Fluoride in Groundwater and its Health Hazards: A Review in Indian Scenario

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ABSTRACT

Fluorine is the lightest member of the halogen group and is one of the most reactive of all chemical elements. The main source of fluoride in groundwater is the rocks which are rich in fluoride. It accounts for about 0.3 g/kg of the Earth's crust and Exists in the form of fluorides in a number of minerals, of which fluorspar, cryolite and fluorapatite are the most common. In 21st century more than 35 million populations of 19 states of India is affected by the high concentration of fluoride in water. The highest concentration observed to date in India is 48 mg/L in Rewari District of Haryana. The most seriously affected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh.15 tribal villages in Rajasthan affected by dental fluorosis with fluoride concentration 0.3 -10.8 mg/L. Skeletal fluorosis affecting between 0.2 and 1 per cent of the population in Andhra Pradesh, where the maximum drinking-water fluoride concentration was 2.1 mg/L. Assam being the most recently identified State with high fluoride levels associated with endemic fluorosis. Since 1987, numerous programmes aimed at fully identifying the problem, along with developing fluoride removal techniques have been implemented. The influence of fluoride on human health is well-studied, but the conclusions drawn from this body of research remain controversial. However, as epidemiological studies continue to refine our understanding of the dose-response relationship and field studies better delineate the areas of potentially high fluoride, efforts to reduce fluoride related health problems should become more effective.

Keywords: Ground water, fluoride, fluorosis, concentration.

1. INTRODUCTION

Fluorine is the lightest member of the halogen group and is one of the most reactive of all chemical elements. It is not, therefore, found as fluorine in the environment. It is the most electronegative of all the elements [1] which mean that it has a strong tendency to acquire a negative charge, and in solution forms F^- ions. Other oxidation states are not found in natural systems, although uncharged complexes may be. Fluoride ions have the same charge and nearly the same radius as hydroxide

ions and may replace each other in mineral structures [1]. Fluoride thus forms mineral complexes with a number of cations and some fairly common mineral species of low solubility contain fluoride. It accounts for about 0.3 g/kg of the Earth's crust and Exists in the form of fluorides in a number of minerals, of which fluorspar, cryolite and fluorapatite are the most common. The main source of fluoride in groundwater is the rocks which are rich in fluoride. Fluoride is commonly associated with volcanic activity and fumarolic gases. Thermal waters, especially those of high pH, are also rich in fluoride [2]. Though fluoride enters the body through water, food, industrial exposure, drugs, cosmetics, etc., drinking water is the major source (75%) of daily intake. Fluoride is an essential element for both humans and animals, and its behaviour in drinking water is vital. Fluorine has high electro negativity and solubility, and hence occurs as F^- in natural waters [3].Fluoride levels in surface waters vary according to location and Proximity to emission sources. Higher levels of fluoride have been measured in areas where the natural rock is rich in fluoride, and elevated inorganic fluoride levels are often seen in regions where there is geothermal or volcanic activity (e.g., 25–50 mg fluoride/L in hot springs and geysers and as much as 2800 mg/L in certain East African Rift Valley lakes). Rock phosphates are converted into phosphate fertilizers by the removal of up to 4.2 per cent fluoride [4]; 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 [5].Optimum content (1.5 mg/L) of fluoride in water is essential for growth of bones and formation of dental enamels. Higher contents (>1.5 mg/L) pose a threat to human health, and can cause severe health problems such as dental and skeletal fluorosis.

