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Hydro-chemical Survey of Groundwater of Hisar City and Assessment of Defluoridation Methods Used in India

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Abstract Ground water quality of Hisar city was assessed for its suitability for drinking purposes. Samples collected from the Bore-wells (forms a part of municipal water supply) and handpumps (direct consumption) were analyzed for the various physico-chemical parameters including pH, electrical conductivity, total dissolved salts, total hardness, total alkalinity, sodium, potassium, calcium, magnesium, carbonate, bicarbonate, chloride and sulfate. The concentrations of magnesium, sodium, potassium, sulfate and especially of chloride were found moderately higher than the WHO standards for the drinking water. Further a comparison of fluoride (F^-) levels in groundwater of various cities and towns of Haryana state was performed. The relatively higher concentrations of F^- in groundwater of Haryana raise the risk of fluorosis and hence groundwater must be used with proper treatment. Promising defluoridation methods using locally available materials and technologies are discussed for the prevention and control of fluorosis. Data were assessed statistically to find the suitable markers of ground water quality as an aid to monitoring groundwater quality.

Keywords Ground water · Drinking water · Water quality parameter · Public health · Fluoride · TDS

1 Introduction

Groundwater is a replenishable source of human water supply and it is estimated that approximately one third of the world's population use groundwater for drinking (United Nations Environment Program 1999). Intensive use of natural resources and increased human activities are posing great threat to groundwater quality (Foster 1995; Mor et al. 2006). Presence of more than 200 chemical constituents in ground water has been documented including about 150 organic and 50 inorganic and radio nucleotides. The reported sources of these chemicals in ground water are both natural as well as anthropogenic (Office of the Technology Assessment 1984). Contaminants in groundwater aquifers exist for hundreds of years due to their slow movement in water aquifers.

In developing countries, contamination of water supplies by organic chemicals is of lesser concern, because most of the health problems are found to be associated with the presence of inorganic chemicals and pathogenic organisms in drinking water (Nash

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and McCall 1995). Due to variations in the regional geology and water/rock interactions, higher concentrations of many elements can occur in water aquifers. Many groundwater exploitation schemes in developing countries are also designed without due attention to quality issues, which may pose a substantial risk to users and to the natural environment.

In India, fluoride (F^-) is one of the most undesired element present in underground water extracted for drinking purposes in many areas. Drinking water containing optimum levels of F^- (0.5–1.5 mg l^{-1}; depending on climatic conditions and the relative contribution of non-aqueous sources of F^- to overall F^- load in individuals) confers protection against dental caries without causing fluorosis, particularly among children. On the other hand due to its strong electronegativity, F^- is attracted by positively charged calcium ions in teeth and bones and hence excessive intake can results in pathological changes in teeth and bones, such as mottling of teeth or dental fluorosis followed by skeletal fluorosis (Brouwer et al. 1988). Based on a review by Kaminsky et al. (1990) and WHO (1997). The health effects of F^- intake in drinking water are encapsulated in Table 1. In addition to F^-, electrical conductivity (EC), total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), nitrate and arsenic are also regarded as critical chemical parameters for water quality assurance. Table 2 shows the desirable and maximum permissible limits for various drinking water quality parameters as recommended by Bureau of Indian Standards (1991).

The routine monitoring of groundwater (Hoko 2005; Hudak and Sanmanee 2003; Kruawal et al. 2005; Robins 2002) can assure the populace that the quality of their drinking water is adequate. It can also be beneficial in detecting deterioration in the quality of drinking water and facilitate appropriate timely corrective actions with minimal negative impacts on population health. Considering this the present study investigates the various physico-chemical parameters in groundwater of Hisar city, which is used in large proportion for drinking, domestic and other purposes by the general public. Further a comparative study of F^- in groundwater of various cities of town of Haryana was also performed and promising defluoridation methods using locally available materials and technologies are discussed to prevent the fluorosis.

