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Groundwater quality in some villages of Haryana, India: focus on fluoride and fluorosis

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Abstract

The fluoride concentration in underground water was determined in four villages of Jind district of Haryana state (India) where it is the only source of drinking water. Various other water quality parameters such as pH, electrical conductivity, total dissolved salts, total hardness, total alkalinity as well as sodium, potassium, calcium, magnesium, carbonate, bicarbonate, chloride and sulfate concentrations were also measured. A systematic calculation of correlation coefficients among different physico-chemical parameters was performed. The analytical results indicated considerable variations among the analyzed samples with respect to their chemical composition. Majority of the samples do not comply with Indian as well as WHO standards for most of the water quality parameters measured. The fluoride concentration in the underground water of these villages varied from 0.3 to 6.9 mg/l, causing dental fluorosis among people especially children of these villages. Overall water quality was found unsatisfactory for drinking purposes without any prior treatment except at eight locations out of 60.

Keywords: Fluoride; Fluorosis; Underground water; Drinking water; India

1. Introduction

The problem of excessive fluoride in groundwater in India was first reported in 1937 in the state of Andhra Pradesh [1]. In India, approximately 62 million people including 6 million children suffer from fluorosis because of consumption of water with high fluoride concentrations [2]. Seventeen states in India have been identified as endemic for fluorosis and Haryana is one of them. Though fluoride enters the body through food, water, industrial

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Table 1
Range of maximum allowable fluoride concentrations as per USPHS

Annual average of maximum daily air temperature (°C)	Recommended fluoride concentration (mg/l)			Maximum allowable fluoride concentration (mg/l)
	Lower	Optimum	Upper	
10–12	0.9	1.2	1.7	2.4
12.1–14.6	0.8	1.1	1.5	2.2
14.7–17.7	0.8	1.0	1.3	2.0
17.8–21.4	0.7	0.9	1.2	1.8
21.5–26.2	0.7	0.8	1.0	1.6
26.3–32.5	0.6	0.7	0.8	1.4

exposure, drugs, cosmetics, etc., drinking water is the major contributor (75–90% of daily intake) [3].

Due to its strong electronegativity, fluoride is attracted by positively charged calcium in teeth and bones. The major health problems caused by fluoride are dental fluorosis, teeth mottling, skeletal fluorosis and deformation of bones in children as well as in adults [4].

According to WHO, 1971, permissible limit for fluoride in drinking water is 1.0 mg/l [5], whereas USPHS, 1962 [6] 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 [7–9]. The maximum allowable fluoride concentrations as established by USPHS are shown in Table 1. Accordingly, the maximum allowable concentration for fluoride in drinking water in Indian conditions comes to 1.4 mg/l while as per Indian standards it is 1.5 mg/l.

The major sources of fluoride in groundwater are fluoride-bearing rocks such as fluorspar, cryolite, fluorapatite and hydroxylapatite [10]. The fluoride content in the groundwater is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, temperature, pH, concentration of calcium and bicarbonate ions in water, etc. [11,12].

Excess fluoride affects plants and animals also. The severity of injury is determined by duration of fluoride exposure and concentration. The fluoride concentrations in groundwater in India vary considerably. In some parts of India, the fluoride levels are below 0.5 mg/l, while at certain other places, fluoride levels as high as 30 mg/l have been reported [13]. This study was undertaken to assess the quality of underground water of four villages in the Jind district in Haryana state.

2. Methods and material

2.1. Study area

The state of Haryana is situated between 27.37°N and 30.35°N latitude and 74.28°E and 77.36°E longitude. Haryana has Uttar Pradesh on its eastern border, Punjab on its western border, Himachal Pradesh and Shivalik Hills on its northern border and Delhi, Rajasthan

Fig. 1. Location of Haryana in India.

and Aravali Hills on its southern border as shown in Fig. 1. Jind district lies in the Haryana between 29.03°N and 29.51°N latitude and 75.53°E and 76.47°E longitude as shown in Fig. 2. The area of the district is 3606 km^2.

The study was undertaken in four villages of Jind district, viz. Butani, Karkhana, Malar and Rojala. The total population of these villages is approximately 20,000. In these villages,

Fig. 2. Location of Jind in Haryana.

groundwater is the only source of drinking water. The water is extracted using handpumps. The water table in the study region varies from 2 to 10 m. Geological formations are alluvial type and the soil is sandy-loam. The area is semi-arid with scanty to normal rainfall.

