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A REVIEW ON FLUORIDE POLLUTION IN DRINKING WATER

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ABSTRACT
Fluoride pollution in the environment occurs through two channels, namely natural and anthropogenic sources. Fluoride is frequently encountered in minerals and in geochemical deposits and is generally released into subsoil water sources by slow natural degradation of fluorine contained in rocks.
KEYWORDS: Fluoride, drinking water, degradation, geochemical deposits

INTRODUCTION

Fluoride pollution: Fluorine, the 13th most abundant element of the earth's crust, represents about 0.3g/kg of earth's crust. Fluorine in the environment is therefore found as fluorides which together represent about 0.06–0.09 per cent of the earth's crust. The average crustal abundance is 300 mg/kg . Fluorides are found at significant levels in a wide variety of minerals, including fluorspar, rock phosphate, cryolite, apatite, mica, hornblende and others . Fluorite (CaF_2) is a common fluoride mineral of low solubility occurring in both igneous and sedimentary rocks. Fluoride is commonly associated with volcanic activity and fumarolic gases. Thermal waters, especially those of high pH, are also rich in fluoride. Minerals of commercial importance include cryolite and rock phosphates. The fluoride salt, cryolite is used for the production of aluminium and as a pesticide. Rock phosphates are converted into phosphate fertilizers by the removal of up to 4.2 % fluoride ; the removed and purified fluoride (as fluorosilicates) is a source of fluoride that in some countries is added to drinking-water in order to protect against dental caries. Fluorine is an important element for human beings, as it helps in growth and prevents the enamel of the teeth from dissolving under acidic conditions. Various dietary components influence the absorption of fluorides from gastrointestinal tract and the absorbed fluorides are distributed throughout the body. Drinking water and sea food are good sources of fluoride. Fluoride is beneficial to health if the concentration of the fluoride ion (F-) in drinking water is less than 1.5 mg/L .

Fluoride is "more toxic than lead and less toxic than arsenic" and is an accumulative toxin. Fluoride has dual significance; if its content is less then it may result in problems like dental caries. World Health Organization (WHO) recommends it in the range of 0.1– 0.5 mg/L. The standard of the United States is between 0.6 and 0.9 mg/L, and of India 1.0 and 1.5 mg/L. Thus the requirement of fluoride content varies among countries and depends on the geography and the age of people involved.

Drinking-water is typically the largest single contributor to daily fluoride intake . However, as noted above, this is not necessarily true in every case . For a given individual, fluoride exposure (mg kg–1 of body weight per day) via drinking-water is determined by the fluoride level in the water and the daily water consumption (litres per day).

The fluoride content of air, water and food determine intake of fluoride depend mainly on the geographical areas. Food seems to be the source of 80%– 85% of fluoride intake, intake from drinking water is 0.03 – 0.68 mg/day and from tooth paste 0.2 mg – 0.3mg .

Fluoride distribution in water: Fluoride is found in all natural water at some concentration. Seawater typically contains about 1mg/L while rivers and lakes generally exhibit concentrations of less than 0.5 mg/L. In ground water, however, low or high concentrations of fluoride can occur, depending on the nature of the rocks and the occurrence of fluoride-bearing minerals. Concentrations in water are limited by fluorite solubility, so that in the presence of 40 mg/L calcium it should be limited to 3.1 mg/L . It is the absence of calcium in solution which allows higher concentrations to be stable. High fluoride concentrations may therefore be expected in ground water from calcium-poor aquifers and in areas where fluoride-bearing minerals are common. Fluoride concentrations may also increase in ground water in which cation exchange of sodium for calcium occurs . Fluorosis has been described as an endemic disease of tropical climates, but this is not entirely the case. Water with high fluoride concentrations occur in large and extensive geographical belts associated with a) sediments of marine origin in mountainous areas, b) volcanic rocks and c) granitic and gneissic rocks.

Geochemistry of fluoride: During the process of chemical weathering dissolution of fluoride species in the natural water is controlled by Ca^{2+} and governed by thermodynamic principles. The $CaCO_3$ equilibrium in the ground water plays an important role in the process. The equilibrium constant with respect to calcite can be evaluated from the reactions:

$CaCO_3 + H^+ \Leftrightarrow Ca^{2+} + HCO_3^-$

$K_{CaCO3} = a(Ca^{2+})\, a(HCO_3^-) / a(H^+)$

$= 97$ at 25^0C (39)

The fluoride equilibrium is given by:

$CaF_2 \Leftrightarrow Ca^{2+} + 2F^-$

$K_{CaF2} = a(Ca^{2+})\, a(F^-)^2$

$= 10^{-10}$ at 25^0C (40)

Dividing the first equation by the second the solubility of calcite and fluoride can be represented by a third constant K:

