Volume-3, Issue-8, August-2014 • ISSN No 2277 - 8160

Research Paper | Microbiology

Fluoride and its Ecological Effects in Water: A Review

Mali Ram Sharma Research scholar, JECRC University, Sitapura, Jaipur

Varsha Gupta Assistant Professor, department of microbiology, JECRC University, Sitapura, Jaipur

ABSTRACT

Fluoride (F–) is an inorganic ion which is found in all type of water from low to high concentrations. Fluoride concentration in water depends on some factors like temperature, pH, and solubility of fluorine-bearing minerals. Degradation of groundwater may be due to natural or anthropogenic processes. Natural causes are intrinsic geological conditions while anthropogenic causes include wastewater from sewage treatment plants, discharge from industries, improper solid waste disposal etc. Increasing Fluoride in groundwater is a major problem in many parts of the world. The fluoride belongs to the halogen group of minerals and it is natural constituents of the environment. Fluoride is the most electronegative elements and is never found in nature in the element form. It is seventeenth in the order of frequency of occurrence of the elements. It represents about 0.06% to 0.09% of the earth's crust fluoride is an essential element for life. At low concentrations fluoride deficiencies can arise but at high fluoride concentrations dental and skeletal fluorosis can certainly emerge. In drinking water fluoride concentration should be 0.5-1.5 mg per liter. World Health Organization recommends that the fluoride content in drinking water should be in the range of 1.0 to1.5 ppm. Higher concentration of fluoride also causes respiratory failure, fall of blood pressure and general paralysis. Loss of weight, anemia, and cochexia are among the common findings in chronic fluoride poisoning. Continuous intake of fluorides causes permanent inhibition of growth.

KEYWORDS : Fluoride, chemistry of fluoride, ecological effects of fluoride, dental fluorosis, skeletal fluorosis

INTRODUCTION

Fluoride (F–) occurs in almost all waters from trace to high concentrations. Fluoride concentration in natural waters depends on some factors like temperature, pH, and solubility of fluorine-bearing minerals. In India, an estimated 62 million people, including 6 million children suffer from fluorosis because of consuming fluoride-contaminated water. Generally, high fluoride contamination in hard-rock land is common due to water quality variation and changes in shallow and deep aquifers zones. The degradation of groundwater may be due to natural or anthropogenic processes. Natural causes are inherent geological conditions while anthropogenic causes include wastewater from sewage treatment plants, discharge from industries, improper solid waste disposal, agrochemicals, runoff from agricultural fields, and leakage from underground storage tanks etc. [1].

Increasing Fluoride in groundwater is a major problem in many parts of the world [2]. The fluorides belong to the halogen group of minerals and are natural constituents of the environment. Fluoride is the most electronegative chemical elements and is never found in nature in the element form. It is seventeenth in the order of frequency of occurrence of the elements and represents about 0.06% to 0.09% of the earth's crust [3]. Fluoride is an essential element for life. At low concentrations fluoride deficiencies can arise but at high fluoride concentrations other harmful effects can certainly emerge. Fluoride concentration should be 0.5 to 1.5 mg per liter in drinking water [4].

Among the water quality parameters, fluoride ion exhibits unique properties as its concentration in optimum dose in drinking water is advantageous to health and if the concentration exceeds the limit, this affects the health [5].

Though fluoride enters the body through water, food, industrial exposure, drugs, cosmetics, etc., drinking water is the major source (75%) of daily intake [6]. Due to its strong electronegativity; fluoride is attracted to positively charged calcium in teeth and bones. Major health problems caused by fluoride are dental fluorosis, teeth mottling, skeletal fluorosis and deformation of bones in children as well as adults [7].

Excess fluoride affects plants and animals also. Fluoride is well recognized as an element of public health concern. Fluoride is present universally in almost every water (higher concentrations are found in groundwater), earth crust, many minerals, rocks etc. It is also present in most of everyday needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes and so on [8,9].

Though a small amount of it is beneficial for human health for preventing dental carries, it is very harmful when present in excess of 1.0 ppm. World Health Organization (WHO) and ISO: 10500 recommend that the fluoride content in drinking water should be in the range of 1.0 to 1.5 ppm. Higher concentration of fluoride also causes respiratory failure, fall of blood pressure and general paralysis. Loss of weight, anorexia, anemia, wasting and cochexia are among the common findings in chronic fluoride poisoning. Continuous intake of fluorides causes permanent inhibition of growth. [10-12].