2.2. Water sampling

There are approximately 80–100 handpumps in each village. A total of 15 samples were collected from different locations of each village. The samples were collected in precleaned sterilized bottles and stored in an icebox. The analyses were carried out according to APHA, 1989 standard methods for various physico-chemical parameters [14]. Analyzed parameters were pH, electrical conductivity, total dissolved salts, total alkalinity, total hardness as well as sodium, potassium, calcium, magnesium, carbonate, bicarbonate, chloride, sulfate and fluoride concentrations.

2.3. Reagents and standards

Analytical grade chemicals were used throughout the study without further purification. To prepare all the reagents and calibration standards, double distilled water was used. All the experiments were carried out in triplicate. The results were reproducible within ±3% error limit.

2.4. Methodology

The pH and electrical conductivity of the water were determined on site. The pH was measured using Eutech-Cybernetics pH scan meter. The conductivity was determined using Eutech-Cybernetics EC scan meter. The TDS were calculated using a formula from the United States Salinity Laboratory, 1954 [15]. Sodium, potassium and calcium concentrations were determined using ELICO CL-220 Flame photometer. Total alkalinity and total hardness were measured by titrimetric method using standard sulfuric acid and standard EDTA solutions, respectively. Fluoride was determined spectrophotometrically using ELICO SL-150 ultraviolet spectrophotometer. Sodium fluoride was used to prepare the standard solutions. Sulfate was determined nephalometrically using ELICO CL-52 Nephalometer. Chloride was determined by argentometric titration method. Statistical analysis was carried out using Statistical Package for Social Sciences (SPSS).

3. Results and discussion

The groundwater had no color, odor and turbidity. Taste of the water was slightly brackish at most of the locations.

Analytical data for the water samples are presented in Tables 2–5. In Table 6, a comparison of groundwater quality of the area under study with drinking water standards (Indian and WHO) is presented. The data revealed considerable variations in the water samples with

Table 2
Physico-chemical properties of groundwater at village Bhutani[a]

Sample no.	pH	EC	TDS	TH	TA	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	F^{-}
1	7.66	4.1	2624	356	736	66	46	576	4	0	897	426	580	3.6
2	7.99	3.01	1926	312	777	48	46	456	04	75	796	185	267	2.0
3	7.64	3.78	2419	309	767	61	38	504	8	21	885	236	540	2.6
4	7.55	3.51	2246	577	616	65	100	456	7	0	752	298	570	2.6
5	8.48	3.91	2502	220	710	49	24	504	4	56	752	253	400	4.2
6	7.58	5.73	3667	848	554	90	151	636	9	0	676	787	960	2.2
7	7.62	6.01	3846	594	689	88	91	684	7	0	841	744	980	3.4
8	7.85	7.74	4954	373	596	52	59	188	5	81	562	270	170	2.2
9	8.33	3.76	2406	366	580	53	56	528	5	75	556	364	690	3.4
10	7.68	3.32	2125	265	793	56	30	468	5	31	904	224	567	3.6
11	7.34	4.75	3040	906	694	83	169	516	9	0	847	639	560	2.0
12	7.54	4.21	2694	488	663	74	73	528	10	0	809	440	698	3.28
13	7.66	4.32	2765	343	767	67	43	540	6	31	872	386	980	3.44
14	7.90	7.37	4717	1265	4615	106	243	732	10	68	549	1210	1000	2.36
15	7.73	3.01	1926	227	767	51	24	504	3	0	935	224	280	4.52

[a] All the values are in mg/l, except pH and EC. Units of EC are mmho/cm.

Table 3
Physico-chemical properties of groundwater at village Karkhana[a]

