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Fluoride in drinking water and human urine in Southern Haryana, India

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Abstract

The objective of this study was to determine the fluoride content in drinking water and urine samples of adolescent males aged 11–16 years living in Southern Haryana, India. A total of 30 drinking water sources in the studied habitations were assessed for fluoride contamination. Fluoride was estimated in the urine of 400 male children randomly selected from these habitations. The fluoride concentration in drinking water and urine samples was determined using USEPA fluoride ion selective electrode method. The mean fluoride concentration in drinking water samples of Pataudi, Haily Mandi and Harsaru villages was 1.68 ± 0.35, 3.22 ± 1.18 and 1.78 ± 0.12 mg/l, respectively. The mean urinary fluoride concentration was 2.26 ± 0.024 mg/l at Pataudi, 2.48 ± 0.77 mg/l at Haily Mandi and 2.43 ± 0.84 mg/l at Harsaru village. The higher fluoride levels in the urine of children may be associated to higher fluoride levels in drinking water. The accuracy of measurements was assessed with known addition method in water and urine. Mean fluoride recovery was 98.0 and 99.1% in water and urine. The levels obtained were reproducible with in ±3% error limit.

Keywords: Fluoride; Children; Urine; Drinking water; Estimation; TISAB; Ion selective electrode

1. Introduction

Fluoride is an essential microelement for human health. Smaller quantities in the order of 1.0 mg/l in ingested water are usually considered good to have a beneficial effect on the rate of occurrence of dental carries, particularly among children [1]. 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 [2]. Along with it metabolic changes have been reported on soft tissues such as thyroid, reproductive organs, brain, liver and kidneys. Fluoride may cause an increase in the concentration of thyroid stimulating hormone (TSH) and a decrease in the concentration of T3 and T4 hormones in the thyroid gland resulting in hypothyroidism [3]. Adverse effects on reproductive potential of humans have also been reported [4]. The levels of mental work capacity and the intelligence quotient of children who were born and raised in fluorosis endemic area have been reported lower than normal [5].

Traditionally fluorosis has been connected with higher intake of fluoride through drinking water. High fluoride concentration may be found in ground water especially in areas with volcanic rocks [6]. According to WHO [1] permissible limit for fluoride in drinking water is 1.0 mg/l, whereas, USPHS [7] has set a range of allowable concentrations for fluoride in drinking water for a region depending on its climatic conditions because the amount of water consumed and consequently the amount of fluoride ingested being influenced primarily by the air temperature. Lesan [8] suggests a limit of fluoride in drinking water as low as 0.6 mg/l under tropical conditions.

Several methods are available to assess the fluoride exposure to human beings. But it is generally accepted that the best indicator of fluoride exposure is the urinary fluoride concentration in the population under investigation [9]. Fluoride levels in urine and hair of occupationally exposed persons and children living in the vicinity of phosphate fertilizer waste were directly proportionate to the fluoride levels in drinking water [10]. It has also been reported that dental fluorosis and fluoride content of enamel, plaque, saliva, urine, nails and hairs are directly related to fluoride levels of drinking water and dietary fluoride intake [11]. The purpose of this investigation was to measure and compare the urinary fluoride levels in adolescent children in a study of the health effects of chronic fluoride exposure from drinking water. We used an ion selective electrode method to determine

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fluoride in drinking water and urine samples. This paper reports the fluoride levels in drinking water sources from three habitations in Southern Haryana (India) and also urinary fluoride levels in children from these habitations.

2. Experiments

2.1. Site specifications and sampling

Study area is situated in Gurgaon district in Southern-East part of Haryana state (Fig. 1). It is bounded in north by Union Territory of Delhi, in west by Rohtak district (Haryana), in east by Mohindergarh district (Haryana) and) in south by Faridabad district (Haryana). The study area lies between longitudes 76°40′ and 77°10′ and between latitudes 27°37′ and 28°30′. The climate of the study area is semi-arid with extreme temperature conditions in summer and winter. Summer spans over April to July and October have moderate temperature conditions. Summer is typified by strong dusty winds.