Dental fluorosis is endemic in 14 states and 150,000 villages in India with the problem most marked in the states of Andhra Pradesh, Bihar, Gujarat, and M.P., Punjab, Rajasthan, Tamil Nadu and Uttar Pradesh [13].

India is among the 23 nations where a large population suffers from dental and skeletal Fluorosis due to high F– concentration in groundwater. India has acute public-health problems induced by utilization of groundwater as a source of drinking water. The health problems arising as a result of fluoride (F–) contamination are far more widespread in India. Fluorosis was first detected in India, among cattle and humans in Andhra Pradesh [14].

1.1 FLUORIDE GEOCHEMISTRY

Fluorine (F) is a halogen, atomic weight 18.998, atomic number 9, valence -1. It is a diatomic gas in its elemental state (F2). Fluorine is the most electronegative element known, and in the gaseous form, F2, is a very powerful oxidizer. Because of the strong oxidizing power of F2, fluorine exists naturally as fluoride ion (F–). In the environment, fluoride flows from the continental drainages to the oceans at an estimated rate of 3.7 million metric tons a year. Mining removes 2 million tons per year, and 0.022 million tons are released to the atmosphere (as HF, SiF4 and metal fluorides) by combustion of fossil fuels and industrial emissions [15].

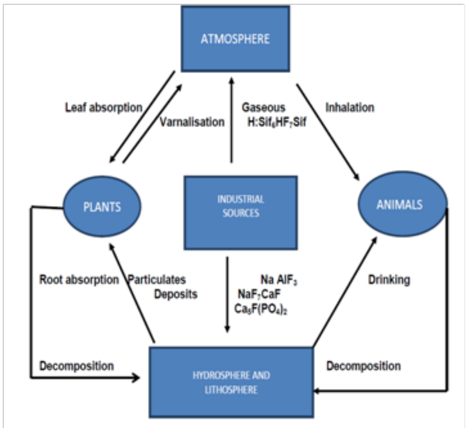

Figure1.1 Fluoride life cycle in the environment[16]

1.2 HYDROGEOCHEMISTRY OF FLUORINE

Three aspects have to be considered:

(i) High fluorine in source rocks: large amounts of fluorine are present in the rocks which can be dissolved during weathering.

(ii) Fluorite stability: The F– concentration in the aqueous solutions is limited by the fluorite solubility. Besides fluorite, fluorapatite solubility could also theoretically govern the concentration of F– in aqueous systems [17].

High F– water is usually HCO3- dominated which favours the dissolution of F– from soils and rocks. Therefore, water with high F– concentration can form in the areas where alkaline, i.e. carbonate-containing, waters are in contact with F– bearing rocks. F–concentrations are relatively independent of the other water soluble components. The F– solubility in soil is lowest in the pH range of 5.0-6.5. At higher pH value, ionic exchange occurs between F–and OH– ions resulting in increase of F– concentration in groundwater. A considerable amount of F– may be contributed due to anthropogenic activities. Remarkable amounts of F– are transferred into agricultural soil by phosphate fertilizer. Phosphate may contain up to 4% of F– depending on its origin and contents of fluorapatite. The steel, aluminum, glass, brick and ceramic industries use F– in their production process that occur with the encounter of F– containing aerosols, dust, wastewater into the surrounding environment [18].

1.3 CHEMICAL PROPERTIES OF FLUORINE

a. Element of Halogen group with molecular weight 19 and atomic number 9.
b. Fluorine is the most electro negative elements.
c. This fluorine exists as a diatomic molecule with low dissociation energy (38 K Cal/mole) [19].

Fluorine is the lightest member of Group 17 (VIIA) of the periodic table. This group, the halogens, also includes chloride, bromine, and iodine. Fluorine occurs as a diatomic molecule, F2, in its elemental form. It has only one stable isotope and its valence in all compounds is -1. Fluorine is the most reactive of all the elements, which may be attributed to its large electro negativity (estimated standard potential +2.85 V). It reacts at room temperature or elevated temperatures with all elements other than nitrogen, oxygen, and the lighter noble gases. Fluorine is also notable for its small size; large numbers of fluorine atoms fit around atoms of another element [20].