Sample no.	pH	EC	TDS	TH	TA	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	F^{-}
1	8.29	2.03	1299	–	834	40	–	140	0	56	904	31	156	4.76
2	7.87	3.98	2547	370	1031	61	53	470	8	93	1068	270	488	2.98
3	7.93	3.69	2362	322	772	69	36	564	4	56	828	344	700	2.6
4	8.10	6.05	3872	231	1057	85	4	708	6	137	1011	602	1160	2.71
5	7.84	4.16	2662	258	826	63	24	600	4	81	859	349	605	2.84
6	7.79	5.40	3456	200	787	73	4	550	6	68	822	613	638	5.08
7	8.06	1.25	800	126	550	30	13	104	1	68	537	1.5	70	2.28
8	8.07	3.89	2490	251	907	72	17	576	3	81	942	355	622	2.44
9	8.03	7.45	4768	421	953	93	46	840	6	137	885	832	580	1.60
10	7.49	2.95	1888	268	782	62	28	495	4	0	954	210	480	1.74
11	8.38	2.00	1280	–	730	37	–	130	160	56	777	28	260	4.7
12	8.38	1.64	1050	176	632	31	24	116	1	81	607	17	80	2.0
13	7.97	2.02	1293	193	793	42	21	180	3	81	803	99	240	2.32
14	7.95	2.18	1395	214	730	42	26	180	3	37	815	114	250	4.0
15	7.78	6.72	4301	376	601	87	39	720	3	62	607	809	880	0.88

[a] All the values are in mg/l, except pH and EC. Units of EC are mmho/cm.

Table 4
Physico-chemical properties of groundwater at village Malar[a]

Sample no.	pH	EC	TDS	TH	TA	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	F^{-}
1	7.61	7.32	4685	512	696	90	70	648	12	34	780	863	940	2.32
2	7.32	4.76	3046	448	714	70	66	528	04	0	872	412	500	1.04
3	8.05	6.30	4032	448	832	75	63	660	08	73	866	582	860	1.62
4	7.26	11.04	7066	1089	578	182	154	1164	72	0	705	1406	2640	1.48
5	8.26	6.49	4154	–	879	77	–	780	01	85	900	693	660	6.90
6	8.44	6.42	4109	828	592	88	148	720	12	11	700	826	1520	1.32
7	7.78	6.18	3955	454	766	85	59	744	22	73	786	738	780	2.60
8	7.83	5.05	3232	441	630	80	58	612	06	68	631	588	1140	3.36
9	7.93	0.77	493	108	118	14	18	22	00	0	143	17	52	0.30
10	7.14	7.82	5005	848	776	104	142	720	12	68	808	1003	680	1.58
11	7.68	2.34	1498	173	639	43	16	420	06	79	619	222	140	6.70
12	7.34	1.78	1139	332	531	43	55	120	01	90	464	74	240	0.96
13	8.00	5.59	3578	807	550	87	143	624	10	62	845	736	998	3.28
14	7.64	3.40	2176	587	790	57	108	372	56	68	826	284	420	2.04
15	7.91	4.50	2880	238	644	65	19	636	07	56	671	443	840	2.12

[a] All the values are in mg/l, except pH and EC. Units of EC are mmho/cm.

Table 5
Physico-chemical properties of groundwater at village Rojala[a]

Sample no.	pH	EC	TDS	TH	TA	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	F^{-}
1	7.31	9.59	6138	1357	855	158	233	888	24	90	860	1480	1500	2.72
2	7.93	1.27	813	234	400	35	35	98	03	62	361	62	79	3.20
3	7.46	7.87	5037	319	630	102	15	912	03	56	654	1218	660	5.90
4	8.24	1.96	1254	173	362	36	20	141	02	62	315	176	170	3.86
5	7.70	8.51	5446	800	719	112	126	840	12	107	659	1281	1820	4.95
6	8.37	0.66	422	149	193	11	29	20	02	28	178	26	32	0.84
7	7.85	5.76	3686	234	743	86	4	570	07	0	906	719	830	5.50
8	7.88	7.05	4512	539	672	97	72	828	06	45	728	892	1440	2.96
9	8.12	3.44	2202	238	494	56	24	984	03	56	487	324	540	3.72
10	7.30	13.53	8659	1536	855	200	251	1200	33	73	895	2045	3100	5.55
11	7.96	5.40	3456	373	710	79	43	648	05	68	728	608	780	2.38
12	8.43	1.98	1267	197	353	37	25	102	02	45	338	122	230	5.40
13	8.04	1.52	973	217	376	33	33	92	03	39	378	60	200	2.50
14	7.68	5.77	3693	454	597	75	65	612	06	51	625	704	730	2.56
15	8.10	2.03	1299	200	432	43	23	171	02	51	424	185	280	3.10

[a] All the values are in mg/l, except pH and EC. Units of EC are mmho/cm.