It has been reported that rocks of Ajaib Garh series form the basement in the eastern part of the study area. The maximum thickness of the alluvium is 238 m which thins out towards the northern part. In the western part around Pataudi Tehsil, the thickness varies around 175–203 m. The unconsolidated alluvium forms the principal aquifer.

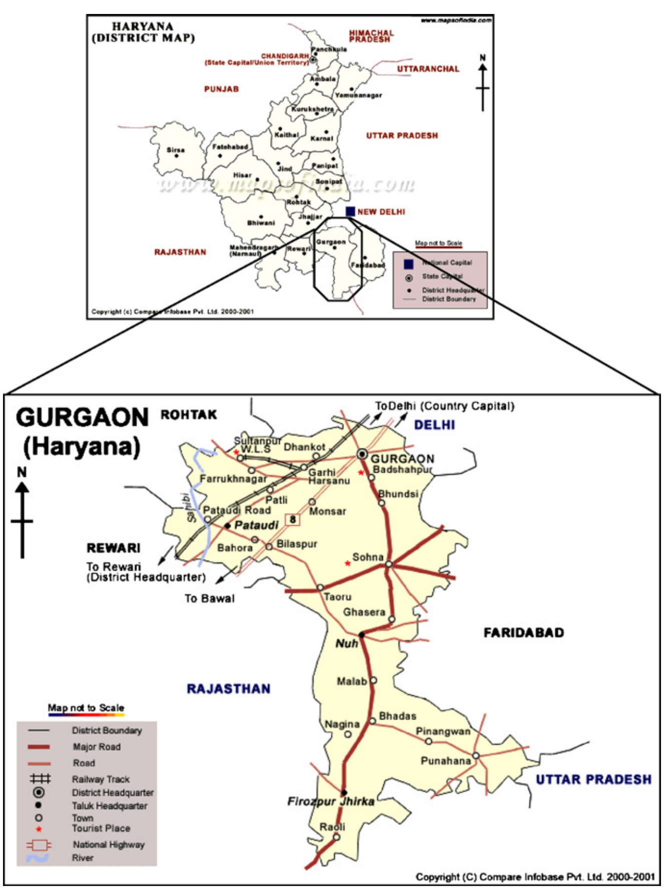

Fig. 1. Location map of study area.

2.2. Water samples

The study area included three villages namely, Pataudi, Haily Mandi and Harsaru in Gurgaon district (Haryana), India. Water samples were collected from 30 different groundwater sources in the month of April to July. Groundwater is the main water source available to the residents of these villages. It is extracted either by hand pumps or tube-wells. The samples were collected after the extraction of water either from privately owned (manually operated hand-pumps) or from electricity operated tubewells (which forms a part of public water supply system of above three habitations). The water was left to run from the sources for about 4–6 min until temperature, conductivity and pH were stabilized. The samples were collected in pre-cleaned, sterilized polyethylene bottles of one litre capacity. The samples were taken by holding the bottle at the bottom to avoid any contamination. The samples were analyzed within 6–12 h after collection [12].

2.3. Urine samples

The first voided urine samples were collected in polyethylene beakers from Pataudi, Haily Mandi and Harsaru villages in the month of April to August. The samples were collected from 418 male school children in the age group of 11–16 years and analyzed on the spot for fluoride concentration. The total number of male school children in the study area was 1654. The urine samples of female children were not made available by the residents of these villages to the authors due to social customs of the study area. Eighteen samples were discarded due to the doubt of contamination at the time of sampling.

2.4. Methodology

The fluoride concentration in water was determined electrochemically, using the USEPA ion selective electrode method. This method is applicable to the measurement of fluoride in drinking water in the concentration range of 0.1–1000 mg/l [13]. The electrode used was an Orion 96-09 fluoride electrode, coupled to an Orion 420 A electrometer. Standards solutions (0.1–10 mg/l) were prepared from a stock solution (100 mg/l) of sodium fluoride. To estimate the fluoride in urine, the method reported by Czarnowaski and Krechnike [10] was followed. Fluoride concentration in the urine samples was determined as given above for water samples. The urines samples were diluted with equal volumes of total ionic strength adjustment buffer (TISAB) of pH 5.2 before fluoride estimation. The composition of TISAB solution was as follows: 58 g NaCl, 4 g of CDTA (Cyclohexylene diamine tetraacetic acid) and 57 ml of glacial acetic acid per litre.

