Chapter 2
Sources of Fluoride Toxicity

Abstract Sources of excess fluoride intake for animals are diverse and include drinking water, fluoride compounds used for household and agricultural purposes, forage and grasses contaminated with industrial fluoride emissions or volcanic ash, and occasionally, poor quality mineral mixture and feed supplements. Soil rich in soluble fluoride may also be responsible for fluorosis in grazing animals, particularly when growing vegetation is small and scanty. Toxicity arising due to airborne fluoride is rare and oral intake remains the major route of excess fluoride uptake. A water fluoride level as low as 1.5 ppm can cause chronic fluoride toxicity in several species, although the literature suggests higher water fluoride tolerance levels in most domestic animals. Volcanic-ash–contaminated pasture has been reported to cause mortality outbreaks in grazing animals in several countries.

Fluoride (F) toxicity can arise due to excessive fluoride intake from a variety of natural or manmade sources. Important F sources for animals include vegetation/forage contaminated by fluoride-rich industrial effluents or windblown or rain-splashed soil with high fluoride content, water high in fluoride content either naturally or due to industrial contamination, mineral mixtures and other feed supplements containing excess fluoride, vegetation grown on soils high in fluoride content, and a combination thereof (Shupe 1980; Swarup and Dwivedi 2002; Fig. 2.1). Fluoride is well absorbed by several routes, however, ingestion is the major mode of fluoride uptake for most animals (Shupe 1980). Soluble fluoride is distributed over the earth’s surface and atmosphere as a result of natural processes such as erosion, hydraulic leaching, volcanic activity, and to a lesser extent by mining and manufacturing processes. Animals when grazing over soluble fluoride-rich soil can ingest toxic doses of fluoride, especially if the pasture is overgrazed and animals are grazing small plants close to the soil (Shupe and Olson 1971). In this chapter, important sources of acute and chronic fluoride toxicity for animals are described in brief.
2.1 Natural Sources

Fluorosis in animals can occur due to high fluoride concentration naturally occurring in dietary substances including feed, fodder, concentrate ration, and drinking water.

2.1.1 Forage, Grasses, and Grains

Soil fluoride concentration is believed to have little influence over fluoride concentration in vegetation, inasmuch as most of the fluoride in soils cannot be assimilated readily by plants. However, a direct relation is reported to exist between F concentration in the soil and selected forage. Fluoride in forage increases by 3 ppm for each 100 ppm increase in soil F up to approximately 2200 ppm (Mascola et al. 1974). Other factors modulating fluoride concentration in fodder plants include height of the plant and season. Fluoride content increases with decrease in plant height. The fluoride concentration is higher in plants grown during winter and spring in comparison to those grown during summer and autumn (Mascola et al. 1974). Fluoride uptake by plant roots from soil occurs by passive diffusion, and
thereafter F is carried to the shoot by transpiration. Most of the plants do not accumulate fluoride in toxic concentrations and the level usually remains below 10 mg per kg dry weight. The tea plants (family Theaceae) can exceptionally accumulate high F concentrations. However, tea plants or their by-products are not a usual ingredient of animal feed. Many plant species, particularly *Acacia georgiana* and *Dichapetalum cymosum* (a South African shrub known as “Gifblaar”) can assimilate soil F and convert them into fluoroacetate, which is extremely toxic for animals (Shupe et al. 1984). Fluoroacetate is converted in vivo in mitochondria into fluorocitrate through condensation of fluoroacetyl-Co-A with oxaloacetate by the enzyme citrate synthetase which normally supplies acetyl-Co-A into the citric acid cycle. Fluorocitrate is a strong inhibitor of aconitase, which is an important enzyme of the Krebs cycle. Thus fluorocitrate inhibits the biochemical pathway for energy production in the organism (Patocka and Strunecka 2002).

It is interesting to note that gaseous fluoride compounds can enter leaves through stomatal pores and in high concentration they may induce toxicity signs in plants, including chlorosis, peripheral necrosis, leaf distortion and malformation, and abnormal fruit development. Long-term exposure to F concentrations greater than 0.2 μg/m³ may cause injury to plants (WHO 1984). It has been observed that air-contaminated forage loses a portion of its fluorine to the atmosphere after cutting and during storage as hay (NRC 1960).