Table 1 Fluoride intake in drinking water and health effects

F^- in drinking water (mg l^{-1})	Health effect	Population affected (%)
<0.5	Dental caries	–
0.5–1.5	Promotes dental health	1–2
1.5–2.5	Dental fluorosis	10
2.5–4.0	Dental fluorosis	33
>4	Dental, skeletal fluorosis	–
>10	Osteosclerosis	–

Table 2 Drinking water quality standards as recommended by BIS and WHO

Parameter	IS standards		WHO standards
	Desirable	Max. permissible	
Color	5	25	–
Odor	Unobjectionable	Unobjectionable	–
Taste	Agreeable	Agreeable	–
pH	6.5–8.5	6.5–8.5	6.5–9.2
TH	300	600	200
TA	200	600	300
TDS	300	1500	500
Cl^-	250	1000	250
SO_4^{2-}	250	400	200
NO_3^-	45	45	50
F^-	1.0	1.5	1.5
Ca^{2+}	75	200	100
Mg^{2+}	30	100	150
K^+	–	–	200
Na^+	–	–	200

Except pH and color (hazen unit) all unit are in mg l^{-1}.

2 Materials and Methods

2.1 Site specifications and sampling

Hisar is one of the fastest industrializing cities of Haryana and lies between 29°10′ N and 75°46′ E, and 215.2 m above mean sea level (Fig. 1). The area of Hisar district is 3,787 km^2 and approximate 166 thousand people live in urban area (http://www.Hisar.nic.in/statistics.htm). A total of 134 sampling sites were selected from 47 localities including various residential, commercial and industrial areas in Hisar

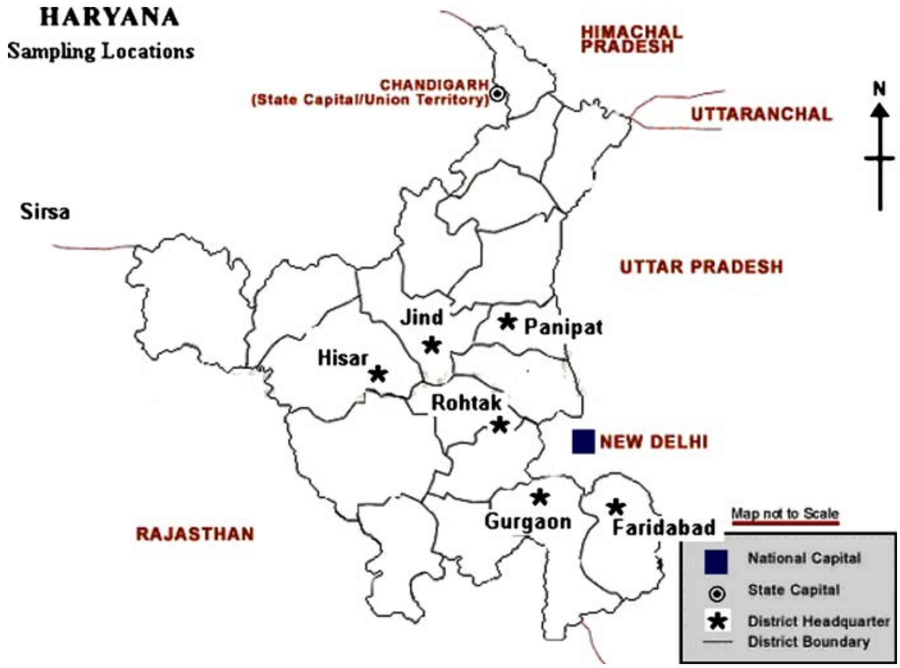

Fig. 1 The location of Hisar city in map of Haryana State

city. The urban area of the city was divided in to five zones i.e. north, south, east, west and central (Table 3).

The samples were collected after the extraction of water either from privately owned manually operated hand-pumps or from electricity operated bore-wells. The water was left to run from the sampling source for 4–6 min to pump out the volume of water standing in the casing before taking the final sample. Then samples were collected in pre-cleaned, sterilized polyethylene bottles of 2 l capacity. The samples were taken by holding the bottle at the bottom to avoid any contamination and were analyzed just after the sampling. The analyzed water quality parameters include pH, EC, TH, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), total dissolved salts (TDS), and total alkalinity (TA).

2.2 Methodology

The analysis of various physico-chemical parameters were performed according to APHA–AWWA–WPCF (1994), as follows – the pH and electrical conductivity of the water were determined on site by using Eutech-Cybernetics pH scan meter and Eutech-Cybernetics EC scan meter. The values of TDS were calculated from EC by multiplying a factor that varies with the type of water. The value of this factor ranges from 0.55 to 0.9. Na^+, K^+, and Ca^{2+}, concentrations were determined using Flame photometer (ELICO CL-220). TA and TH were measured by titrimetry method using standard hydrochloric acid and standard EDTA solutions, respectively. Cl^- was measured by argentometry, where as SO_4^{2-} by nephalometry. The Levels of F^- in groundwater were extended from the Ravindra and Garg (2006) and were measured by the Ion-electrode method.

