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Fluoride contamination in drinking water in rural habitations of Central Rajasthan, India

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Abstract Fluoride concentration in groundwater sources used as major drinking water source in rural area of block Nawa (Nagaur District), Rajasthan was examined and the toxic effects by intake of excess fluoride on rural habitants were studied. In block 13, habitations (30%) were found to have fluoride concentration more than 1.5 mg/l (viz. maximum desirable limit of Indian drinking water standards IS 10500, 1999). In five habitations (11%), fluoride concentration in groundwater is at toxic level (viz. above 3.0 mg/l). The maximum fluoride concentration in the block is 5.91 mg/l from Sirsi village. As per the desirable and maximum permissible limit for fluoride in drinking water, determined by World Health Organization or by Bureau of Indian Standards, the groundwater of about 13 habitations of the studied sites is unfit for drinking purposes. Due to the higher fluoride level in drinking water, several cases of dental and skeletal fluorosis have appeared at alarming rate in this region. There is an instant need to take ameliorative steps in this region to prevent the population from fluorosis. Groundwater sources of block Nawa can be used for drinking after an effective treatment in absence of other safe source. The evaluation of various defluoridation methods on the basis of social and economical structure of India reveals that the clay pot chip, activated alumina adsorption, and Nalgonda techniques are the most promising.

Keywords Drinking water · Groundwater · Fluoride · Fluorosis · Defluoridation · Nawa · Nagaur · Rajasthan

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Introduction

The groundwater contains variety of substances in different concentration either in suspension or in solution (Day 1987; Hussain 2001). Fluoride is an essential microelement for human health. Smaller quantities (<1.0 mg/l) in drinking water are usually considered good to have a beneficial effect on the rate of occurrence of dental carries, particularly among children (WHO 1997; Hussain et al. 2004, 2010). On the other hand, due to its strong electronegativity, fluoride is attracted by positively charged calcium ions in teeth and bones. Excessive intake results in pathological changes in teeth and bones, such as mottling of teeth or dental fluorosis followed by skeletal fluorosis (Shusheela 1993; Hussain et al. 2002; USEPA 1995; USPHS 1991; WHO 1984).

Fluorosis is a considerable health problem worldwide, which is afflicting millions of people in many areas of the world, for example East Africa (Nanyaro et al. 1984; Gaciri and Davies 1993; Gizaw 1996), Turkey (Oruc 2003), India (Hussain 2001, 2005; Subba and John 2003; Gupta et al. 2005), southeastern Korea (Kim and Jeong 2005), and northern China (Wang and Reardon 2001).

The permissible limit of fluoride in drinking water is 1.0 mg/l as per WHO (1997). Per day fluoride intake is directly related with the daily water intake. Therefore, in year 1962, USPHS set a range of allowable concentrations for fluoride in drinking water according to the climatic conditions (especially temperature).

Rajasthan is the largest state in India having 342,239 km^2 area with relatively low population density, i.e., 165 persons per square kilometer. According to physiographic divisions, the north and western part of the state is under the Great Plain of north India, while south and middle as well as eastern part is classified under the Peninsular Plateau. In the state, *Thar Desert* occupies about 61% of the total area. Groundwater is a major source for drinking and domestic and irrigation purpose (Census 2001). In groundwater, the natural concentration of fluoride depends on the geological, chemical, and physical characteristics of the aquifer, porosity, and acidity of the soil and rocks, temperature, and the depth of source. It has been observed that low calcium and high bicarbonate alkalinity favor high fluoride content in groundwater. Figure 1 depicts the general mechanism of formation of fluoride.

Many workers (Hussain et al. 2000, 2003, 2005; Gupta et al. 1983; Choubisa et al. 1995) have reported the level of fluoride concentration in different districts of Rajasthan; however, in Nagaur, a centrally located district, no studies have been undertaken yet in the study area with regard to fluoride and fluorosis problem. Therefore, the objective of this study was to investigate the quality of drinking water (underground water) with special reference to the concentration of fluoride in some rural habitations of Central Rajasthan, India.