$a(HCO_3^-)/a(H^+)\, a(F^-)^2 = K$

$\Rightarrow (a\text{-}F^-)^2 = K'\, a(HCO_3^-)/a(H^+)$

Where $K' = 1/K$

$\Rightarrow a F^- \alpha\ (HCO_3^-) / (H^+)$

It is evident that if pH remains constant the activity of the fluoride ion will be proportional to that of bicarbonate ion. Thus following the principle of ionic activity product, if the concentration of calcium and fluoride in natural water exceeds the solubility product of fluoride ($10^{-10.58}$ at 25^oC) CaF_2 precipitates, before reaching saturation state. Calcium ion shows (+)ve correlation with fluoride ion and after this stage there will be a (–)ve correlation between Ca^{2+} and F^- ions. In fact, the total concentration of fluoride in a solution generally will be somewhat greater due to the presence of other electrolytes (ionic and Complexing effect). But it appears that high fluoride concentration is more likely to occur in water with low calcium concentration. Das gupta summed up characteristics of ground water having fluoride content dissolved from minerals as bellow:

1. Negative correlation of Ca^{2+} and F^-
2. Positive Correlation of HCO_3^- and F^-
3. Close the saturation with respect to CaF_2^-
4. Saturated with respect to $CaCO_3$.

Guidelines and standards for fluoride: In 1984, WHO conducted an extensive review and found that there were insufficient data to conclude that fluoride produces cancer or birth defects. In addition, WHO noted that mottling of teeth (i.e. dental fluorosis) is sometimes associated with fluoride levels in drinking-water above 1.5 mg/L and crippling skeletal fluorosis can ensue when fluoride levels exceed 10 mg/L. A guideline value of 1.5 mg/L was therefore recommended by WHO as a level at which dental fluorosis should be minimal. It is particularly important to consider climatic conditions, volume of water intake and other factors when setting national standards for fluoride . As per Indian standards the permissible limit of fluoride in it is 1.5 mg/L. There have been many incidences of fluorosis where fluoride in drinking water is less than the prescribed standards. In such cases food has been identified as main source of fluoride and hence food born fluorosis has been stressed upon and it has been reported in recent times. In fact, permissible limits of fluoride in drinking water are known to be dependent on the environmental temperature relationship as is given . It is seen from the that the optimum fluoride concentration decreases with increasing temperature.

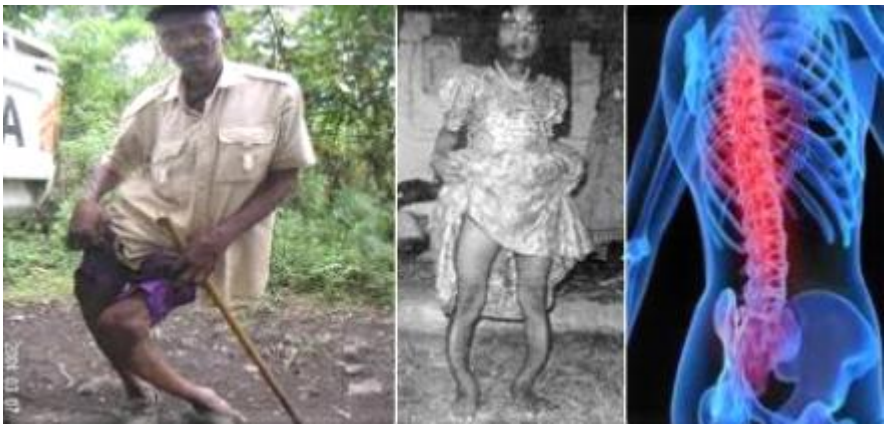
Table : Standards for fluoride in drinking water

Recommending authority	Permissible limit of F^- ion, mg/L
1. ISI recommendation	1.5
2. Indian medical council of medical research	1.0 1.0
3. Public Health Engineering manual and code of practice constituted by government of India.	
4. United States Public Health Standards	0.8 0.5 –1.5
5. WHO standards for drinking water.	

Table: mean maximum temperature and corresponding recommended optimum fluoride concentration

Mean maximum temperature, ^{0}C	Recommended fluoride concentration (mg/L)
50.0 – 53.7	1.2
53.8 – 58.3	1.1
58.4 – 63.8	1.0
63.9 – 70.6	0.9
70.7 – 79.2	0.8
79.3 – 90.5	0.7

Effect of fluoride ingestion in human beings-Fluorosis: A disease caused by ingestion of fluoride in excess through water, food, and air is a serious health problem. Fluoride ingested with water goes on accumulating in bones up to age of 55 years (Figure 1.2). Depending upon the amount and period of ingestion, illness of varying degree like dental fluorosis, skeletal fluorosis and non-skeletal fluorosis would occur. Calcification of certain ligaments, renders the movement of joints difficult and it is usually associated with at least 10 mg/L of fluoride in drinking water.