2. SOURCES OF FLUORIDE IN GROUNDWATER:

Fluoride always occurs in combined form of minerals as fluoride because it's high reactivity and represents about 0.06 to 0.09% of the earth's crust [6]. Fluoride is mainly affected by the local and regional geological condition. Drinking-water is typically the largest single contributor to daily fluoride intake [4]. Fluoride is found in all natural waters at some concentration. Seawater typically contains about 1mg/L while rivers and lakes generally exhibit concentrations of less than 0.5 mg /L. In groundwater, 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 [1]. High fluoride concentrations may therefore be expected in groundwater from calcium-poor aquifers and in areas where fluoride-bearing minerals are common. Fluoride concentrations may also increase in groundwater in which cation exchange of sodium for calcium occurs [2]. Waters 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. High groundwater fluoride concentrations associated with igneous and metamorphic

rocks such as granites and gneisses have been reported from India. Robinson and Edington (1946)[7] reported that the main source of fluorine in ordinary soil consists of clay minerals. The weathering and leaching process, mainly by moving and percolating water, play an important role in the incidence of fluoride in groundwater. When fluoride rich minerals, which are present in rocks and soils, come in contact with water of high alkalinity, they release fluoride into groundwater through hydrolysis replacing hydroxyl (OH^-) ion. Rameshan and Rajagopalan (1985) [8] suggested that topographic features also play an important role in the control of fluoride. The existence of some of the dykes such as doleritic, intrusion normally acts as a natural barriers against the flow of underground water making the groundwater making the groundwater stagnated in fractures and pores .If the groundwater is more alkaline and stagnant for longer time, all the fluoride minerals in basic dyke rocks, and the overlying soil that are rich in mafic minerals undergoes greater ionization facilitating the groundwater to get enriched with fluoride. The degree of ionization increases with depth resulting in increase in total dissolved salts and alkalinity. The rocks are the natural aggregation of minerals and contain fluoride in abundant quantity. Endemic fluorosis remains a challenging and extensively studied national health problem in India

3. DISTRIBUTION OF FLUORIDE IN INDIA:

In 21th century, India more than 35 million populations of 19 states (Table 1) is consuming fluoride above permissible limit through drinking water. In 1991, 13 of India's 32 states and territories were reported to have naturally high concentrations of fluoride in water [9], but this had risen to 17 by 1999 [10]. The most seriously affected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh [11, 12]. The highest concentration observed to date in India is 48 mg/L in Rewari District of Haryana [10]. The high concentrations in groundwater are a result of dissolution of fluorite, apatite and topaz from the local bedrock, and Handa (1975)[13] noted the general negative correlation between fluoride and calcium concentrations in Indian groundwater. Efforts to address the problem of fluoride in rural water supplies in India have been led by the Rajiv Ghandi National Drinking Water Mission, with considerable support from external agencies, particularly UNICEF. However, even with the great interest in fluoride in India, it is not easy to arrive at an accurate or reliable estimate of the number of people at risk. This is because of the difficulty of sampling groundwater from India's many millions of hand-pumps. Existing sampling has been selective but unstructured, taking some villages from districts and some of the many pumps in each village [10]. In India, an estimated 62 million people, including 6 million children suffer from fluorosis because of consuming fluoride-contaminated water. Further, there have been no comprehensive health surveys for dental fluorosis from which the overall extent of the problem could be assessed. Nevertheless, in the most affected states listed above, half or more of the districts have some villages with groundwater supplies

having high fluoride concentrations. In these states, 10 to 25 per cent of the rural population has been estimated to be at risk, and perhaps a total of 60–70 million people in India as a whole may be considered to be so [10]. In India many district affected by fluoride .The figure 1 showing the map of India with all district showing fluoride range in drinking water. A survey conducted by the human rights organization (NGO) on the health hazards of the human population found that the dental and skeletal disorders are due to the fluoride content in groundwater in many parts of India.

