J. Mater. Environ. Sci. 4 (4) (2013) 520-525
ISSN : 2028-2508
CODEN: JMESCN

Fluoride contamination in estuary water villages located around SIPCOT Industrial Zone, Cuddalore District, Tamil Nadu, India

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Received 24 Dec 2012; Revised 2 Feb 2013; Accepted 2 Feb 2013
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Abstract
Presence of high concentration of fluoride in drinking water causes dental and skeletal fluorosis in humans in several parts of the world. In India presence of high concentration of fluoride in water is reported from different corners of the country. In the present study we investigated fluoride levels in the Uppanar estuary water in Cuddalore, Tamil Nadu, India. Forty five water samples from different villages located near SIPCOT Industrial Zone, Cuddalore, were collected and analysed for fluoride contamination. Water samples were collected during May to June in 2008. It was recorded that in the water of Thaikkal village fluoride concentration were ranged between 1.8 and 2.4 mg/l, and in Kudikadu values of fluoride concentration were between 01.1and 2.1 mg/l. Moreover, the fluoride concentration in water near the SIPCOT Zone ranged between 1.0 and 1.7 mg/l. The concentration of fluoride (2.4mg/l) recorded from these sites were higher than the WHO recommended safe levels of fluoride in drinking water resources. Since the fluoride concentration recorded in the present study are above 1 mg/l, it may lead to skeletal fluorosis which has no treatment or cure at present and hence appropriate steps have to be taken to prevent such fluorosis in these villages.

Key words: Estuary water, fluoride, fluorosis, Cuddalore, Tamil Nadu, India

1. Introduction
Water is the basic requirement for sustenance of all kinds of life forms. Water containing dissolved ions beyond the WHO permissible limit is harmful and not suitable for domestic use and irrigation. Fluoride beyond desirable concentration that is (0.6 to 1.5 mg/l) in water is a major health problem in many parts of the world. About 200 million people from 25 nations have health risks because of high fluoride in ground water [1].

Human health effects
Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking water can give rise to a number of adverse effects ranging from mild dental fluorosis to crippling skeletal fluorosis [2]. About 75–90 per cent of fluoride ingested by human being is converted into hydrogen fluoride (HF) in an acidic stomach and out of this upto 40 % is absorbed by stomach or intestine [3]. Once absorbed, fluoride readily distributes throughout the body with blood and approximately 99 per cent of the body burden of fluoride retained in calcium rich areas such as bone and teeth (dentine and enamel) where it is incorporated into the crystal lattice [2]. In infants about 80 to 90 % of the absorbed fluoride is retained but in adults this level falls to about 60%. Bone fluoride is considered to be a reflection of long-term exposure to fluoride [2]. Fluoride crosses even placenta and is found in mother’s milk at low levels [4].

High levels of fluoride present in concentrations up to 10 mg/l are associated with dental fluorosis (yellowish or brownish striations or mottling of the enamel) while low levels of fluoride, less than 0.1 mg/l are responsible for high levels of dental decay [5]. Concentrations in drinking-water of about 1 mg/l are associated with a lower incidence of dental caries particularly in children, whereas excess intake of fluoride can result in dental fluorosis. In severe cases this can result in erosion of enamel [2]. As fluoride concentration increased further (upto 2.6 mg/l) dental decay continues to fall [6]. Dental fluorosis is a cosmetic effect that ranges in appearance from scarcely discernible to a marked staining or pitting of the teeth in severe forms. It is caused by an elevated fluoride level in, or adjacent to, the developing enamel [3]. Belyakova and Zhavoronkov [7] suggested that fluorosis might be one of the most widespread of endemic health problems associated with natural geochemistry. Endemic fluorosis is now known to be global in scope, occurring on all continents and affecting many millions of people. Although no precise figures for the global number of persons affected are available, some figures at national levels have been given in the literature [8].

Endemic skeletal fluorosis is well documented and is known to occur with a range of severity in several parts of the world, including India, China and northern, eastern, central and southern Africa. It is primarily associated with the consumption of drinking water containing elevated levels of fluoride. Crippling skeletal fluorosis, which is associated with the higher levels of exposure, can result from osteosclerosis, ligamentous and tendinous calcification and extreme bone deformity [2].