Fig. 2 Village census code wise concentration of fluoride. **a** Fluoride concentration below 1.0 mg/l. **b** Fluoride concentration between 1.0 and 1.5 mg/l. **c** Fluoride concentration between 1.51 and 3.0 mg/l. **d** Fluoride concentration between 3.01 and 5.0 mg/l. **e** Fluoride concentration above 5.0 mg/l

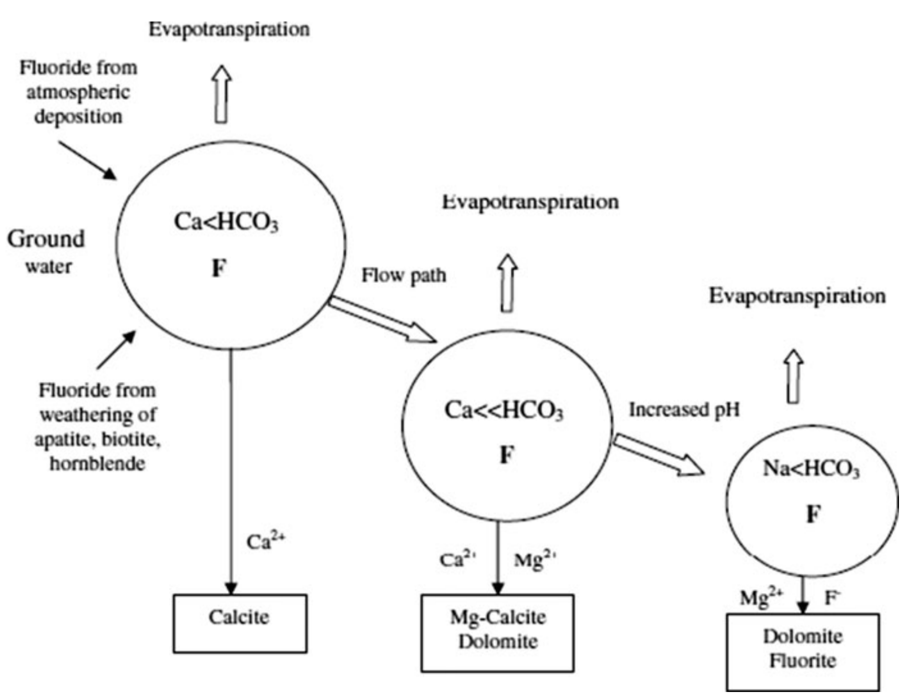
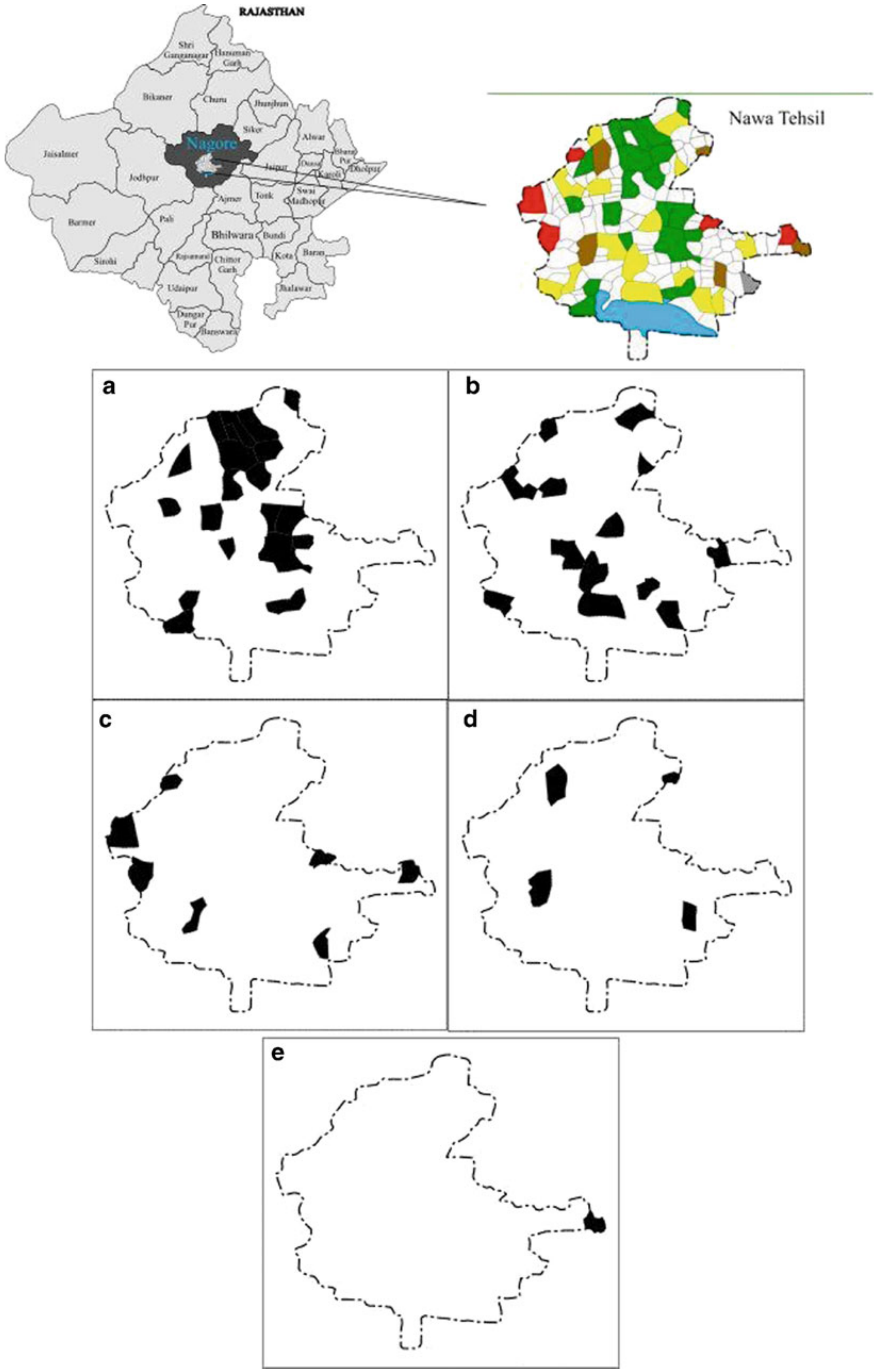