AR 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 and the results were found reproducible within ±3% error limit. The analytical results were used as input for Special Package for Social Science (SPSS) software for correlation matrix.

3 Results and Discussions

Hisar city falls in hot and semi-arid South-western zone of Haryana State. The subsoil water in Hisar is stored in sand and gravel beds. The depth of water table varies from 6 to 30 m. Manually operated hand-

Table 3 Average concentration of various physico-chemical parameters in Hisar city

	pH	EC	TDS	TH	TA	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	[a]F^-
North Zone (*n*=31)													
Police Line	8.0	2.2	1,408.0	382.0	534.0	350.0	14.0	38.5	69.5	618.5	206.0	298.0	0.6
Sunder nagar	7.4	3.6	2,304.0	553.3	755.7	896.7	12.7	80.0	86.0	889.0	378.7	602.7	1.2
New Grain market	7.6	2.5	1,621.3	780.0	450.3	273.3	30.0	98.7	539.7	516.7	245.3	380.0	0.7
Cloth market	7.6	2.1	1,365.3	821.3	445.7	203.3	24.3	122.7	149.3	544.0	216.0	252.0	0.5
Parav bazar	7.4	5.1	3,242.7	1,577.3	386.0	548.3	93.3	217.7	251.0	471.0	544.3	714.7	0.8
Bharat nagar	7.5	3.0	1,920.0	604.0	513.3	355.0	5.7	81.7	97.3	631.0	382.7	318.3	1.4
Vinod Nagar	7.4	2.7	1,728.0	421.3	541.7	398.3	5.3	51.3	71.0	646.0	242.3	537.3	1.5
Tibba danna Sher	8.2	5.0	3,200.0	696.0	419.5	760.0	7.0	81.5	119.5	490.0	451.5	683.5	1.9
Govt Colony D.C.M	7.8	4.8	3,050.7	612.0	522.3	751.7	7.3	84.3	97.7	637.0	838.7	728.0	0.6
Indrapreasth Colony	7.5	2.4	1,557.3	753.3	505.0	230.0	16.3	80.0	134.3	616.0	70.7	244.0	0.2
Auto Market	7.2	2.9	1,856.0	1,702.7	414.3	154.3	69.3	225.7	141.0	505.3	64.0	297.2	1.2
East Zone (*n*=30)													
Thandi Sarak	6.9	2.3	1,493.3	1,092.0	528.0	131.0	78.3	123.7	190.3	644.0	67.3	154.7	1.2
Shanti Nagar	7.0	1.9	1,216.0	896.0	388.7	105.7	30.3	133.7	136.3	474.3	52.7	123.0	1.1
Kunjlal garden	7.2	0.7	426.7	382.7	336.0	35.7	18.3	80.0	44.7	410.0	4.0	87.7	0.9
Dhani Sham lal	7.5	1.9	1,216.0	624.0	508.7	166.7	6.7	78.3	104.0	622.3	121.3	276.0	0.4
Indira Colony	7.6	2.0	1,280.0	561.3	509.0	210.0	7.0	75.3	70.3	626.0	112.7	285.0	0.9
Hari nagar	7.9	1.3	853.3	448.0	435.3	170.3	7.7	97.7	49.3	472.0	196.7	167.5	0.7
Nirankari Bhawan	7.8	1.8	1,130.7	478.7	458.0	287.0	9.0	80.0	68.0	497.0	262.0	241.0	1.6
Model Town	7.9	2.1	1,344.0	429.3	481.0	392.3	12.3	76.7	57.7	521.3	282.0	365.3	4.1
Vidyut Nagar	7.6	2.5	1,621.3	888.0	515.0	388.3	12.3	62.0	178.3	564.0	496.3	414.3	3.3
