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.

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 – 0.3 mg.

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:

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

$K_{CaCO_3} = a(Ca^{2+})\, a(HCO_3^-)/ a(H^+)$

$= 97$ at 25^oC [39]

The fluoride equilibrium is given by:

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

$K_{CaF_2} = a(Ca^{2+})\, a(F^-)^2$

$= 10^{-10}$ at 25^oC [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
3. Public Health Engineering manual and code of practice constituted by government of India.	1.0
4. United States Public Health Standards	0.8
5. WHO standards for drinking water.	0.5 –1.5

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.

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