Fig. 1 General mechanism of the formation of fluoride groundwater in India. The figure illustrates the hydrochemical changes and precipitation of secondary minerals as the groundwater flows from recharge areas to discharge areas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Sirohi
Udaipur
Jhalawar
Nawa Tehsil
a
b
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Material and methods

Groundwater samples of 44 habitations located in Nawa block of Nagaur District were collected in pre-cleaned polythene bottles following standard sampling techniques. The fluoride concentration in water was determined electrochemically, using fluoride ion-selective electrode (APHA 1991). This method is applicable to the measurement of fluoride in drinking water in the concentration range of 0.01–1,000 mg/l. The electrode used was an Orion fluoride electrode, coupled to an Orion electrometer. Standards fluoride solutions (0.1–10 mg/l) were prepared from a stock solution (100 mg/l) of sodium fluoride. As per experimental requirement, 1 ml of total ionic strength adjusting buffer grade III (TISAB III) was added in 10 ml of sample. The ion meter was calibrated for a slop of −59.2±2. The composition of TISAB solution was 385.4 g ammonium acetate, 17.3 g of cyclohexylene diamine tetraacetic acid, and 234 ml of concentrate hydrochloric acid per liter. All the experiments were carried out in triplicate and the results were found reproducible with ±2% error. A general observation was also conducted with respect to the incidence of dental and skeleton fluorosis.

Study area

Nagaur District is located at latitude 26°25′ to 27°40′ N and longitude 73°18′ to 75°15′ E. Its average elevation is about 300 m, ranging below 250 m in the south and 640 m in the north. There are 1,396 habitations in the district. The main lithological units include gneisses, schists, granites, quartzites, phyllites, and limestones belonging to the Bhilwara and Delhi Supergroup of rocks of Archaean and Proterozoic ages, respectively. Although groundwater occurs mainly under water table condition in all the formations, the quaternary alluvium forms good aquifers in Nagaur District. In hard rock terrain, the occurrence and movement of groundwater are controlled by secondary porosity such as fractures, fissures, joints, foliation, etc.

Results and discussion

Fluoride concentration in groundwater of 44 habitations of Nawa block was examined. The village census code wise concentration of fluoride is shown in Fig. 2a–e. All the habitations were categorized according to following concentration range (Table 1):

Category I Fluoride concentration below 1.0 mg/l
Category II Fluoride concentration between 1.0 and 1.5 mg/l
Category III Fluoride concentration between 1.5 and 3.0 mg/l
Category IV Fluoride concentration between 3.0 and 5.0 mg/l, and
Category V Fluoride concentration above 5.0 mg/l.