Analytical grade chemicals were used throughout the study without further purification. To prepare all the reagents and calibration standards, double glass distilled water was used. Each sample was analyzed thrice and the results were found reproducible within ±3% error. For quality control purposes, known addition method was used together with the collected water as well as urine samples [14]. Mean fluoride recovery was 98.0% in water samples and 99.1% in urine samples. The analytical results were used as input for special package for social sciences (SPSS) for statistical analysis [15].

3. Results and discussion

Haryana is a relatively smaller state of the Indian Union. The total geographical area of the state is 44212 km^2 which constitutes 1.4% of the country's geographical area. The state is bounded in the north by Shivalik hills and in the south and southwest by Aravalli hills. The study area has undulating landscape. The central region is more or less a plain Indo-Gangatic area. The river Yamuna flows along the eastern boundary of Haryana and is the only perennial river of the state. The average population density of state is 478 km^{-2}. Haryana state is in disadvantageous position with regard to rainfall pattern, surface water quantum and groundwater quality. On an average, the state receives 545 mm rainfall annually, as compared to the environmental requirement of 1550 mm.

Fluorine is the 13th most abundant element in earth's crust. Human body is exposed to fluoride mainly through consumption of water. Fluoride enters the human body through gastrointestinal tract and remains there as hydrofluoric acid. Table 1 shows the number of ground water samples and their fluoride concentration. The fluoride concentration ranged from 0.95 to 2.42 mg/l at Pataudi, 1.90–5.20 mg/l at Haily Mandi and 1.65–1.90 mg/l at Harsaru, respectively. The maximum acceptable concentration of fluoride in drinking water may be extended to 1.5 mg/l if alternative source of water is not available, while in present study 87% of the samples exceeded the maximum permissible limit. Fluoride could have originated from fluoride bearing minerals such as fluorite in the rocks. Apambire et al. [16] have suggested that the main source of ground water fluoride in granitic rocks is the dissolution and anion exchange with micaceous minerals and their clay products. Presence of fluoride bearing minerals in the host rocks and their interaction with water is considered to be the main cause for fluoride in ground water. The decomposition, dissociation and dissolution are the main chemical processes for the occurrence of fluoride in ground water. During rock water interaction, concentration of fluoride in rocks, aqueous ionic species and residence time of interaction are also important parameters [17]. The geological formation in the study area ranges from pre-Cambrian to recent times. Aravalli system is the oldest formation present in the study area. They are composed of quartzite sandstone, mica schists, phyllites, silica sand, china clay, ordinary sand, crystalline limestone etc [18].

In the summer the temperature ranges in study area from 25 to 45 °C and a higher ingestion of water is expected. According to the recommendations from the World Health Organization, the optimal concentration of fluoride in drinking water should be 0.5–0.7 mg/l in regions with extreme climates [19]. Taking into account the BIS recommended fluoride concentration (1.5 mg l^{-1}) in drinking water, people in such habitations be advised to adopt some defluoridation technique prior to use of groundwater for drinking purposes. Another problem for the people living in study area is the availability of drinking water from electricity operated tubewells which forms the part of public water supply and as observed before these sources contain higher levels of fluoride. Only at four sampling points, the fluoride concentration was lesser than 1.5 mg l^{-1}.

The authors have observed that water consumption is approximately 2.5 l per children per day during the months of April to August. If we take average fluoride concentration in the different water sources into consideration then the fluoride intake by children from ingested water could be 4.20, 4.45 and 8.05 mg fluoride/person/day at Pataudi, Harsaru and Haily Mandi villages, respectively. These values are higher than the recommended fluoride intake from the diet by a person. It has been observed that absorption of fluoride from water ranges from 86 to 97% [20]. The dietary fluoride allowances are in the range of 0.1 to 1.0 mg/person/day for children under the age of one year; 0.5 to 1.5 mg/person/day for children between one and three; up to 2.5 mg/person/day for children under 12 and 1.5–4.0 mg/person/day for adults [21]. It is evident from the results that the people in study area are chronically exposed to higher levels of fluoride from drinking water. The problem is further aggravated by the fact that the residents of the study area neither have access to bottled water nor economically so well off that they can afford the bottled water.