2. ECOLOGICAL EFFECTS IN WATER

Fluoride may be an essential element for animals and humans. For humans, however, the essentiality has not been demonstrated clearly, and no data indicating the minimum nutritional requirement are available. To produce signs of acute fluoride intoxication, minimum oral doses of at least 1 mg of fluoride per kg of body weight were required.

Many epidemiological studies of possible adverse effects of the long-term ingestion of fluoride via drinking-water have been carried out. These studies clearly establish that fluoride primarily produces effects on skeletal tissues (bones and teeth). Low concentrations provide protection against dental caries, especially in children.

2.1 EFFECTS ON FLORA

Fluorides in general, are accumulated in the plant tissues over long times. They are first accumulated in the leaves and then are translocate towards tips and margins of the leaves. The injury symptoms are produced only after a critical level of fluoride is attained. Due to such accumulation over long times, fluorides generally and HF particularly can induce injury at very low atmospheric concentrations. Critical concentration for fluoride injury is 0.1 ppm for several days.

The fluoride enters the leaf through the stomata and is moved to the margins where it accumulates and causes tissue injury. Note, the characteristic dark band separating the healthy (green) and injured (brown) tissues of affected leaves. Studies of usceptibility of plant species to fluorides show that apricot, barley (young), blueberry, peach (fruit), gladiolus, grape, plum, prune, sweet corn and tulip are most sensitive. Resistant plants include alfalfa, asparagus, bean (snap), cabbage, carrot, cauliflower, celery, cucumber, eggplant, pea, pear, pepper, potato, squash, tobacco and wheat [21].

In industrial areas, atmospheric hydrogen fluoride pollution can be a serious case of fluoride toxicity to plants. Several workers in different plants of India have reported chronic endemic Fluorosis, due to fluoride toxicity. Occidientalis, Prunus persica, Pinus contorta, Sylvestris, Pinuspinus, Pinusmugho, Pinus ponderosa, Prunus domestica, Picea pungens, Tulipa gesneriana, Acer negundo, Vaccinium sp., Pseudotsuga taxifolia, Gladiolus sp.,Vitus vinifera, Mahonia repens, Larix etc. are sensitive from Fluoride [22].

Benedict and Breen have used weeds in evaluating vegetation damage caused by air containing hydrogen fluoride and other air pollutants. Ten weeds that grow more or less commonly throughout the United States were selected for fumigation studies: annual bluegrass (Poa annua), cheese weed (Malva parviflora), chickweed (Stellaria media), dandelion (Taraxacum officinale), Kentucky bluegrass (Poa pratensis), lamb's-quarters (Chenopodium album), mustard (Brassica arvensis), nettle-leaf goosefoot (Chenopodium murale), pigweed (Amaranthus retroflexus), and sunflower (Helianthus annuus). The weeds were seeded on the top of well-mixed loam in boxes six inches square and four inches deep and kept under favorable conditions until they germinated. after ten days, the plants were thinned to five per box, except for grasses of which .twenty was allowed to grow for three and six weeks in moist soil and six weeks in dry soil [23].

The effect of ecological factors on photosynthesis has been reviewed · by Thomas. He and his associates have used photosynthesis as a yardstick for evaluating the effect of fumigation of plants with toxic gaseous substances. It has been assumed that if photosynthesis in plant is not affected by a fumigation treatment, it is unlikely a plant will be injured. .Thomas and associates found that plants could tolerate sub lethal concentrations of hydrogen fluoride for long periods without interference with assimilation. In most species there was a rapid translocation of absorbed fluoride to the tips or margins of the leaves, where toxic concentrations accumulated, causing necrotic areas. Photosynthesis was reduced by the extent of the injured areas, but the green portions of the leaf remained fully functional. The range of "sub-lethal" concentrations with different species was marked. In gladioli, as much as 10 ppb in many six to eight hour daily fumigations could be disposed of by translocation to permit green areas to function fully [24].

In cotton, 400 to 500 ppb could be similarly tolerated. Other species gave intermediate values. Higher concentrations than these caused a reduction in photosynthesis in excess of apparent leaf injury. Recovery from this inhibition of photosynthesis was relatively slow. 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 and phosphates [25].