Fluorosis symptoms

Fluoride Bearing Illness :

The effects on behavior related directly to plasma fluoride levels , fluorides do not pass the blood - brain barriers , which only reflect short-term situations. Fluorides are cumulative, and short-term studies are specifically designed by proponents in a weak attempt to circumvent biological data , fluorides are general protoplasmic poisons, with the capacity to modify the metabolism of cells by inhibiting certain enzymes. Sources of fluorine intoxication include drinking water containing 1.0 mg/L or more of fluorine the potentialities for harm outweigh those for good . Chinese investigations have found that levels of fluoride in water from 3-10 mg/L effect the nervous system directly without first causing physical deformations from skeletal fluorosis .

Long-term consumption of water containing < 0.5 mg of fluoride per liter leads to dental fluorosis. White and yellow glistening patches on the teeth are seen which may eventually turn brown. The yellow and white patches when turned brown present itself has horizontal streaks. The brown streaks may turn black and effect the whole tooth and may get pitted, perforated and chipped off at the final stage. Dental fluorosis not only posses cosmetic problems but has serious social problems too, in terms of matrimonial problems of the children.

Skeletal fluorosis:This has been observed in persons when water contains more than 3-6 mg/L fluoride. Skeletal fluorosis effects young and old alike. Severe pain or stiffness in backbone, joints and hip region and increase in density of bones besides calcification of ligaments and some severe neurological problems, are caused due to Fluorosis. Further, Fluoride can also damage the foetus- if the mother consumes water and food with a high concentration of fluoride during pregnancy/breast feeding, infant mortality due to calcification of blood vessels can also occur.

The relation between concentration of fluoride and the biological effects are summarized .

Fluoride concentration of approximately 1.0 mg/L

Fluoride has been shown to reduce tooth decay when children 5 - 9 years of age receive an adequate level. Below 0.5 mg/L there is little evidence of this benefit but above 1.5 mg/L, little additional benefit is derived.

Fluoride concentration over 2.0 mg/L

Above approximately 2 mg/L, staining of tooth enamel is possible. EPA categorizes staining as an aesthetic concern and thus requires that customers of public water systems be notified of the fluoride level when the concentration exceeds 2.0 mg/L.

Table: Concentrations of fluorides and biological effects

Concentration of fluoride (mg/L)	Medium	Effect
0.002	Air	Injury to vegetation

1	Water	Dental caries
2 or more	Water	Mottled enamel
8	Water	10 % osteosclerosis
50	Food and water	Thyroid changes
100	Food and water	Growth retardation
120	Food and water	Kidney changes

Fluoride concentration over 4.0 mg/L

At concentrations above 4.0 mg/L, studies have shown the possibility of skeletal fluorosis. In its most severe form, skeletal fluorosis is characterized in irregular bone deposits that may cause arthritis and crippling when occurring at joints. EPA recognizes skeletal fluorosis as a health concern and thus requires that public water systems not only notify their customers but also treat the water to lower the fluoride level.

Fluorosis-world scenario

The latest information shows that fluorosis is endemic in at least 25 countries across the globe . The total number of people affected is not known, but a conservative estimate would number in the tens of millions. In 1993, 15 of India's 32 states were identified as endemic for fluorosis . In Mexico, 5 million people (about 6% of the population] are affected by fluoride in groundwater. Fluorosis is prevalent in some parts of central and western China and caused not only by drinking fluoride in groundwater but also by breathing airborne fluoride released from the burning of fluoride laden coal. Worldwide, such instances of industrial fluorosis are on the rise.

Figure indicates the probability of occurrence of excessive concentrations of fluoride in groundwater in Asia, on a scale of high-medium-low. In India, the chances of occurrence of fluoride has been rated as medium, and the regions are concentrated in Andhra Pradesh, Karnataka, Tamil Nadu, Gujarat and South Rajasthan

Toxicity of fluoride –Indian scenario

Presence of various hazardous contaminants like fluoride, arsenic, nitrate, sulfate, pesticides, other heavy metals etc. in underground water has been reported from different parts of India. Endemic fluorosis is a public health problem in India. Sixty two million people including 6.0 million children in the country in nearly 25 states, 150 districts are affected with dental, skeletal or non skeletal fluorosis. Medical advice recommends the drinking water should not contain more than 1.5 mg/l of fluoride. Concentration of fluoride below 1.5 mg/l is helpful in prevention of tooth decay, and such level of fluoride also assists in the development of perfect bone structure in human and animals. However, doses of fluoride above 1.5 mg/l increase the severity of tooth mottling and induce the prevalence of osteoporosis and collapsed vertebrae. Fluorosis has no treatment and is considered to be deadly disease. High fluoride content in water even causes change in shape and color of the fruits and vegetation.