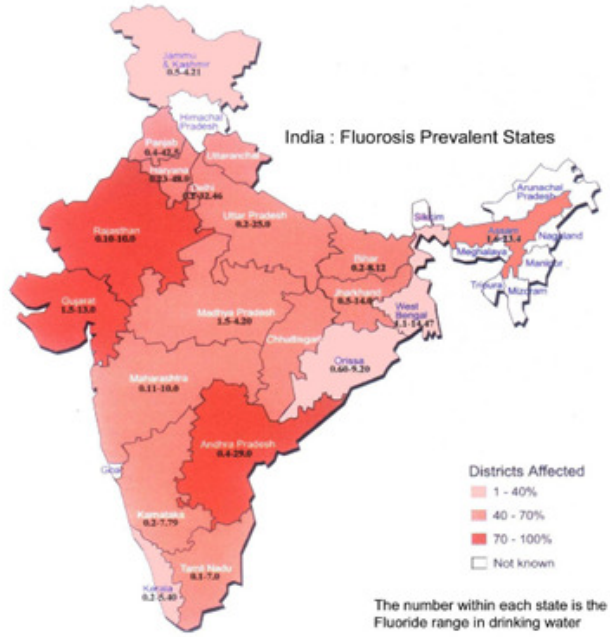

Fig.1 Map showing Fluorosis prevalent states

4. HUMAN HEALTH EFFECTS

Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is a significant cause of morbidity in a number of regions of the world. A number of studies have reported on the acute effects of fluoride exposure following fluoridation overdosing. However, the effects of long-term exposure to naturally occurring fluoride from drinking-water and other environmental sources are the major concern with regard to human health. A large number of epidemiological studies have been conducted in many countries concerning the effects of long-term

exposure to fluoride. A total of 17 (out of 32) States are reported to have endemic fluorosis in India [14, 15]. In 1987, it was estimated that 25 million people were suffering from fluorosis [15].

4.1 Dental fluorosis

The prevalence of dental fluorosis has been investigated in Rajasthan by Choubisa *et al*. (1997) [16]. Prevalence rates were observed in 15 tribal villages with fluoride concentrations of 0.3–10.8 mg/L. At mean fluoride concentrations of 1.4 and 6 mg/L, dental fluorosis was seen in 25.6 per cent and 84.4 per cent of school children (< 16 years) and 23.9 per cent and 96.9 per cent of adults respectively. Kodali *et al*. (1994) [17] reported dental mottling in 76 per cent of children in the 5–10 year age group and 84 per cent of children in the 10–15 year age group in Kodabakshupally, Sarampet and Sivannagudem. Yadav and Lata (2003) [18] examined the prevalence of dental fluorosis at lower drinking-water fluoride concentrations (mean concentrations between 1.93 and 2.14 mg/L) in the Jhajjar district, Haryana. Over 50 per cent of the children examined were found to be affected by dental fluorosis. Reddy and Prasad (2003) reported dental fluorosis levels of 43 per cent in the Anantapur district of Andhra Pradesh, where drinking- water fluoride concentrations ranged between 1.2 and 2.1 mg/L.

4.2 Skeletal fluorosis

Endemic skeletal fluorosis was reported from India in the 1930s. It was observed first in Andhra Pradesh bullocks used for ploughing, when farmers noticed the bullock's inability to walk, apparently due to painful and stiff joints. Several years later the same disease was observed in humans (Short *et al*., 1937) [19]. Choubisa *et al*. (1997) [16] examined the prevalence of skeletal fluorosis in Rajasthan in adults exposed to mean fluoride levels of 1.4 and 6 mg/L. At 1.4 mg/L over 4 per cent of adults were reported to be affected, while at 6 mg/L, 63 per cent of adults were reported to be affected. The prevalence was found to be higher in males and increased with increasing fluoride levels and age. In Andhra Pradesh, (Reddy and Prasad (2003) found skeletal fluorosis affecting between 0.2 and 1 per cent of the population examined, where the maximum drinking-water fluoride concentration was 2.1 mg/L.

4.3 Renal effects

The renal system is responsible for excreting most of the body's excess fluoride and is exposed to higher concentrations of fluoride than are other organs [20]. This suggests that it might be at higher risk of fluoride toxicity than most soft tissues. The chronic ingestion of fluoride can have non-carcinogenic effects on the kidney, and both pertain to the incidence of kidney stones [21]. More than 18,700 people living in a region of India where fluoride Concentrations in the drinking water ranged from 3.5 to 4.9 mg/l and found that patients with clear signs of skeletal fluorosis were 4.6 times more likely to develop kidney stones.

