R., Bhardwaj, N. and Saini, Y. (2010). Fluoride accumulation by vegetables and crops grown in Nawa Tehsil of Nagaur district (Rajasthan, India). *J. Phytol.*, 2, 80–85.

35. Bhargava, D. and Bhardwaj, N. (2009). Study of fluoride contribution through water and food to human population in fluorosis endemic villages of North-Eastern Rajasthan. *Afr. J. Basic Appl. Sci.*, 1, 55–58.
36. Raghavachari, S., Tripathi, R.C. and Bhupathi R.K. (2008). Endemic fluorosis in five villages of the Palamau district, Jharkhand, India. *Fluoride*, 41, 206–211.
37. Ramteke, D. S., Onkar, R., Pakhide, D. and Sahasrabudhe, S. (2007). Assessment of Fluoride in Groundwater, Food and Soil and its Association with Risk to Health. Proceedings of the 10th International Conference on Environmental Science and Technology, Kos Island, Greece.
38. Yadav, R.K., Sharma, S., Bansal, M., Singh, A., Panday, V. and Maheshwari, R. (2012). Effects of fluoride accumulation on growth of vegetables and crops in Dausa district, Rajasthan, India. *Adv. Biores.*, 3, 14–16.
39. Kabata Pendias, A. and Pendias, H. (2001). *Trace Elements in Soils and Plants*, 3rd edn, p. 413. Boca Raton, FL: CRC Press.
40. Cronin, S.J., Manohara, V., Hedley, M.J. and Loganathan, P. (2000). Fluoride: A review of its fate, bioavailability, and risks of fluorosis in grazed-pasture systems in New Zealand. *N. Z. J. Agri. Res.*, 43, 295–321.
41. Jha, S.K. (2012). Geochemical and spatial appraisal of fluoride in the soils of indo-gangetic plains of India using multivariate analysis. *Clean Soil Air Water*, 40, 1392–1400.
42. Mishra, P.C., Meher, K., Bhosagar, D. and Pradhan, K. (2009). Fluoride distribution in different environmental segments at Hirakud Orissa (India). *Sci. Technol.*, 3, 260–264.
43. Jha, S.K., Nayak, A. K., Sharma, Y.K., Mishra, V.K. and Sharma, D.K. (2008). Fluoride accumulation in soil and vegetation in the vicinity of brick fields. *Bull. Environ. Contam. Toxicol.*, 80, 369–373.
44. Chaudhary, V., Sharma, M. and Yadav, B.S. (2009). Elevated fluoride in canal catchment soils of Northwest Rajasthan, India. *Res. Rep. Fluoride*, 42, 46–49.
45. Anbuvel, D., Kumaresan, S. and Margret, R.J. (2014). Flouride analysis of soil in cultivated areas of Thovalai channel in Kanyakumari District, Tamilnadu, India: Correlation with physico-chemical parameters. *Int. J. Basic Appl. Chem. Sci.*, 4, 20–29.
46. Yadav, A.K., Kaushik, C.P., Haritash, A.K., Singh, B., Raghuvanshi, S.P. and Kansal, A. (2007). Determination of exposure and probable ingestion of fluoride through tea, toothpaste, tobacco and pan masala. *J. Hazard. Mater.*, 142, 77–80.
47. Kumar, R. and Yadav, S.S. (2014). Fluoride content in pan masala, chewing tobacco, betel nuts (supari), toothpaste and tooth-powder items used and consumed in rural and urban parts of Rampur District, Uttar Pradesh, India. *J. Sci. Technol. Manag.*, 2, 38–47.
48. Viragh, E., Viragh, H., Laczka, J. and Coldea, V. (2006). Health effects of occupational exposure to fluorine and its compounds in a small-scale enterprise. *Ind. Health*, 44, 64–68.
49. Taiwo, O.A., Sircar, K.D., Slade, M.D., Cantley, L.F., Vegso, S.J., Rabinowitz, P.M., Fiellin, M.G. and Cullen, M.R. (2006). Incidence of asthma among aluminium workers. *J. Occup. Environ. Med.*, 48, 275–282.
50. Ehrnebo, M. and Ekstrand, J. (1986). Occupational fluoride exposure and plasma fluoride levels in man. *Int. Arch. Occup. Environ. Health*, 58, 179–190.

51. Kono, K., Yoshida, Y. and Yamagata, H. (1987). Urinary fluoride monitoring of industrial hydrofluoric acid exposure. *Environ. Res.*, 42, 415–520.
52. Chan-Yeung, M., Wong, R., Earnson, D., Schulzer, M., Subbarao, K., Knickerbocker, J. and Grzybowski, S. (1983). Epidemiological health study of workers in an aluminum smelter in Kitimat, B.C. II. Effects on musculoskeletal and other systems. *Arch. Environ. Health*, 38, 34–40.