Table 6
Comparison of groundwater quality at the villages under study with drinking water standards (Indian and WHO)[a]

Parameters	Values from collected samples			Indian standards		WHO standards
	Minimum	Maximum	Mean	Acceptable	Maximum	
pH	8.48	7.14	7.85	7–8.5	6.5–9.2	6.5–9.2
EC	13.53	0.66	4.67	300	–	–
TDS	8659	422	2987	500	1500	500
TH	1536	108	445	200	600	500
TA	4615	118	741	200	600	–
Ca^{2+}	200	11	68	75	200	75
Mg^{2+}	298	4	72	30	–	150
Na^{+}	1200	20	518	–	–	200
K^{+}	160	0	11	–	–	–
CO_3^{2-}	137	0	52	–	–	–
HCO_3^{-}	1068	143	720	–	–	–
Cl^{-}	2045	1.5	498	200	1000	500
SO_4^{2-}	3100	32	688	200	400	–
F^{-}	6.9	30	3.0	1.0	1.5	–

[a] All the values are in mg/l, except pH and EC. Units of EC are mmho/cm.

respect to their chemical composition. The pH of all the water samples was slightly alkaline. There was a large variation in electrical conductivity even in the samples collected from the same village. According to a salinity classification by Rabinove et al. [16], groundwater was non-saline at five locations, slightly saline at 28 locations and moderately saline at 27 locations (Table 7). According to Durfor and Becker's [17] classification of total hardness,

Table 7
Classification of the water samples on the basis of total dissolved salts

Sample no.	Classification of groundwater	Total dissolved salts (mg/l)	No. of samples
1	Non-saline	<1000	5
2	Slightly saline	1000–3000	28
3	Moderately saline	3000–10000	27
4	Very saline	>10000	–

Table 8
Classification of the water samples on the basis of total hardness

Sample no.	Description	Hardness (mg/l)	No. of samples
1	Soft	0–60	–
2	Moderately hard	61–120	1
3	Hard	121–180	5
4	Very hard	>180	51

water was very hard at all the locations except at one site (Table 8). The calcium content in all the water samples was beyond acceptable limit.

The WHO acceptable limit for alkalinity in drinking water is 200 mg/l. In all the villages, the total alkalinity was higher than the acceptable limit. Carbonate was either absent or present in negligible amounts. Bicarbonate ranged from 143 to 1068 mg/l in these villages. Except at two locations, sodium was higher than the WHO acceptable limit of 50 mg/l. Lower concentration of calcium compared to that of sodium indicated the absence of readily soluble calcium minerals or the action of base exchange, whereby calcium originally present in the water had been exchanged by sodium [18]. Chloride concentration ranged from 1.5 to 2045 mg/l. Except at 15 locations, the chloride content was higher than the WHO acceptable limit. Sulfate concentration varied from 32 to 3100 mg/l and was found to be within acceptable limits only at nine locations.

At most of the locations, fluoride concentration was higher than the permissible limit as evidenced from Fig. 3. At village Butani, all locations had fluoride concentration greater than the permissible limit, whereas at Rojala and Karkhana, only one location in each village had fluoride concentration within the acceptable range. At Malar, six locations had fluoride concentration within acceptable range.

The statistical analysis (Table 9) showed that EC has a positive and significant correlation with TDS, TH, Ca^{2+}, Na^{+}, $SO_4{}^{2-}$ and Mg^{2+}. Total hardness was positively and significantly correlated with Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$ and Cl^{-}. Fluoride was not significantly correlated with any of the studied parameters. The regression equations among the significantly correlated parameters are given in Table 10.