4.4 Effect of fluoride on animals

Although the literature on fluorosis in cattle is extensive, information about fluorosis in horses is almost nonexistent. In 1974, US National Academy of Science report on effect of fluoride in animals. Most of horses in Justus Farm in Pagosa Springs, Colorado, affected by fluorosis due to consumption artificially fluorinated water, concentration up to 1.3 to 3.4 ppm. Fluorosis affected horses symptoms were dental fluorosis, crooked legs, hyperostosis and enostosis, hoof deformities and reduced bone resorption [22]. In Rajasthan dungarpur district natural occurrence of fluorosis was observed in a survey of domesticated dromedary camels. Among these eight camels were affected with mild to severe dental fluorosis [23]. Osteo- dental and non skeletal fluorosis was observed in domesticated cattles living in Chani village, Bikaner district of Rajasthan. Fluoride in drinking water of this village varies between 1.5 and 2.5 ppm [24]. In Rajasthan herbivores animals were affected by dental and skeletal fluorosis due to excess of high fluoride concentration in water [25]. The highest fluoride concentration found in invertebrates detritivores, compared to invertebrate Herbivores and carnivores [26].

4.5 Exposure, fluorosis and fluoride concentrations

At least 17 States are affected by elevated fluoride levels in drinking-water, namely; Andhra Pradesh, Assam, Bihar, Delhi, Gujarat, Haryana, Jammu and Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh and West Bengal.

Table 2. Fluoride concentrations reported in groundwater of India.

Region/State	Fluoride concentration (mg l–1)	Maximum severity of fluorosis observed
North-West India	0.4 – 19	Severe
Central India	0.2 – 10	Moderate
South India	0.2 – 20	Severe
Deccan Province	0.4 – 8	Moderate

Sources: Agarwal et al. (1997); Yadav et al. (1999)

These have been progressively identified since the first report by Short *et al*. (1937) [19], with Assam being the most recently identified State with high fluoride levels associated with endemic fluorosis. Not all States are equally affected and the number of districts with endemic fluorosis within each State varies [15]. Nine out of eighteen districts in West Bengal were recently identified as having fluoride contaminated groundwater (Ministry of Water Resources, 2004) [27]. It has been Estimated that the total population consuming drinking-water containing elevated levels of fluoride is over 66 million [15]. The distribution of fluoride in Indian groundwater is shown in Table 2. In Rajasthan, fluoride concentrations have been found to vary between 0.6 mg/L and 69.7 mg/L [28]. In Haryana, the highest fluoride Concentration was found in the village of Karoli and was recorded

at 48 mg/L. Meenakshi *et al*. (2004) [29] reported fluoride levels of between 0.3 and 6.9 mg/L in four villages in the Jind district of Haryana.

5. CONCLUSION

The influence of fluoride on human health is well-studied, but the conclusions drawn from this body of research remain controversial. Although the presence of trace levels of fluoride in the diet is clearly associated with fewer dental caries and the formation of stronger bones, there is also a number of acute and chronic health problems associated with the intake of fluoride in high doses. Impacts of fluoride on humans and animals are discussed. Dental fluorosis, skeletal fluorosis, crippling fluorosis, renal effects are discussed with their exceeding limit fluoride in water. For that, In India populations have been facing high health risk on fluorosis. In worldwide the millions of people affected by dental fluorosis and skeletal fluorosis. Effect of fluoride on humans, animals, plants and marine ecosystem due to the release of fluoride from industries like, Coal mining, aluminium smelter and etc. Today, there are several fluoride containing dental restoratives available in the market including glass isomers, resin modified glass isomer cement and tooth paste. So to overcome the fluorosis in

Worldwide by safe drinking and avoid the discharge of industries waste to water bodies.

Even in developed nations, where governmental health agencies regulate the fluoride content of public drinking water, private water supplies, dietary choices, dental products, industrial emissions, and/or occupational exposure can cause an individual's total fluoride intake to exceed safe doses. However, as epidemiological studies continue to refine our understanding of the dose-response relationship and field studies better delineate the areas of potentially high fluoride, efforts to reduce fluoride related health problems should become more effective

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