The mean fluoride concentration of mineral soils is around 0.2–0.3 g/kg, whereas that of organic soil is usually lower. The fluoride content of topsoil increases by the addition of fluoride containing phosphate fertilizers, pesticides, and irrigation water or by deposition of gaseous and particulate emissions from industry. In New Zealand, it was found that long-term use of phosphorus fertilizers resulted in an increase in total surface soil (0–75 mm depth) fluoride concentration up to 217–454 mg per kg (Loganathan et al. 2001). Fluoride uptake by grazing animals through plant consumption is expected to be much lower than F uptake directly by soil ingestion because most plants do not accumulate F. Therefore, reducing soil ingestion by maintaining good pasture cover can reduce the risk of fluorosis in herbivores (Loganathan et al. 2008). Forage and grasses grown in industrial areas are often contaminated by fluoride-rich industrial effluents or by windblown or rain-splashed soil having a high fluoride concentration. Most industrial fluoride emissions are airborne and fluoride-rich dust, ash, and fumes may contaminate soil, water, and vegetation not only in the industrial vicinity, but also up to a considerable distance from the source of emission (Radostits et al. 2000). In such conditions F concentration in plants depends upon (1) the amount of fluorine released into the atmosphere, (2) the distance between the F emission source and the pasture area, (3) the type of vegetation, and (4) the distribution pattern as affected by the wind and topography (NRC 1960). Plants grown in areas where F is emitted into the atmosphere may contain 500–1000 ppm fluoride. Hence, animals should not be allowed to graze in pasture close to industries such as brick-kiln plants, rock phosphate processing plants, aluminum industry, and so on. Fodder plants grown in polluted areas should be harvested, soaked, and washed with water before offering to animals. This practice will substantially reduce the available F to animals.
Grains usually do not contain toxic concentrations of fluoride. Corn, wheat, oats, and barley grown on F-rich soil have very low F concentrations (less than 10 ppm) and nearly equal those grown on soil low in F (NRC 1960). Nevertheless, sorghum (Sorghum bicolor) consumption in human beings has been found to increase the risk and severity of osteo and dental fluorosis (Krishnamachari and Krishnaswamy 1973; Hari-Kumar et al. 2007). Sorghum grown in fluorotic areas contains a high molybdenum concentration. Molybdenum reduces urinary fluoride excretion and enhances fluoride retention (Stookey and Muhler 1962). A sorghum-based diet therefore increases F retention in human beings (Lakshmaiah and Srikantia 1977) and rats (Lakshmi and Lakshmaiah 1999). It is surprising to note that sorghum plants are more susceptible to hydrogen fluoride gas exposure than wheat plants (Mac-Lean et al. 1984).

2.1.2 Water

The fluoride concentration of natural groundwater depends upon geological factors, consistency of the soil, porosity of rocks, pH and temperature of the soil, complexing action of other elements, depth of wells, leakage of shallow groundwater, and chemical and physical characteristics of water (Li et al. 2014). Both surface and groundwater may have high F concentration in a particular locality, but the level is often higher in groundwater than the surface water. When groundwater percolates through rocks containing fluoride-rich compounds, fluoride leaches out and concentration may increase far above the safe level. The mean fluoride content of rocks varies between 0.1 and 1.0 g/kg. Important fluoride-containing minerals are fluorspar, cryolite, and apatite. However, in most soils, F is associated with micas and other clay minerals that make them less soluble and hence less toxic. Sodium fluoride and magnesium fluoride are also found as natural minerals. Fluoride contamination occurs through a natural process in which fluoride-bearing rocks crumble and break down, but the process can be speeded up if the chemistry of the aquifer is disturbed. Climatic conditions may also influence rate and degree of fluoride dissolution in water from rocks and soil. High F concentration in shallow zone groundwater is largely due to the geochemical F deposition in the vicinity of the groundwater extraction structures. The toxicity potential of fluoride-rich water is also influenced by the ambient temperature; alkalinity; and calcium, copper, and magnesium concentrations in water.

Water having a fluoride concentration up to 1.0 mg/L is safe, levels in between 1.1 and 2.5 mg/L are marginally contaminated, whereas above 2.6 mg/L are considered highly contaminated and dangerous for drinking purposes for human beings (Susheela 1999). It is estimated that total fluoride intake by a person when potable water contains 1 ppm fluoride would be from 0.05 to 0.10 mg per kg of body weight per day (NRC 1960). Most terrestrial animals, particularly domestic herbivores, are supposed to tolerate F in water higher than these threshold levels. However, many reports indicate the appearance of toxic symptoms in cattle, buffalo, and other livestock reared in areas where mean water fluoride concentration is equal to or slightly above 1.5 ppm (Choubisa 1999; Maiti et al. 2003; Ranjan et al. 2009).
2.1 Natural Sources