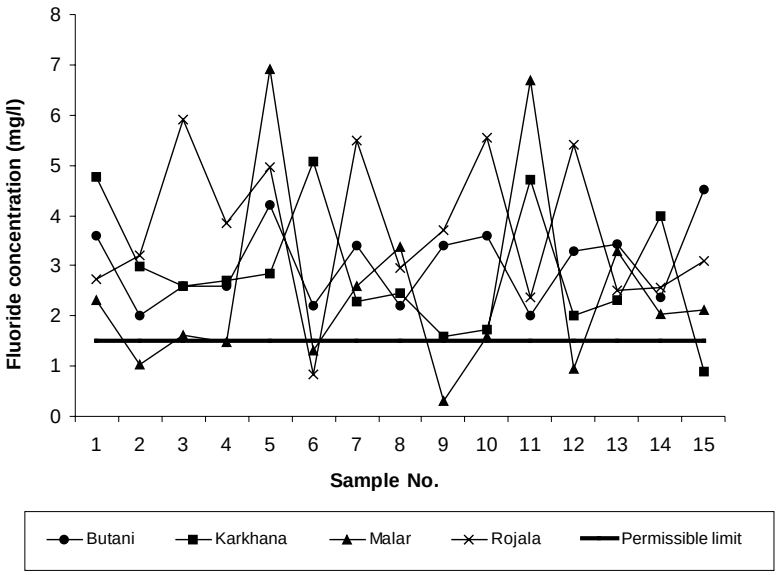

Fig. 3. Fluoride concentration of underground water in the four villages as compared to the maximum allowable limit for drinking water in India.

Table 9
Correlation matrix for different water quality parameters

	pH	EC	TDS	TH	TA	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	F^{-}
pH	1.0	−0.4697*	−0.4697	−0.5004*	−0.0502	−0.569*	−0.446*	−0.4198*	0.0326	−0.3033	−0.4669	−0.3894	0.1422
EC		1.0	1.0	0.7755*	0.2606	0.9417*	0.6601*	0.8589*	0.1568	0.3726	0.9503*	0.8562*	0.0824
TDS			1.0	0.7755*	0.2606	0.9417*	0.6601*	0.8589*	0.1568	0.3725	0.9503*	0.8562*	0.0824
TH				1.0	0.4016	0.8442*	0.9818*	0.6336*	0.5925*	0.2384	0.8191*	0.7690*	−0.511
TA					1.0	0.2588	0.4213*	0.2472	0.0319	0.2002	0.3042	0.1601	0.0081
Ca^{2+}						1.0	0.7273*	0.8689*	0.2155	0.4068	0.9526*	0.9221*	0.0802
Mg^{2+}							1.0	0.5039*	0.5378*	0.1509	0.7123*	0.6596*	−0.1108
Na^{+}								1.0	0.0776	0.4684*	0.8567*	0.8095*	0.1264
K^{+}									1.0	0.1253	0.1394	0.2354	0.0743
HCO_3^{-}										1.0	0.2651	0.3029	0.1799
Cl^{-}											1.0	0.8785*	0.1295
SO_4^{2-}												1.0	0.0708
F^{-}													1.0

*Indicates highly significant correlation (i.e. $P \leq 0.001$).

Table 10
Least square of the relation ($x = A + By$) among significantly correlated parameters

x (dependent)	y (independent)	Correlation	A	B
EC	TH	0.7755	1.904	0.0064
EC	Ca^{2+}	0.941 7	−0.313	0.0708
EC	Na^{+}	0.8589	0.55	0.0079
EC	Cl^{-}	0.9503	1.77	0.0058
EC	SO_4^{2-}	0.8562	1.98	0.0039
TH	TDS	0.7755	−3.15	0.147
TDS	Ca^{2+}	0.9417	−200.5	45.35
TDS	Na^{+}	0.8589	353.88	5.08
TDS	Cl^{-}	0.9503	1133.99	3.72
TDS	SO_4^{2-}	0.8562	1270.65	2.496
TH	Ca^{2+}	0.8442	−103.76	7.65
TH	Mg^{2+}	0.9819	110.514	5.182
TH	Cl^{-}	0.8191	130.85	0.608
TH	SO_4^{2-}	0.7690	145.146	0.421
Ca^{2+}	Mg^{2+}	0.7273	44.229	0.4234
Ca^{2+}	Na^{+}	0.8689	14.966	0.1068
Ca^{2+}	Cl^{-}	0.9526	31.566	0.077
Ca^{2+}	SO_4^{2-}	0.9221	31.66	0.0558
Mg^{2+}	Cl^{-}	0.7123	12.698	0.1003
Na^{+}	Cl^{-}	0.8567	235.65	0.566
Na^{+}	SO_4^{2-}	0.8095	243.7	0.398
Cl^{-}	SO_4^{2-}	0.8785	48.196	0.654

4. Conclusion

Most of the water samples, collected from the four villages of Jind district do not meet the water quality standards for fluoride concentration and many other quality parameters. Hence it is not suitable for consumption without any prior treatment. A handpump attached filter based on Nalgonda technology or activated alumina adsorption might be the solution to this problem.

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