2.2 EFFECTS ON FAUNA

In aquatic animals, fluoride tends to be accumulated in the exoskeleton of invertebrates and in the bone tissue of fishes. The toxic action of fluoride resides in the fact that fluoride ions act as enzymatic poisons, inhibiting enzyme activity and, ultimately, interrupting metabolic processes such as glycolysis and synthesis of proteins. Fluoride toxicity to aquatic invertebrates and fishes increases with increasing fluoride concentration, exposure time and water temperature, and decreases with increasing intraspecific body size and water content of calcium and chloride. Freshwater invertebrates and fishes, especially net-spinning caddis fly larvae and upstream-migrating adult salmons, appear to be more sensitive to fluoride toxicity than estuarine and marine animals. Because, in soft waters with low ionic content, a fluoride concentration as low as 0.5 mg/l can adversely affect invertebrates and fishes, safe levels below this fluoride concentration are recommended in order to protect freshwater animals from fluoride pollution [26].

Increasing population in developing countries and high industrialization of the advanced countries are creating environmental problems. Fluoride contamination of drinking water is one of such problems Worldwide. At present, twenty nine countries, are reported to be affected with fluorosis, the fluoride related disease. The problem in India is known for quite a long time. More than 23 countries in the world, including India, have problems with F– in the drinking water. The problems are most pronounced in the states of Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu and Uttar Pradesh while excess F– may induce hypocalcaemia. In India; about 62 million people are at risk of developing fluorosis from drinking high fluoride groundwater. Fluoride is important for the development of teeth and the bones. Small doses of fluoride have beneficial effects on the teeth by hardening the enamel and reducing the increase of caries, but excessive intake of fluoride results in dental and skeletal fluorosis and other disorders may also occur. The maximum tolerance limit of fluoride in drinking water specified by the World Health Organization is 1.5 mg/l. Dental and skeletal fluorosis has been reported in many countries of the world. In these countries fluoride levels in the range of 10-60 mg/l in groundwater have been reported [18].

2.2.1 DENTAL FLUOROSIS

Generally ingestion of water having a fluoride concentration above 1.5 – 2.0 mg/l may lead to dental mottling, an early sign of dental fluorosis which is characterized by white patches on teeth. In advanced stages of dental fluorosis, teeth display brown to black staining followed by pitting of teeth surfaces. Dental fluorosis produced considerable added dental costs (tooth deterioration) and significant physiological stress for affected population. Dental fluorosis is endemic in 14 states and 1, 50,000 villages in India. The problems are most marked in the states of Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu and Uttar Pradesh.

2.2.2 SKELETAL FLUOROSIS

Skeletal fluorosis may occur when fluoride concentrations in drinking water exceed 4-8 mg/l, which leads to increase in bone density, calcification of ligaments rheumatic or arthritic pain in joints and muscles along with stiffness and rigidity of the joints, bending of the vertebral column and excessive bone formation or osteosclerosis, a basis symptom of skeletal fluorosis. Crippling skeletal fluorosis can occur when a water supply contains more than 10 mg/l.

CONCLUSIONS:

The chief source of fluoride content in ground water is the leaching of fluoride from the fluoride-bearing minerals of the earth's crust. In order to enable sustainable development of groundwater resources, it is necessary to delineate the safe and unsafe zones with reference to F-content. Fluoride contamination being a prominent and widespread problem in several parts of the world and as causes for this are mostly natural and unpreventable, educating the people and defluorinating the groundwater before consumption are essential for a healthy world. Fluoride in drinking water is known for both beneficial and detrimental effects on health. The problems associated with the excess fluoride in drinking water are highly endemic and widespread in countries like India. Fluorosis - a disease caused by ingestion of fluoride in excess through water, food, and air is a serious health problem. Many rivers flowing through more than half a dozen states in India are reported to have fluoride contents varying from 0.1 to 12.0 ppm. The detrimental effects of excessive fluoride can be controlled by defluoridation of natural waters. A number of methods of defluoridation are available; however not all the methods are suitable for all circumstances.