Industrial Area	8.0	2.4	1,304.7	429.3	505.3	468.3	88.7	64.3	65.0	547.3	419.7	344.3	9.2
West Zone (*n*=15)													
Old grain market	7.3	4.1	2,645.3	780.0	512.7	373.7	62.7	144.7	101.7	625.7	140.0	498.7	0.4
Aggarwal colony	7.5	4.6	2,965.3	952.0	499.7	470.7	32.0	155.7	137.0	610.0	198.7	674.7	0.9
Prem Nagar	7.6	2.3	1,493.3	480.0	477.3	231.7	62.3	76.0	70.7	582.7	63.3	278.0	1.0
Devi Bhawan	7.4	4.9	3,136.0	890.7	431.7	433.3	72.7	166.0	115.7	527.0	172.0	617.3	0.2
Rishinagar	7.6	2.0	1,408.0	728.0	406.7	153.3	24.3	115.0	107.0	490.7	62.7	281.3	0.1
South Zone (*n*=28)													
Krishna Nagar	7.4	1.7	1,088.0	434.7	582.7	238.3	11.3	54.0	72.7	705.7	37.3	181.3	2.2
Jat Colege Area	7.9	1.3	832.0	345.3	560.7	182.0	7.0	27.7	67.3	610.0	56.7	79.7	1.2
Canal Colony	7.7	1.0	640.0	438.7	507.3	81.3	15.3	69.0	80.3	594.7	53.3	52.0	1.6
Lajpat nagar	8.0	1.1	704.0	564.0	497.7	138.3	8.7	36.3	115.0	533.0	32.0	100.0	1.2
Jawahar nagar	7.4	2.4	2,026.7	686.7	440.7	394.7	6.3	118.0	95.0	508.0	331.7	419.3	2.1
Sector 15A	7.7	1.4	874.7	618.7	309.7	170.3	5.3	107.3	85.3	348.3	132.7	336.0	1.4
Sector 15 A H. B.	7.7	1.3	1,600.0	453.3	469.0	248.3	52.3	55.7	76.3	513.0	131.7	140.3	4.0
Patel nagar	7.3	3.7	1,254.7	916.0	502.7	2142.0	111.7	103.7	159.3	613.0	791.7	506.0	1.3
Mini secretriate	7.4	2.4	2,080.0	1,484.0	341.5	153.5	12.5	378.0	161.0	387.5	277.5	732.5	1.3
Saket Colony	6.7	2.7	884.0	1,216.0	523.0	310.0	9.0	198.0	175.0	637.0	384.0	400.0	3.9
Friends Colony	7.5	2.6	884.0	460.0	531.0	390.0	37.0	72.0	68.0	598.0	364.0	608.0	2.9
Central Zone (*n*=30)													
Rajguru market	7.3	2.4	1,514.7	833.3	333.7	205.7	49.0	114.0	133.3	385.3	54.0	177.3	0.9
Dogran mohalla	7.2	4.1	2,645.3	1,330.7	378.7	370.0	143.3	140.3	238.3	462.0	90.0	356.0	1.8
Multani chowk	6.9	3.8	2,432.0	1,516.0	482.0	293.3	81.7	172.0	264.0	588.3	86.0	313.3	1.3
Saniyan Mohalla	7.0	4.1	2,602.7	1,306.7	474.7	333.3	145.3	156.3	207.0	579.0	113.3	380.0	1.5
Nai sabji mandi	6.9	3.2	2,048.0	1,292.0	540.3	210.3	76.7	175.0	207.3	659.3	90.7	250.7	1.5
Sant Nagar	7.2	1.3	832.0	533.3	434.3	108.3	9.0	82.7	79.3	548.3	36.0	125.3	1.8
Adarsh Nagar	7.5	2.9	1,834.7	937.3	535.3	327.0	15.0	142.3	141.3	610.0	59.3	278.7	1.3
Rampura Mohalla	7.3	3.3	2,090.7	921.3	527.7	381.7	82.3	133.3	143.0	606.7	83.3	243.3	1.6
Barwali Dhani	7.4	0.9	597.3	437.3	388.7	71.0	9.0	61.7	68.7	474.3	16.0	80.0	3.0
Jhajpul	7.6	2.4	1,536.0	836.0	523.7	188.3	61.3	121.0	129.7	638.7	217.3	226.7	1.2