The distribution of fluoride in the groundwater of Nawa block is shown in Fig. 2a–e. Fluoride concentration ranges from 0.3 to 5.9 mg/l. The minimum concentration was recorded for Rajliya village while maximum concentration was recorded from Sirsi village (5.9 mg/l). Data on the concentration of fluoride in different samples of Nawa block indicate that maximum habitations have fluoride concentration between 0.4 and 1.5 mg/l (Fig. 3). The present investigation reveals that 19 habitations (43%) fall in category I (Fig. 2a) in which fluoride concentration is below 1.0 mg/l, a maximum desirable limit of standards for drinking water recommended by Bureau of Indian Standard (BIS) in IS 10500 (1991). There is no possibility of fluorosis in these habitations because this concentration of fluoride is beneficial for calcification of dental enamel especially for children below 10 years of age. Once fluoride is incorporated into teeth, it reduces the solubility of the enamel under acidic conditions and thereby provides protection against dental carries.

Out of 44 habitations of Nawa block, 13 habitations (30%) have fluoride concentration between 1.0 and 1.5 mg/l and fall in category II (Fig. 2b). The maximum permissible limit of fluoride in standard for drinking water is 1.5 mg/l (IS 10500; BIS 1991). In 32% population of these habitations, fluoride intake through drinking water is more than 4 mg/day in an individual. Therefore, an incidence of first and second degree dental fluorosis is possible in local residents of these habitations (Fig. 4).

About 17% of population of 7 habitations (16%) consumes water with fluoride concentration between 1.5 and 3.0 mg/l, which is above the maximum permissible limit as recommended by BIS (Fig. 2c). Therefore, dental fluorosis is common in these habitations. At this

Table 1 Fluoride categorization of villages of Nawa Tehsil

Category I (below 1.0 mg/l)	Category II (above 1.0 mg/l and below or equal to 1.5 mg/l)	Category III (above 1.5 mg/l and below or equal to 3.0 mg/l)	Category IV (above 3.0 mg/l and below or equal to 5.0 mg/l)	Category V (above 5.0 mg/l)
Chawandiya (0.92)	Parewadi (1.44)	Karkeri (2.40)	Ghandi gram (3.12)	Sirsi (5.91)
Adaksar (0.73)	Lalas (1.08)	Rasal (1.73)	Sargoth–Padampura (4.20)	
Todas (0.81)	Kotra (1.32)	Rooppura Torda (2.11)	Piprali (4.12)	
Nalot (0.75)	Jiliya (1.14)	Shyamgarh (2.25)	Thikariya Khurd (4.21)	
Charanwas (0.72)	Panchwa (1.23)	Kooni (2.13)		
Chitawa (0.52)	Rewasa (1.31)	Mindha (2.01)		
Sabalpura (0.51)	Lichana (1.21)	Prempura (3.03)		
Aspura (0.79)	Panchota (1.25)			
Gogor (0.57)	Mandawara (1.06)			
Bhanwata (0.61)	Kasari (1.10)			
Ulana (0.41)	Govindi (1.05)			
Kukanwali (0.88)	Bhatipura (1.07)			
Nagwara (0.82)	Deoli (1.42)			
Rajliya (0.33)				
Nuwana (0.62)				
Maroth (0.55)				
Jeenwar (0.74)				
Bawali gurha (0.45)				
Nanana (0.91)				

concentration, teeth lose their shiny appearance and chalky black, gray, or white patches develop known as mottled enamel (Dean 1942). In some cases, the pre-stage of skeletal fluorosis may occur after 45 years of age (Ziauddin 1974). In four habitations (9%), fluoride concentration in groundwater is above 3.0 mg/l and below 5.0 mg/l, and this fall in category IV (Fig. 2d). The intake of fluoride per day by an adult in these habitations is very high. About 6% population of these habitations may have all degree of dental fluorosis (mild, moderately, moderately severe, and severe fluorosis) including skeletal fluorosis after 30 years of age. However, the probability of second stage skeletal fluorosis age may be common after the age of 45 (Olsson 1979). In the entire survey, Sirsi was the only village that falls in category V (Fig. 2e), which contributes 1% population of Nawa block (Fig. 4). In this village, fluoride concentration is above 5.0 mg/l, which may result in all types of fluorosis among inhabitants. In the second clinical stage, the affected persons may have pain in bones, which causes further calcification in ligaments. It has been reported that such persons may suffer from stiffness in joints. At this concentration, the vertebrae partially fuse together crippling the patient which is known as "crippling skeletal fluorosis". A detailed survey of health hazards particularly fluorosis-induced symptoms and empirical data on affected population are required in Nawa.