2.1.3 Volcanic Activities

Domestic and wild animals often suffer from severe fluorosis by ingestion of water and plants contaminated with volcanic ash (Araya et al. 1990; Bellomo et al. 2007). Volcanic ash usually has a very high soluble fluoride concentration and can be deposited over a large geographical area. In volcanic areas, the fluoride concentrations in water and pasture grass may remain high for years even after cessation of volcanic activities (Araya et al. 1993). The fluoride concentration in volcanic ash emitted by the Hekla volcano, Iceland, was up to 2000 ppm and the forage covered by ash had fluoride concentrations of 350–4300 µg/g (Thorarinsson 1979). In Chile in 1988, fluoride-bearing ash arising from the Lonquimay volcano affected more than 10,000 farm animals and resulted in the death of more than 4000 goats, sheep, cattle, and horses (SEAN 1989). Likewise, the death of thousands of sheep in 1995–1996 was attributed to ashfall from the Ruapehu volcano eruptions in Mexico (Armienta et al. 2011). In Argentina, the ash (“tephra”) released from the Puyehue–Cordon Caulle volcanic eruption in June 2011 reached up to a distance of 1400 km. Severe fluorotic dental lesions were observed in wild red deer who died after the volcanic eruption, which was attributed to consumption of grasses contaminated with volcanic ash (Flueck and Smith-Flueck 2013). In Iceland, thousands of sheep, cattle, horses, and other domestic and wild animals died due to repeated volcanic eruptions over the years (Armienta et al. 2011). Occasionally, acute toxicity in animals may occur after inhalation of hydrogen fluoride released from volcanoes (Weinstein and Davison 2004).

2.2 Anthropogenic Sources

Anthropogenic sources are also responsible for fluoride toxicity in animals. Some of them have been described in this chapter.

2.2.1 Mineral Mixture and Other Feed Supplements

There are several reports documenting mineral supplements as a major source of fluoride toxicity in livestock (Griffith-Jones 1977; Hillman et al. 1979; Singh and Swarup 1995). In a cattle herd numbering 120 animals, introduction of a commercial salt lick with fluoride concentration 1400 mg per kg resulted in the development of fluorotic lesions after one year. The fluoride concentrations in water and pasture samples were within the normal range suggesting the salt lick as the sole source of excess fluoride intake (Schultheiss and Godley 1995). In northern Australia, up to 15 % of cattle in a herd revealed signs of lameness due to use of fertilizer-grade monoammonium and diammonium phosphate as a mineral supplement. The affected animals were given large quantities of the mineral supplement thinking that the lameness was due to a phosphorus deficiency as it was an endemic
problem in that area (Jubb et al. 1993). Chronic ingestion of gypsum that was included in a feed supplement and also ingested from fertilizer dumps in paddocks resulted in the death of 226 cattle at a farm over a period of 18 months. Here, direct toxicity of gypsum as well as the effect of excess fluoride was incriminated as the cause of heavy mortality in the cattle herd (Bourke and Ottaway 1998).

The starting material for almost all chemically processed phosphates in mineral mixture and animal feed supplements is rock phosphate which contains approximately 13–14 % phosphorus and 3–4 % fluoride. The rock phosphate is first converted into phosphoric acid which is used for chemical synthesis of various types of feed phosphates. Phosphoric acid is synthesized from rock phosphate either by heating the rock phosphate in an electric furnace (dry process) or by treating the rock phosphate with sulphuric acid (wet process). The phosphoric acid produced by the electric furnace process has a very low F concentration and can be directly used for chemical synthesis of feed phosphates. In phosphoric acid produced by the dry heat process, the P:F ratio is usually greater than 2000:1 (Thompson 1980). However, the energy requirement per unit of phosphorus produced is approximately eight times greater in the dry process as compared to the wet process. Hence, the cost of production of phosphoric acid by the dry process is almost double that of the wet process. Wet process production methods therefore account for approximately 93 % of the total industrial production of phosphoric acid (Thompson 1980). The phosphoric acid produced by the wet process should always be defluoridated before use in feed phosphate synthesis. Defluoridation of phosphoric acid is done by addition of silicon dioxide and heat is supplied in the form of steam. The defluoridation process increases the cost of the feed phosphates, hence some manufacturers skip this step and use the phosphoric acid produced by the wet process directly for synthesis of feed phosphates. This may lead to high fluoride concentrations in mineral mixtures and animal feed supplements. Livestock, particularly dairy cattle may suffer from fluorosis after consuming such mineral mixtures or feed supplements (Singh and Swarup 1995). The phosphoric acid which has a P:F ratio of at least 100:1 is considered safe for production of feed phosphates for livestock.