In an epidemiological study in China the relationship between fluoride intake via drinking water and all other sources and all fractures, followed a U shaped dose response with higher rates of fracture at very low intakes below 0.34 mg/l l–1 and high intakes above 4.32 mg/l l–1 (total intake 14 mg per day) [9]. It was concluded by the IPCS that for a total intake of 14 mg per day there is a clear excess risk of skeletal adverse effects and there is suggestive evidence of an increased risk of effects on the skeleton at total fluoride intakes above about 6 mg per day [2].

In spite of the large number of studies conducted in a number of countries, there is no consistent evidence to demonstrate any association between the consumption of controlled fluoridated drinking water and either morbidity or mortality from cancer [2,4,6,10]. However, Hamilton has reported that fluoride at high concentration may act as a carcinogen also [11].

Acute fluoride intoxication occurred when minimum oral doses of atleast 1 mg fluoride per kg of body weight are ingested [4] and this could be expected from water with a fluoride concentration of approximately 30 mg/l. Incidents of acute intoxication have been reported following overdosing in water supplies where fluoride levels have ranged from 30–1,000 mg/l [12].

In India too water quality is at risk due to high concentration of various ions in water [2]. Among other chemical ions, long exposure to fluoride in water are known to cause health hazards including skeletal and dental fluorosis, dental caries, teeth mottling as well as deformation of bones both in humans and animals [3]. In India about 62 million people are living at risk of high fluoride concentration in drinking water [2]. Dental fluorosis is endemic in 14 states and 150,000 villages in India with the problem most pronounced in Andhra Pradesh, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu and Utter Pradesh states (Table 1) [13].

Table 1. Fluoride concentrations reported in ground waters of India

Region/State	Fluoride concentration (mg/l)	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*. [14]; Yadav *et al*. [15]

According to WHO [4] permissible limit of fluoride in drinking water is 0.1 mg/l. In temperate regions, where water intake is considerably low fluoride upto 1.5 mg/l are acceptable [16]. When the concentration of fluoride is more than 3.5 mg/l, mottling has been noted and high concentration may even cause other physiological problems in human as well as animals [4]. Water quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities [17, 18]. The main source of fluoride in water is rocks such as fluorspar, fluorite, cryolite, fluoroapatite and hydroxyapatite [19]. Ahmed *et al*. [20] have compared the analytical results of ground water in Rajshahi city of Bangladesh with the recommended limits suggested by World Health Organization. Knowledge in hydrochemistry is more important to assess the quality of ground water for understanding its suitability for various needs. Anbazhagan and Nair [21] have been used the geological information systems to represent and understand the spatial variation of various geochemical elements. Moreover, occurrence of fluoride in water is a function of factors such as availability and solubility of fluoride minerals, velocity of flowing water, pH, temperature and concentrations of calcium and bicarbonate ions in water [22, 23,24]. Seventeen states in India have been identified as endemic for fluorosis and Tamil Nadu is one of them where 23 out of 28 districts are prone to fluorosis in drinking water [21]. In Tamil Nadu, the high concentration of fluoride in water is found to be in Dharmapuri and Salem district followed by Coimbatore, Madurai, Trichy, Dindugal and Chidambaram districts. The districts having low fluoride are Thirunelveli, Pudukottai, North Arcot, and Ramnad districts. If we are going to see the level of severity, the status of Dharmapuri and Salem districts are more severe than Coimbatore, Madurai, Trichy, Dindugal and Chidambaram (moderate), whereas, Thirunelveli, Pudukottai, North Arcot and Ramnad are the least affected districts by fluoride content in water [25]. Tirunelveli District of Tamilnadu is reported to have drinking water containing high concentration of fluoride (3.84 mg/l) and causes disease namely fluorosis [26]. Pollutants, especially toxic heavy metals and inorganic chemicals like fluoride are of great concern in the coastal environments like estuaries and backwaters [27]. Fluoride is one of the naturally occurring chemical components in addition to chloride, sodium, sulphide, magnesium, bromide etc in seawater. Another major source of fluoride to the coastal environment is the wastewater from industries manufacturing fluoride chemicals [25]. The wastewater from such industries contains fluoride ranging from several hundred to several thousands of mg/l in raw effluents [25]. Therefore, present study was started with the aim of investigating fluoride concentration in water of the Uppanar estuary situated at Cuddalore, Tamil Nadu, India.