Fluorosis was first detected in India , when the disease was prevalent in 4 states, namely Andhra Pradesh, Tamil Nadu, Punjab and Uttara Pradesh. During the period 1960-1986, nine more states have been identified as endemic Global environmental pollution problems are not just problems that affect many people. Instead, they are those immense problems that affect the entire planet Earth. These problems may or may not affect all people at the same time or to the same level. These pollution problems may have commenced many decades or centuries ago and are the result of additive, interconnected events that are manifested in a more complex present-day problem. It may also be true that the problem is generated at a relatively simple level of complexity but evolved into a more complex problem, requiring a complex solution. Water is one of the most basic requirements for human daily life. However, with rapid development of modern industries, the problem of water pollution is turned more serious day by day and on the other hand, the higher quality of water has been demanded with increasingly stringent environmental quality standards.

REFERENCES:

1) Yuan B L, Wang H J. Principle and Application of New Technology in Water Treatment (in Chinese). Beijing: Chemical Industry Press, 2006
2) Li F T, Zhang S F, Zhao Y. Coagulants and Flocculants (in Chinese).Beijing: Chemical Industry Press, 2005
3) Sanjay kumar and Krishna Gopal; Water quality technologies for smaller communities; J. of Rural Tech. Vol. 1 No. 1 Sept. 2003
4) WHO, the guidelines: A Framework For Safe Drinking-Water, chapter 2, Geneva, Page 35, 2004
5) US Geological circular 1200, 1995, chapter six, ground water quality, page 50.
6) Christopher R. Schulz and Daniel A. Okun. 1984. Surface water treatment for communities in developing countries. John Wiley & Sons, New York.
7) WHO, 1970. Fluoride and human health. Monograph Series 59, Geneva.
8) WHO, 1971. International standards for drinking water quality, 3rd Edition, World Health Organization, Geneva.
9) WHO, 1978. Nitrates, nitrites and N – nitroso compounds, Environmental Health Criteria – 5, Geneva.
10) WHO, 1984 a. Guidelines for drinking water quality (Recommendations). World Health Organization, Geneva, 1: 130.
11) WHO, 1984. Guidelines for drinking water quality (Health criteria and other supporting informations), Geneva, 8: 121.
12) WHO, 1985. Guidelines for drinking water quality (Drinking water quality control in small community supplies). Geneva, 8: 121.
13) Rajiv Gandhi National Drinking Water Mission (1986, 1993). "Prevention and control of Fluorosis in India" no. 8 and 9.
14) Cengeloglu, Y., Esengul, K. and Ersoz, M. (2002) Removal of fluoride from aqueous solution by using bauxite wastes. Sep &Pur Tech. 28, 81 – 86.
15) Murray J.J. [Ed.] 1986 Appropriate Use of Fluorides for Human Health, World Health Organization, Geneva
16) Haikel, Y. et al. 1986 Fluoride content of water, dust, soils and cereals in the endemic dental fluorosis area of Khouribga (Morocco). Archives of Oral Biology, 31(5), 279–286.
17) Haikel, Y. et al. 1989 The effects of airborne fluorides on oral conditions in Morocco.Journal of Dental Research, 68(8),1238–1241.
18) Cao, J., Bai, X., Zhao, Y., Zhou, D., Fang,S., Jia, M. and Wu, J. 1997 Brick tea consumption as the cause of dental fluorosis among children from Mongol, Kazak and Yugu populations in China. Food and Chemical Toxicology, 35(8), 827–833.
19) Chen, M.J. 1991 An investigation of endemic fluorine poisoning caused by food contaminated by smoke containing fluorine [Article in Chinese; reference based on English Abstract]. Chung Hua Yu Fang I HsuehTsaChih, 25(3), 171–173.
20) Mabelya, L. 1997 Dental fluorosis and the use of a high fluoride-containing trona tenderizer (magadi), Community Dentistry and Oral Epidemiology, 25(2),170–176
21) Environmental Health Directorate 1977 Tap Water Consumption in Canada: Ministry of Health and Welfare, 77-EHD-18.
22) Ershow, A.G. and Cantor, K.P. 1989 Total Water and Tapwater Intake in the United States:Population-Based Estimates of Quantities and Sources, National Cancer Institute Order#263-MD-810264.
23) Hopkin, S.M. and Ellis, J.C. 1980 Drinking Water Consumption in Great Britain, Technical Report TR 137, Water Research Centre, Medmenham, UK