Table 1
Fluoride content in drinking water samples of study area (mg F^-/l)

Sample no.	Pataudi	Haily Mandi	Harsaru
1	1.60	2.35	1.90
2	2.42	2.20	1.65
3	2.12	4.00	1.80
4	1.60	3.90	
5	1.10	2.35	
6	1.71	1.90	
7	1.20	5.20	
8	1.44	3.90	
9	1.71		
10	0.95		
11	1.71		
12	1.90		
13	1.52		
14	1.90		
15	1.80		
16	1.80		
17	1.90		
18	1.90		
19	1.71		
Range	0.95–2.42	1.90–5.20	1.65–1.90
Mean	1.68	3.22	1.78
±S.D.	0.35	1.180	0.125

Table 2
Urinary fluoride concentration in the study area

Village	Fluoride		*n*	±S.D.
	Range (mg/l)	Mean (mg/l)		
Pataudi	1.00–3.20	2.261	200	0.024
Haily Mandi	0.90–3.25	2.482	100	0.770
Harsaru	1.00–3.15	2.430	100	0.845
Total	0.90–3.25	2.358	400	0.486

Table 3
Age dependent urinary fluoride concentration in children from study area (mg F^{-}/l)

Village	Age (years)				
	11	12	14	15	16
Pataudi					
Range	1.05–3.20	1–3.15	1.60–3.15	1.10–3.10	1–3.15
Mean	2.26	2.13	2.17	2.33	2.19
±S.D.	0.08	0.07	0.03	0.056	0.332
n	40	40	40	40	40
Haily Mandi					
Range	1.10–3.00	0.90–3.25	1–3.10	1.40–3.00	1–2.90
Mean	2.16	2.20	1.98	2.29	2.85
±S.D.	0.676	0.640	0.590	0.446	3.617
n	20	20	20	20	20
Harsaru					
Range	1.15–3.10	1–3.00	1.10–3.15	1–2.65	1–3.00
Mean	2.19	2.09	2.25	1.76	2.00
±S.D.	0.540	0.713	0.641	0.425	0.629
n	20	20	20	20	20

Human body is exposed to fluoride through other edible products also. Ingestion pattern of fluoride varies for each product. Only a fraction of these is ingested in the body. Levels of fluoride in tea, toothpaste, tobacco and pan masala have been reported by other workers [20]. Tea exposes human body to 3.88–137.09 μg of fluoride per gram of tea and the same quantity of toothpaste exposes the human body to 53–338 μg of fluoride. The range of exposure varies 28–113 $\mu g\, g^{-1}$ with a mean value of 75 $\mu g\, g^{-1}$ for tobacco, while it was 16- 306 $\mu g\, g^{-1}$ with a mean value of 114 $\mu g\, g^{-1}$ for pan masala with tobacco.

The persons, who are not exposed to excessive levels of fluoride, the fluoride concentration in their urine is usually in the range of 1.0–1.5 mg/l [22]. Urinary fluoride concentrations in the urine of the children of Pataudi, Haily Mandi and Harsaru villages are given in Table 2. The mean urinary fluoride concentration at Pataudi was 2.26 ± 0.024 mg/l; at Haily Mandi was 2.48 ± 0.77 mg/l and at Harsaru was 2.43 ± 0.84 mg/l. The mean urinary fluoride concentration of children from all the three habitations was significantly higher.

The fluoride content in the studied urine samples ranged from 0.90 to 3.25 mg/l. The results showed that majority of the children had abnormally higher levels of fluoride in urine. For 90% of the children, the urinary fluoride concentration was in the range of 1.0–2.5 mg/l. The mean urinary fluoride excretion was 2.35 ± 0.48 mg/l. This higher fluoride concentration in urine may be associated to the high fluoride content in drinking water in study area. Children from Haily Mandi had maximum urinary fluoride excretion. In addition to this, no age dependent differences in urinary fluoride excretion were found in any of the three habitations (Table 3).