2. Study area

The present study was conducted in Uppanar estuary of Cuddalore district of Tamil Nadu, India. The Uppanar estuary is located at Cuddalore district (Lat 11º 43'N; Long 79º 49'E)**.** The estuary originates from the north eastern part of the Shervarayan hills and opens into the Bay of Bengal near Cuddalore. Uppanar estuary receives municipal sewage and industrial effluents from SIPCOT (Small Industries Promotion Corporation of Tamilnadu) Industrial complex. Most of industries are wet process industries and hence consume large quantity of water. The area was very fertile with an annual landing of about 2000 tons of fish before the establishment of the SIPCOT **(Fig – 1).**

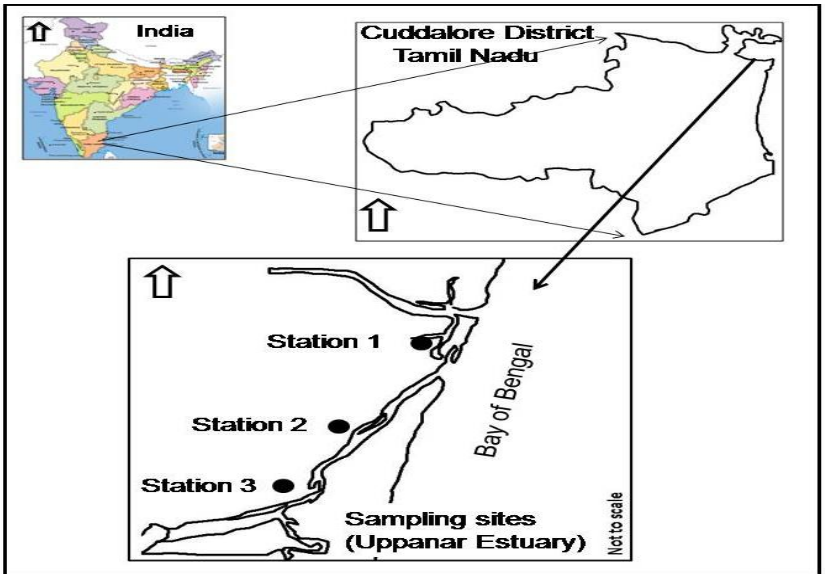

Figure 1. Study area and sample sites location

The estuary water is used by local people for drinking and cooking so that fluoride pollution in the coastal environment may have great human health implications.

3. Materials and Methods

3.1. Sampling technique

Water samples were collected using random sampling from 3 selected stations in the Uppanar estuary; one near to human settlement of SIPCOT complex; second from Kudikadu which is situated 2 km upstream of the waste disposal point and third stations was selected 2 km downstream near to Thaikkal village.

Acid washed one litre polythene cans were used for collection of sample water were closed tightly, labelled and transported to the laboratory of Department of Marine Biology, Annamalai University, Tamil Nadu, India. After arrival to the laboratory, the water samples were centrifuged and refrigerated at 4° C until used for Fluoride analysis.

3.2. Fluoride Analysis

The method used for fluoride ion determination was "Colorimetric Method (SPADNS, APHA)"[28]. The Colorimetric methods are subjected to errors due to the presence of interfering ions. So, it was necessary to distil the sample before estimating the fluoride. The addition of the prescribed buffer (TISAB-Total Ionic Strength Adjustment Buffer) frees the electrode from the interference caused by the common ions such as aluminium, hexametaphosphate and orthophosphate that adversely affect the calorimetric methods simultaneously. The distillation procedure is carried out in the following manner 400ml of distilled water was taken in the distillation flask and 200ml of concentrated sulphuric acid was added to it carefully. The mixture was swirled and homogenized, then 25-30 glass bits were added (to control the excess boil) and then the apparatus was connected with electric power supply. The apparatus was heated slowly at first and then rapidly until the temperature of the flask reaches exactly 180^0C. Then, the distillates were discarded. This process removes the fluoride contamination and adjusts the acid water ratio for subsequent distillations.