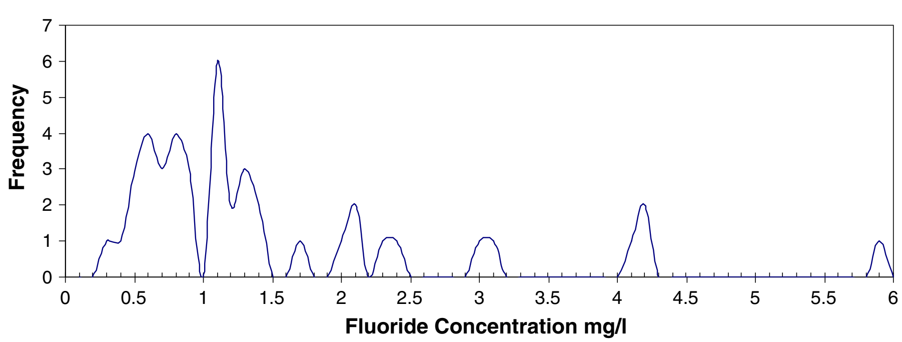

Fig. 3 Fluoride concentration in Nawa block (Nagour), Rajasthan

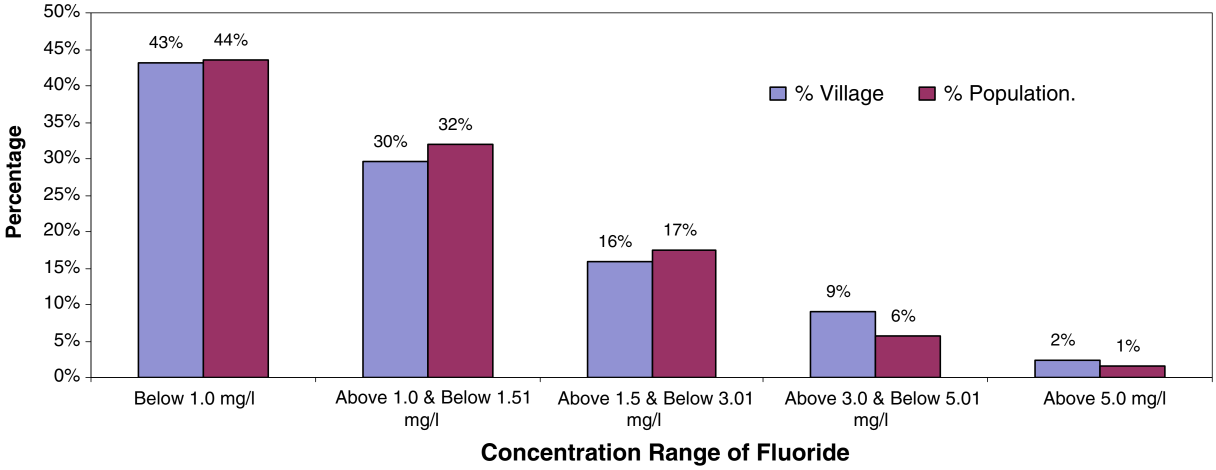

Fig. 4 Percentage distribution of village and population in various concentration range

Control and prevention of fluoride and fluorosis

The lack of resources and low-cost efficient technology acceptable to the affected populations restrict the development of an effective fluoride and fluorosis control and prevention program in developing countries. Precipitation and adsorption are most preferred methods for the defluoridation. Precipitation process is based on the addition of chemicals and removal of insoluble compounds as precipitates. A comparative account of various common defluoridation methods has been summarized in Table 2; many of these methods are discussed in detail by Heidweiller (1990) and references within. Nalgonda technique of community defluorida-