REFERENCES

1. R.N. Janardhan, S. Deay and K. Das (2009), "Fluoride contamination in groundwater's of Sonbhadra District, Uttar Pradesh, India", 96(7), 979- 985. | 2. K. Brindha, R. Rajesh, R. Murugan and L. Elango(2010), "Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India", Environ Monit Assess, DOI 10.1007/s 10661–010–1348-0. | 3. K. Wedepohl (1974), "Hand book of geochemistry", Springerverlage berlin (Ed.: Heidelberf) New York, 2, 9 K-1. | 4. W. M. Edmunds and P.L. Smedley (1996), "Ground water geochemistry and health: An overview", (Eds: J.D. Appleton, R. Fuge, G.J.H. Mc call), Environmental geochemistry and health, London: Geological Society, Special Publication 113, 91-105. | 5. M.S. Venkata and S. Reddy (1995), "Determination of fluoride content in drinking water and development of a model in relation to some water quality parameters", Fresenius Envir Bull, 4, 297-302. | 6. K. Sarala and P. Rao (1993), "Endemic fluorosis in the village Ralla Anantapuram in Andhra Pradesh – An epidemiological study", 26, 177-180. | 7. A. Kumar, M. Betnagar and M. Bahadur (1993), "Prevalence of endemic fluorosis with gastro-intestinal manifestations in people living in some north-Indian villages", 26, 97-104. | 8. C. Thatte (1994), "Matching of water supply with growing demands", J. IWWA, 26(2), 67-71. | 9. S.N. Rao, P. Rao, J. Niranjan, and K. Rao (1997), "Hydro geochemical zoning in crystalline terrain and its significance to water quality", Jour.Geol. Soc. India, 49(6), 715-719. | 10. S. A. Andezhath and G. Ghosh (1999), "Fluorosis management in India: The impact due to networking between health and rural drinking water supply agencies", AHS-AISH Publication, 260, 159-165. | 11. K. Pillai, and V. Stanley (2002), "Implications of fluoride-an endless Uncertainty", Journal of Environmental Biology, 23, 81-87. | 12. V. Ramesam and K. Rajagopalan (1985), "Fluoride ingestion into the natural water of hard rock areas, Peninsular India", Jour. Geol. Soc. India, 26, 125-132. | 13. S.N. Rao (1992), "Factors affecting optimum development of groundwater's in crystalline terrain of the Eastern Ghats, Visakhapatnam area, Andhra Pradesh, India", Jour. Geol. Soc. India, 40(5), 462-467. | 14. H. Short, M. Robert, T. Bernard and A. Mannadinayar (1937), "Endemic fluorosis in the Madras, Presidency", Indian Journal of Medical Research, 25, 553–561. | 15. JoeEugene L. and Richard A. (2000), "Impact of Fluoridation of the Municipal Drinking Water Supply", 850, 474. | 16. Dash and Mishra (2001), "Fluoride life cycle in the environment", Asian journal of experimental biological science. | 17. A. Pekdeger, N.H. Özgür and J. Schneider (1992), "Hydrogeochemistry of fluorine in shallow aqueous systems of the Gölcük area", SW. | 18. M. Beg (2009), "Geospatial analysis of fluoride contamination in ground water of | Tamnar area, Raigarh District, Chhattisgarh State", 7-9. | 19. G.R. Vishwanathan (1935), "Annual Report Madras, Indian council of Agricultural Research, New Delhi", Quoted from Indian Institute of Science, 33A (1). | 20. V. Sanitha and M. Reddy (2008), "Fluoride in ground water and fluorosis", 1-3. | | 21. G. Iuliana and L. Barbu (2011),"the Effects of Air Pollutants on Vegetation and the Role of Vegetation in Reducing Atmospheric Pollution", 18-19. | 22. P. Kumar and M. Rani (2011),"Impact of Fluoride on Flora in and around Hindalco Industries Ltd., Renukoot (India)", Text Road Publication1(5), 81-83. | 23. H. M. Benedict, and W. H. Breen (1955),"The use of weeds as a means of evaluatingvegetation damage caused by air pollution. In Proc. of the third national air pollution symposium", Los Angeles, California, 177-190. | 24. M. D. Thomas (1955)," Effect of ecological factors on photosynthesis", Annual Rev. Plant Physiol.,6, 133-156. | 25. A.G. Delbert (1956), "Some Effects of Inorganic Fluoride on Plants, Animals, and Man", 8-12. | 26. J.A. Camargo (2003), "Fluoride toxicity to aquatic organisms: a review", Chemosphere., 50(3),251-64. |