### 2.2.2 Airborne Fluoride

The mean F concentration in ambient air in unpolluted or nonindustrial areas is generally less than 0.1 µg/m³. The levels may be slightly higher in areas near aluminum smelters or other industries, but should not exceed 2–3 µg/m³. The current “ceiling” value for F (in the form of hydrogen fluoride) in ambient air, as recommended by the National Institute for Occupational Safety and Health (NIOSH), Washington, DC, is 2.5 mg/m³ (Weinstein and Davison 2004).

Fluoride is released in the atmosphere by natural processes and human activities in both gaseous and particulate forms. Gaseous forms include hydrogen fluoride, silicon tetrafluoride, hexafluorosilicic acid, and sulfur hexafluoride. Particulate forms include sodium aluminum fluoride (cryolite), aluminum fluoride, calcium fluoride, sodium hexafluorosilicate, lead fluoride, and calcium phosphate fluoride (fluorapatite). Natural
dispersal of gaseous and particulate fluoride into the air has been recognized in regions of volcanic activity (USEPA 1980). Other natural sources include dust from soil and seawater droplets carried up into the atmosphere by winds (WHO 1984). Coal contains a substantial amount of arsenic, silicon, and fluorine. Hence, coal-fired power plants are important sources of anthropogenic hydrogen fluoride emissions. Fluoride concentration in coal may range 4–40 g/kg (McDonald and Berkeley 1969). According to an estimate, total air emissions of hydrogen fluoride by electrical utilities in 1998, 1999, 2000, and 2001 were 64.1, 58.3, 58.3, and 55.8 million tons, respectively. In many parts of China, coal burning for household purposes was documented as the cause of endemic fluorosis in the human population (Guijian et al. 2007). Small kilns used for making bricks and tiles are another source of airborne fluorosis in China and India. The fluoride concentration in coal and mud used for making bricks and tiles may exceed 10,000 mg/kg, hence a high emission of fluoride in the air occurs after firing (WHO 2000).

2.2.3 Industrial Effluents

More than 28 industries release fluoride-rich fumes and effluents into the environment (Swarup and Dwivedi 2002). Important among them are the aluminum industry, steel production plants, superphosphate plants, ceramic factories, coal-burning power plants, brickworks, glassworks, and oil refineries (WHO 1984). Livestock including cattle (Swarup et al. 2001), buffaloes (Patra et al. 2000), sheep (Sahoo et al. 2003), goats (Sahoo and Ray 2004), and camels (Karram and Ibrahim 1992) living in the vicinity of such industries often suffer from chronic fluoride toxicity. Pasture contaminated with rock phosphate dust emitted from a fertilizer factory resulted in the occurrence of fluorosis in sheep living in adjoining areas (Zumpt 1975). Wild herbivores are also reported to suffer from industrial fluorosis (see Chap. 5).

Hydrofluoric acid is used in the alkylation process for the production of high-octane fuels by refineries of crude petroleum. Waste products generated from such refineries are mostly disposed of by land treatment, wherein waste products are applied onto or into the soil for biodegradation of organic wastes, immobilization of inorganics, and avoidance of bioaccumulation of hazardous compounds (Loehr and Malina 1986). This practice results in an increase in soil fluoride concentration and may cause fluorosis in animals living on such soil. For example, fluorotic lesions along with high bone fluoride concentration in cotton rats (Sigmodon hispidus) living in such petroleum-waste–treated areas was reported from some parts of the United States (Paranjpe et al. 1994; Rafferty et al. 2000).

2.2.4 Agrochemicals and Household Products

Both organic and inorganic fluoride compounds are used for agricultural and domestic purposes. For example, sodium fluorosilicate can be used as a rodenticide and sodium fluoride as a feed premix for treatment of roundworms in pigs.
A few decades back, many fluoride compounds including sodium fluoride, cryolite, and sodium fluorosilicates were widely used for pest control in agriculture. Accidental exposure to these compounds can cause acute toxicity in man and animals. Mass poisoning and death of about 800 dogs occurred after consumption of poultry meat contaminated with fluoroacetate or fluoroacetamide in Israel (Egyed 1979). But these compounds are now rarely used and hence are of little significance as a source of fluoride toxicity in animals.

References

Egyed MN (1979) Mass poisoning in dogs due to meat contaminated by sodium fluoroacetate or fluoroacetamide (special reference to the differential diagnosis). Fluoride 12:76–84
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