53. NIOSH. (1989). National occupational exposure survey (1980–1983). Cincinnati, OH: National Institute for Occupational Safety and Health, Department of Health and Human Services.
54. Arshad, M. and Shanavas, P. (2013). Comparison of serum and urinary fluoride levels among fertilizer and wood industry workers in Mangalore city, India. *Res. Rep. Fluoride*, 46, 80–82.
55. Sharma, Y.K., Kulkarni, P.K., Shah, A.R., Patel, M.D. and Kashyap, S.K. (1991). Occupational exposure to inorganic fluorides. *Indian J. Ind. Med.*, 37, 13–22.
56. Susheela, A.K., Mondal, N.K. and Singh, A. (2013). Exposure to fluoride in smelter workers in a primary aluminum industry in India. *Int. J. Occup. Environ. Med.*, 4, 61–72.
57. Myers, H.M. (1978). Fluorides and dental fluorosis. *Monogr. Oral. Sci.*, 7, 1–76.
58. Davis, W.L. (1972). Ambient air fluorides in Salt Lake County, Rocky Mountain. *Med. J.*, 69, 53–56.
59. Hudak, P.F. (1999). Fluoride levels in Texas groundwater. *J. Environ. Sci. Heal. A*, 34, 1659–1676.
60. WHO. (1984). Fluorine and Fluorides, Environmental Health Criteria 36. Geneva, Switzerland: World Health Organization.
61. Jędra, M., Sawilska-rautenstrauch, D., Gawarska, H. and Starski, A. (2011). Fluorine content in total diets samples of small children. *Rocz. Panstw. Zakl. Hig.*, 62, 275–281.
62. de Almeida, B.S., da Silva Cardoso, V.E. and Buzalaf, M.A. (2007). Fluoride ingestion from toothpaste and diet in 1- to 3-year-old Brazilian children community. *Dent. Oral Epidemiol.*, 35, 53–63.
63. Tomori, T., Koga, H., Maki, Y. and Takaesu, Y. (2004). Fluoride analysis of foods for infants and estimation of daily fluoride intake. *Bull. Tokyo Dent. Coll.*, 45, 19–32.
64. Ponikvar, M., Stibilj, V. and Žemva, B. (2007). Daily dietary intake of fluoride by Slovenian military based on analysis of total fluorine in total diet samples using fluoride ion selective electrode. *Food Chem.*, 103, 369–374.
65. Vaidya, R., Bhalwar, R. and Bobdey, S. (2009). Anthropometric parameters of armed forces personnel. *Med. J. Armed Forces India*, 65, 313–318.
66. Nohno, K., Sakuma, S., Koga, H., Nishimuta, M., Yagi, M. and Miyazaki, H. (2006). Fluoride intake from food and liquid in Japanese children living in two areas with different fluoride concentrations in the water supply. *Caries Res.*, 40, 487–493.
67. Levy, F.M., Olympio, K.P., Philippi, S.T. and Buzalaf, M.A. (2013). Fluoride intake from food items in 2- to 6-year-old Brazilian children living in a non-fluoridated area using a semiquantitative food frequency questionnaire. *Int. J. Paediatr. Dent.*, 23, 444–451.
68. Zohouri, F.V. and Rugg-Gunn, A.J. (2000). Sources of dietary fluoride intake in 4-year-old children residing in low, medium and high fluoride areas in Iran. *Int. J. Food Sci. Nutr.*, 51, 317–26.

69. Dessalegne, M. and Zewge, F., (2013). Daily dietary fluoride intake in rural villages of the Ethiopian Rift Valley. *Toxicol. Environ. Chem.*, 95, 1056–1068.
70. Bouaziz, H., Ketata, S., Jammoussi, K., Boudawara, T., Ayedi, F., Ellouze, F. and Zeghal, N. (2006). Effects of sodium fluoride on hepatic toxicity in adult mice and their suckling pups. *Pestic. Biochem. Physiol.*, 86, 124–130.
71. Bouaziz, H., Amara, I. Ben, Essefi, M., Croute, F. and Zeghal, N. (2010). Fluoride-induced brain damages in suckling mice. *Pestic. Biochem. Physiol.*, 96, 24–29.
72. Iano, F.G., Ferreira, M.C., Quaggio, G.B., Fernandes, M.S., Oliveira, R.C., Ximenes, V.F. and Buzalaf, M.A.R. (2014). Effects of chronic fluoride intake on the antioxidant systems of the liver and kidney in rats. *J. Fluor. Chem.*, 168, 212–217.
73. Turner, C.H., Owan, I., Brizendine, E.J., Zhang, W., Wilson, M.E. and Dunipace, A. J. (1996). High fluoride intakes cause osteomalacia and diminished bone strength in rats with renal deficiency. *Bone*, 19, 595–601.