Absorption of fluoride in the body depends on chemical and physical nature of the ingested fluoride. Soluble fluoride present in the food is efficiently absorbed. Fluoride is distributed in plasma, all tissues and other organs in the human body. But the soft tissues do not accumulate fluoride and hence most of the fluoride in the human body (99%) is found in mineralized tissue. Fluoride is incorporated into the crystal lattice structure in the form of fluorapatite or fluorhydroxyapatite [23]. Absorption of fluoride in stomach and small intestine takes place through passive diffusion. Body absorbs sodium fluoride very rapidly during fasting [24]. This is because fluoride in stomach, primarily, present as weak hydrogen fluoride diffuses from the stomach and easily reaches the blood [25]. In plasma, fluoride is transported as ionic fluoride and non-ionic fluoride. Ionic fluoride does not bind to plasma proteins, and is easily excreted with the urine. However, in the form of HF, about 35–45% is reabsorbed and returned to the systemic circulation. pH of tubular fluid and urinary flow are the main factors which influence reabsorption [24,25]. The amount of urinary fluoride excreted from the body reflects the amount of fluoride ingested. A report from WHO [23] has reported that absorbed fluoride is excreted mainly through kidney [23]. It has been documented that the urinary excretion of fluoride (age group 3–6 years) is 32–80% of total fluoride intake [26–28]. The fluoride excreted in faeces, is that fraction which is not absorbed in the body [29].

4. Conclusions

Urinary fluoride concentration is well-established indicator of fluoride intake by individuals and should regularly be estimated to detect the danger of fluoride toxicity in a population. In the present study it is reported that urinary fluoride concentration increases with increasing fluoride concentration in drinking water. The higher fluoride levels in the urine of children from the study area have been linked to a chronic exposure of fluoride from drinking water. Analysis of drinking water from the different sources in this study showed that fluoride concentration in drinking water from Haily Mandi was 3.5 times higher than permissible limit. Groundwater is the only source of drinking water from the study area and entire population is exposed to excessive fluoride. The population of the study area is at a higher risk due to excessive fluoride intake especially when they are unaware of the amount of fluoride being ingested due to lack of awareness.

Chronic exposure to high fluoride in this population represents a concern due to possible health effects from their long-term exposure.

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References

[1] WHO (World Health Organization), Guideline for Drinking Water Quality Health criteria and other supporting information, vol. 2, 2nd ed., World Health Organization, Geneva, 1997.

[2] D. Sarala Kumari, P.R. Rama Krishna, Endemic fluorosis in the village Ralla Anantpuram in Andhra Pradesh: an epidemiological study, Fluoride 26 (1993) 177–180.

[3] D. Raja-Reddy, Handbook of Neurology, North Holland Publishing Co., Amsterdam, 1979, p. 465.

[4] S.C. Freni, Exposure to high fluoride concentrations in drinking water is associated with decreased birth rates, J. Toxicol. Environ. Health 42 (1) (1994) 109–121.

[5] Y. Lu, Z.R. Sun, L.N. Wu, X. Wang, W. Lu, S.S. Liu, Effect of high fluoride water on intelligence in children, Fluoride 33 (2) (2000) 74–78.

[6] H. Kloos, R. Tekle-heinanot, Fluorosis, in: H. Kloos, Z.A. Zein (Eds.), The Ecology of Health and Disease in Ethiopia, West View Press, Oxford, 1993, pp. 455–462.

[7] USPHS (United State Public Health Service), Drinking Water Standard-1962, USPHS, Publication 956, USGPO, Washington, DC, 1962.

[8] W.R. Lesan, Dental fluorosis: A review of literature with comments on tropical characteristic, E. Afr. Med. J. 64 (1987) 493–497.