After cooling the acid mixture to 120°C or below, 300ml of water sample was added, thoroughly mixed and distilled before the temperature reaches 180°C. After the distillation of sample water (assuming that the concentration of fluoride is high in the samples) the still was flushed with 300 ml of distilled water and then the two fluoride distillates were combined. Similarly, after the periods of inactivity, the still was flushed and the distillate was discarded.

The prepared samples were ready for reading the fluoride concentration. Reagent of 10 ml of acid Zirconyl SPADNS was added to all the samples. The sample was mixed well and then read the optical density of bleached colour at 570 nm using reference solution (for setting zero absorbance). Sample of 1 ml was added with 10 ml of acid Zirconyl - SPADNS reagent, the solution was mixed well and percentage transmission or absorbance was recorded and fluoride concentration was calculated using Spectrophotometer in mg/l.

4. Results and Discussion

The overall fluoride concentration in water samples is given in Table 2 and classification of water based on the type of health problems due to fluoride concentration hazard in waters is shown in Table 3. The fluoride concentration in the study sites varies from 1.0 to 2.4 mg/l.

The level of fluoride recorded during present study was lower at first station located upstream (average 1.32 mg/l at SIPCOT COMPLEX) than the second station located downstream (average 1.52 mg/l at Kudikadu). The concentration of fluoride increased further as we go further to station three (average 2.4 mg/l at Thaikkal). It is obvious that with the increase in number of industries, release of their pollutants in estuary will also increase and probably this was one of the most important reasons [29].

Table 2. Fluoride concentration in water samples collected from different sites during – Month 2008

Site No.	Water sampling sites	Fluoride concentration in mg/l		
		Min	Max	Mean ± SE
1	Near SIPCOT Complex	1.0	1.7	1.32 ± 0.04
2	Kudikadu	1.1	2.1	1.52 ± 0.07
3	Thaikkal	1.8	2.4	1.68 ± 0.09

All water samples were found to fall under fluoride hazard zone as the concentration of fluoride ranges from 1.0 mg/l – 2.4 mg/l If we consider mean value (1.32 ± 0.04) SIPCOT Zone can only be the safer zone (Table 2). Water with fluoride concentration less than 1.5 mg/l is considered normal, whereas fluoride concentrations beyond 1.5 mg/l are represented as high fluoride region with high incidence of fluorosis [4]. Excessive fluorides in drinking water damage teeth forming cells leading to a defect in the enamel and causing dental fluorosis which again result in extensive pitting, chipping, fracturing and decay of teeth [30]. According to Bureau of Indian Standard [31] the desirable range of fluoride concentration in drinking water is from 0.6 to 1.2 mg/l. Thus, if the concentration of fluoride is below 0.6 and above 1.2 mg/l, the water is not suitable for drinking purposes. If we consider the minimum value of fluoride contents (1.0mg/l) recorded in this study, only area near to SIPCOT complex falls under this category. Based on the concentration of fluoride, the water samples obtained from the region have been classified into two groups as medium (0.6-1.5 mg/l) and high (1.5-3.0 mg/l). However, it is suggested that the maximum permissible limit can be extended upto 1.5 mg/l [24].

The possible reason for fluoride contamination in this region may be due to pollutants released by industries or by a natural process, i.e. leaching of fluorine minerals [30]. Fluorite, fluorapatite, mica, hornblende and various other minerals take part during rock-water interaction and liberate fluoride into the groundwater. The semi-arid climate with high temperature and low rainfall and the alkaline nature of soil are contributing factors to enhance the fluoride contamination of water bodies in the study areas [32]. The area is devoid of hard rock and hence the possibility of a source in the common fluoride bearing minerals [30]. Furthermore, pH may also be responsible for the dissolution of fluorides from fluoride bearing rocks during the weathering processes with in the aquifers [33]. The concentration of fluoride in water is not uniform in the area. This may be due to the differences in the presence and accessibility of fluorine-bearing minerals to the circulating water and also due to the weathering and leaching activities [34]. The other reason may be volume of pollutants released by different industry.