74. Sogaard, C.H., Mosekilde, L., Schwartz, W., Leidig, G., Minne, H.W. and Ziegler, R. (1995). Effects of fluoride on rat vertebral body biomechanical competence and bone mass. *Bone*, 16, 163–169.
75. Shanthakumari, D., Srinivasalu, S. and Subramanian, S. (2004). Effect of fluoride intoxication on lipidperoxidation and antioxidant status in experimental rats. *Toxicology*, 204, 219–228.
76. Varner, J., Jensen, K.F., Horvath, W. and Isaacson, R.L. (1998). Chronic administration of aluminum-fluoride or sodium-fluoride to rats in drinking water: Alterations in neuronal and cerebrovascular integrity. *Brain Res.*, 784, 284–298.
77. Sun, L., Gao, Y., Zhang, W., Liu, H. and Sun, D. (2014). Effect of high fluoride and high fat on serum lipid levels and oxidative stress in rabbits. *Environ. Toxicol. Pharmacol.*, 38, 1000–1006.
78. Han, H., Du, W., Zhou, B., Zhang, W., Xu, G., Niu, R. and Sun, Z. (2014). Effects of chronic fluoride exposure on object recognition memory and mRNA expression of SNARE complex in hippocampus of male mice. *Biol. Trace Elem. Res.*, 158, 58–64.
79. Ghosh, D., Das, S., Maiti, R., Jana, D. and Das, U.B. (2002). Testicular toxicity in sodium fluoride treated rats: Association with oxidative stress. *Reprod. Toxicol.*, 16, 385–390.
80. Mishra, P.C. and Mohapatra, K. (1998). Haematological characteristics and bone fluoride content in *Bufo melanostictus* from an aluminium industrial site. *Environ. Pollut.*, 99, 421–423.
81. Hemens, J. and Warwick, R.J. (1972). The effects of fluoride on estuarine organisms. *War. Res.*, 6, 1301–1308.
82. Johnstone, A.D.F. and Hawkins, A.D. (1982). The effects of an industrial waste (cryolite recovery sludge) upon the Atlantic salmon, *Salmo salar* (L). *Water Res.*, 16, 1529–1535.
83. Shi, X., Zhuang, P., Zhang, L., Feng, G., Chen, L., Liu, J., Qu, L. and Wang, R. (2009). The bioaccumulation of fluoride ion (F^-) in Siberian sturgeon (*Acipenser baerii*) under laboratory conditions. *Chemosphere*, 75, 376–380.
84. Sharma, M.R. and Gupta, V. (2014). Fluoride and its ecological effects in water: A review. *Global J. Res. Anal.*, 3, 2277–8160.
85. Bellomo, S., Aiuppa, A., D'Alessandro, W. and Parello, F. (2007). Environmental impact of magmatic fluorine emission in the Mt. Etna area. *J. Volcanol. Geotherm. Res.*, 165, 87–101.

86. Greenwood, D.A. (1956). Some Effects of Inorganic Fluoride on Plants, Animals, and Man, *USU Faculty Honor Lectures*. Paper 41. http://digitalcommons.usu.edu/honor_lectures/41.
87. Weinstein, L.H. (1977). Fluoride and plant life. *J. Occup. Med*., 19, 49–78.
88. Klumpp, A., Klumpp, G., Domingos, M. and Silva, M.D. (1996). Fluoride impact on native tree species of the Atlantic Forest near Cubatao, Brazil. *Water Air Soil Poll*., 78, 57–71.
89. Davison, A. and Weinstein, L.W. (1998). The effects of fluorides on plants. *Earth Island J*., 13, 257–264.
90. Kessabi, M., Assimi, B. and Braun, J.P. (1984). The effects of fluoride on animals and plants in the south Safi zone. *Sci. Total Environ*., 38, 63–68.
91. Zouari, M., Ben Ahmed, C., Fourati, R., Delmail, D., Ben Rouina, B., Labrousse, P. and Ben Abdallah, F. (2014). Soil fluoride spiking effects on olive trees (*Olea europaea* L. cv. Chemlali). *Ecotoxicol. Environ. Saf*., 108, 78–83.
92. Singh, M. and Verma, K.K. (2013). Influence of fluoride-contaminated irrigation water on physiological responses of poplar seedlings (*Populus deltoides* L. clone-S7C15). *Fluoride*, 46, 83–89.
93. Hobbs, C.S., Moorman, R.P, Griffith, J.M., West, J.L., Merriman, G.M., Hansard, S.L., Chamberlain, C.C., MacIntire, W.M., Hardin, L.J. and Jones, L.S. (1954). Fluorosis in cattle and sheep. *Tenn. Agr. Exp. Sta. Bull*., 235.
94. WHO. (2003). Fluoride in Drinking-Water. Background document for preparation of WHO Guidelines for drinking-water quality. Geneva, Switzerland: World Health Organization.