Table 2 A comparative accounts of fluoride removal methods from drinking water

Removal method	Capacity/dose	Working pH	Interferences advantages	Disadvantage	Relative cost
Precipitation alum	150 mg/mg F^-	Nonspecific	Established process	Sludge produced, treated water is acidic, residual Al present	Medium–high
Lime	30 mg/mg F^-	Nonspecific	Established process	Sludge produced, treated water is alkaline	Medium–high
Alum + lime (Nalgonda)	150 mg alum+7 mg lime/mgF$^-$	Nonspecific, optimum 6.5	Low tech, process	Sludge produced, high-chemical dose, residual Al present	Medium–high
Gypsum + fluorite	5 mg gypsum+<2 mg fluorite/mg F^-	Nonspecific	Simple	Requires trained operators, low efficiency, high residual Ca^{2+}, SO_4^{-2}	Low–medium
Adsorption activated carbon	Variable	<3	Many	Large pH changes before and after treatment	High
Plant carbon	300 mg F^-/kg	7	Locally available	Requires soaking in potassium hydroxide	Low–medium
Zeolite	100 mg F^-/kg	Nonspecific	–	Poor capacity	High
Defluoron-2	360 gF^-/m^3	Nonspecific	Alkalinity	Disposal of chemicals used in resin regeneration	Medium
Clay pots	80 mg F^-/kg	Nonspecific	Locally available	Low capacity, slow	Low
Activated alumina	1,200 gF^-/m^3	5.5	Alkalinity effective, well-established	Needs trained operators, chemicals not always available	Medium
Bone	900 gF^-/m^3	>7	Arsenic locally available	May give taste, degenerates, not universally accepted	Low
Bone char	1,000 gF^-/m^3	>7	Arsenic locally available, high capacity	Not culturally accepted	Low
Other electrodialysis	High	Nonspecific	Turbidity can remove other ions. Used for high salinity	Skilled operators high cost. Not widely used	Very high
Reverse osmosis	High	Nonspecific	Turbidity can remove other ions. Used for high salinity	Skilled operators high cost	Very high

tion is the most common available method in India, which is based on precipitation process. Although it is a very efficient and cost-effective technique, the main limitations of this technique are daily additions of chemicals, large amount of sludge production, and least effective with water having high TDS and high hardness (Apparao et al. 1990). Furthermore, it converts a large portion of ionic fluoride (67–87%) into soluble aluminum complex and practically removes only a small portion of fluoride in the form of precipitate (18–33%). The risk of secondary contamination by metal ions such as aluminum and the search for simple, low-cost methods has sustained to use local materials as adsorbent (Table 2). This material includes the use of plant residue such as coconut shell carbon (Arulanantham et al. 1992), activated alumina (Kumar 1995), chemically activated carbon (Muthukumaran et al. 1995), bone media and clay (Heidweiller 1990), fishbone charcoal (Killedar and Bhargava 1993), natural zeolites (Shrivastava and Deshmukh 1994), burnt clay (Karthikeyan et al. 1999), and other low-cost adsorbents. Although the low-cost defluoridation methods have received increasing attention, these are not yet technically feasible and culturally acceptable. Although based on the field test, economical evaluation and religious consideration clay pot chip, activated alumina adsorption, and Nalgonda methods seem more promising for defluoridation in India.

Provisions of alternative water sources such as the delivery of water from low fluoride sources have also been considered for fluorosis prevention strategies. A major problem in the delivery of water from low fluoride sources and defluoridated water is the scarcity of piped distribution systems in rural communities. Construction of piped networks for the purpose of distributing alternative water supplies initially may cost more than the defluoridation but it is economically feasible during the operation and maintenance phases in the absence of treatment systems. Furthermore, it is suggested that the sources of municipal water supply must be established in a region where adequate levels of fluoride have been observed (Ravindra and Garg 2006). One more way to avoid excessive fluoride intake is rainwater harvesting. The dilution of high fluoride water with rainwater will make small amount of rainwater to last long.

Community participation has been identified as an important factor in the success and sustainability of community water programs. Motivating local people to participate in community-based fluorosis prevention efforts has been difficult due to a combination of the chronic nature of fluorosis, lack of awareness of its progressive course and irreversible pathology, and the general deficiency and failure of fluorosis control programs.

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