Table 3. Classification of water based on fluoride hazard (WHO 1996)

Fluoride concentration (mg/l)	**Effects on Human Health**
0.1-0.6	Low limit (dental caries)
0.6-1.5	Safe limit (bone development and prevent dental caries)
1.5-3.0	Dental fluorosis (discoloration mottling and pitting teeth)
3.0-4.0	Stiffened and brittle bones and joints
>4.0	Crippling fluorosis (deformities in knee and hip bones and finally leads to paralysis)
>10	Crippling skeletal fluorosis, Cancer

In this study area main source of fluoride intake by human may probably be the drinking water, which supplies 75-90% of the daily intake by each household [34]. During summer with the high temperature water intake raises, so the chance of higher ingestion of fluoride is expected. Therefore the concentration of fluoride in drinking water is an important factor for controlling daily intake. If fluoride water is consumed over a period of time, it affects the human health. Excessive intake of fluoride affects the teeth and the bones. In large quantities fluoride can also affect the kidney, thyroid gland and in most extreme cases it may lead to death [35].

The effects of fluoride on human health can be either positive or negative depending on the amount of fluoride that has been ingested. Small amounts of fluoride can have a positive health effect [36]. WHO recommended that drinking water should contain 0.5-1.0 mg/l fluoride, as it helps to prevent dental caries and specially effective on children with developing teeth [33]. When teeth are fully developed fluoride still helps to protect the teeth. It also dissolves in the saliva and helps to repair teeth that have been attacked by dental caries. The fluoride can also attach to the surface of the teeth and then be released to help and protect the teeth when needed [33]. The negative effects on excessive ingestion of fluoride over a long period of time will lead to a chronic fluoride poisoning; fluorosis. The first sign of fluorosis is generally mottling of teeth. At first the spots are white but with time and more exposure to fluoride the spots will turn into brownish discolouration. These signs are observed when drinking water contains 1.1-2.0 mg/l fluoride [37]. If the fluoride concentration is above 2.5 mg/l the enamel will cease to be smooth and the brownish mottling will spread to larger area of the teeth. If the drinking water has a fluoride concentration of 3-6 mg/l deformation of bones, skeletal fluorosis, can be observed [38].

It is observed that people from the study area consume non-potable water, which has fluoride contamination and probably because of it people are suffering from yellow, cracked teeth and joint pains. During this survey it was found that males and children (12-16 years age group) have a higher occurrence of dental fluorosis, above this age gradual decrease in the prevalence was observed in this region. Very few are exempted in this region from being affected by fluoride contamination in water, irrespective of the category children, adult, young men, women and elderly people. Even toothpaste and brush could not help them in removing the mottling. These results in deteriorated self esteem of the locals with which they do not even open their mouth to talk and even to throw a smile. There is no paste or physician that could help them, and so that people are stigmatized as 'yellow teethed'. Above all the problem of getting married is disgusting as young men who come to see women just refuse to marry them as they have mottling.

5. Conclusion

The range of fluoride contents in water samples of this area falls under the safe limit (bone development and prevent dental caries) and "Dental fluorosis" (discoloration mottling and pitting teeth) limit. The excess fluoride concentration in this area may be attributed to the geological formation and release of industrial pollutants and municipal waste. The fluoride content present in water is causing serious environmental degradation. The social impact of dental fluorosis amounts from personality disorder as mottling deprives one of their self confidence and users self contempt.

6. Recommendations

There are several options available for providing fluoride-free water to the people of this area. People can harvest rain water from their own rooftop for meeting the drinking and cooking requirements. Building of large number of groundwater recharge structures for diluting the fluoride levels in aquifers at appropriate locations are another option to minimise the problem. A government based common treatment plant will have to be installed to supply fluoride free water for public. Conducting awareness programmes and educating people on fluorosis and promotion of calcium and phosphorus rich diet are recommended which are directly associated with a reduced risk of dental fluorosis. Vitamin C ingestion also safeguard against the risk of fluorosis. Apart from this, free medical camps can be arranged to provide right treatment to the victims.

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