[9] M. Watanable, K. Kono, Y. Orita, T. Dote, K. Usuda, Y. Takahashi, Influence of dietary fluoride intake on urinary fluoride concentration and evaluation of corrected levels in spot urine, in: Proceedings of the 20th Conference of the International Society for Fluoride Research, September 5–9, Beijing, China, 1994, p. 246.

[10] W. Czarlowski, J. Krechniak, Urinary fluoride of school children in Gdansk, Fluoride 35 (2002) 239–243.

[11] A. Ruiz-Payan, M. Ortiz, M. Duarte-Gardea, Determination of fluoride in drinking water and in urine of adolescents living in three countries in Northern Chihuahua Mexico using a fluoride ion selective electrode, Microchem. J. 81 (2005) 19–22.

[12] R. Khaiwal, V.K. Garg, Distribution of fluoride in groundwater and its suitability assessment for drinking purpose, Int. J. Environ. Health Res. 16 (2006) 163–166.

[13] USEPA, Methods for Chemical Analysis of Water and Wastes, Fluoride, Environmental Protection Agency (EPA), Cineinnati, OH, 1991.

[14] M.M.M. Delgado, A.H. de la Torre, R.A. Marante, Direct potentiometric determination of fluoride in beverages. Comparative study of different buffering solutions, Food Chem. 46 (1993) 85–88.

[15] M.J. Norusis, SPSS for Windows Professional Statistics 7.5, SPSS Inc./Prentice Hall, Englewood Cliffs, 1997.

[16] W.B. Apambire, D.R. Boyle, F.A. Michel, Geochemistry, genesis, and health implications of fluoriferous ground waters in the upper regions of Ghana, Environ. Geol. 33 (1997) 13–24.

[17] V. Saxsena, S. Ahmed, Inferring the chemical parameters for the dissolution of fluoride in ground water, Environ. Geol. 43 (2003) 731–736.

[18] A. Singh Study of Subsurface Isotherm, Sohna Hot-Spring Area, Gurgaon district, Haryana, Geothermal Energy in India, Geological Survey of India Special Publication No. 45, 1996.

[19] J. Murray, Appropriate Use of Fluoride for Human Health, World Health Organization, Ginebra, 1986, p. 3.

[20] A.K. Yadav, C.P. Kaushik, A.K. Haritash, B. Singh, S.P. Raghuvanshi, A. Kansal, Determination of exposure and probable ingestion of fluoride through Tea, Toothpaste, Tobacco and Pan Masala, J. Hazard. Mater. 142 (2007) 77–80.

[21] NRC (National Research Council), Recommended Dietary Allowances, 10th ed., NRC (National Research Council), 1989, p. 239.

[22] WHO, Fluorine and Fluorides, Environmental Health Criteria 36, WHO, Geneva, 1984.

[23] World Health Organization, Fluorides and Oral Health, Report of WHO Expert Committee on Oral Health Status and Fluoride Use, WHO, Geneva, 1994.

[24] J. Ekstrand, Relationship between fluoride in the drinking water and the plasma fluoride concentration in man, Caries Res. 12 (1978) 123–127.

[25] G.M. Whitford, D.H. Pashley, G.I. Stringer, Fluoride renal clearance: a pH-dependent event, Am. J. Physiol. 230 (1976) 527–532.

[26] M. Haftenberger, G. Viergutz, V. Neumeister, G. Hetzer, Total fluoride intake and urinary excretion in German children aged 3–6 years, Caries Res. 35 (2001) 451–457.

[27] A. Villa, M. Anabalon, L. Cabezas, The fractional urinary fluoride excretion in young children under stable fluoride intake conditions, Commun. Dent. Oral Epidemiol. 28 (2000) 344–355.

[28] F.V. Zohouri, A.J. Rugg-Gunn, Total fluoride intake and urinary excretion in 4-year old Iranian children residing in low-fluoride areas, Br. J. Nutr. 83 (2000) 15–25.

[29] J. Ekstrand, Fluoride metabolism, in: O. Fejerskov, J. Ekstrand, B.A. Burt (Eds.), Fluoride in Dentistry, Copenhagen, Munksgaard, 1996, pp. 55–68.