n Number of sampling sites in each zone; Except pH and EC (mmho cm^{-1}) all unit are in mg l^{-1}

[a] From Ravindra and Garg (2006).

pumps can easily be installed in study area and are extensively used to pump out the groundwater. Water is pumped out from shallow aquifers by manually operated hand-pumps (installed at approximately 30 m depth) and from deep aquifers by electricity operated bore-wells (installed at approximately 110 m depth).

3.1 Suitability assessment of groundwater

Groundwater extracted from the hand-pumps is used by near-by residents, whereas the tub-wells forms a part of Public Water Supply system to near-by residential communities. There was no significant variation in the groundwater quality samples obtained either from hand-pumps or from electrically operated bore-wells and hence the average groundwater quality of each locality was used to discuss health effects. The health effects of various physico-chemical parameters were referred from WHO (1997) and Bureau of Indian Standards (1991).

The physico-chemical characteristics of the groundwater samples varied significantly in Hisar city (Table 3). In the studied localities groundwater samples were free from color and odor. The taste was found slightly to moderately saline at some of the locations. The pH of all the water samples ranges from 6.7 (Saket Colony) to 8.6 (Tibba Dana Sher), which shows slightly alkaline nature of water. The pH value in Industrial area (8.0±0.7) and Auto market (7.17±0.64) shows maximum variations in individual samples, likely indicate the impact of nearby activity. pH and total heavy metal content in water samples shows an inverse relation, and hence can govern the heavy metal dissolution in water (Virkutyte and Sillanpaa 2006). EC and TDS signify the inorganic load of any water body. The EC of the groundwater varied from 0.7 (Kunjlal Graden) to 5.1 (Parav Bazar) mmho cm^{-1}, while TDS value ranged from 427 (Kunjlal Graden) to 3,243 mg l^{-1} (Parav Bazar). Higher EC may be attributed to high salinity and high mineral content at the sampling points. The higher EC of the water samples is the result of ion exchange and solubilisation in the aquifer (Sanchez-Perez and Tremolieres 2003). As per the TDS classification of Rabinove et al. (1958), 33 samples were slightly saline category (TDS value range between 1,000 and 3,000 mg l^{-1}). Higher concentrations of TDS decrease the palatability and may cause gastro-intestinal irritation in human and may also have laxative effect particularly upon transits.

CO_3^{2-} was absent in most of the water samples. The HCO_3^- ion concentration in groundwater of Hisar city varied from 348 (Sector 15A) to 706 mg l^{-1} (Krishna Nagar) and found to be relatively high. The high alkalinity imparts water with unpleasant taste, and may be deleterious to human health with high pH, TDS and TH. The TA of water ranges from 310 (Sector 15A) to 756 (Sunder Nagar) mg l^{-1} (as $CaCO_3$) in ground water. The TH of ground water varied from 382 (Cloth Market) to 1577 mg l^{-1} (Parav Bazaar). According to Durfor and Becker's (1964) classification of TH (i.e. 0–60, soft; 61–120, moderately hard; 121–180, hard; and >180 very hard), very hard groundwater is dominant in the aquifers of Hisar city, which may raise the risk of calcification of arteries, urinary concretions, diseases of kidney or bladder or stomach disorder. The high value of TH in supply water may cause corrosion of pipes, resulting in the presence of certain heavy metals, such as cadmium, copper, lead, and zinc, in drinking-water. The degree to which this corrosion and solubilization of metals occurs also depends on the pH, alkalinity, and dissolved oxygen concentration.

Ca^{2+} and Mg^{2+} are important ions for total hardness. Ca^{2+} concentration in ground water ranged from 28 (Jat Collage) to 378 mg l^{-1} (Mini Secretariat). Ca^{2+} is usually associated with carbonate mineral, viz., calcite and dolomite, which commonly occur in veins and secondary minerals in granite. Ca^{2+} and SiO_2 may also be contributed by the dissolution of concrete in streets and the side walks. The concentration of Ca^{2+} in most of the samples was with in desirable limit, only few samples showed comparatively high concentration. The concentration of Mg^{2+} ions varied from 44 (Kunjlal Garden) to 540 mg l^{-1} (Grain Market). A concentration of 30 mg l^{-1} is recommended for Mg^{2+} in drinking water, whereas all the studied samples exceeded this maximum permissible limit in Hisar city. The higher concentrations of Mg^{2+} may be due to the specificity of the minerals at the sampling site. Mg^{2+} is essential as an activator of many enzyme systems but Mg^{2+} salts are cathartic and diuretic and high concentration may cause laxative effect, while deficiency may cause structural and functional changes.

The concentration of Na^+ ranges from 36 (Kunjlal Garden) to 2,142 (Patel Nagar) mg l^{-1} in ground water samples, most of the samples exceeded the maximum permissible limit of Na^+ in groundwater samples. The higher concentration of Na^+ may pose a risk to the persons suffering from cardiac, renal and circulatory diseases. The concentration of K^+ varies from 5 to 145 mg l^{-1} with significant fluctuation. K^+ is an essential nutrient but if ingested in excess may behave as a laxative. Based on the above evaluation of cationic ions, Na^+ is dominant in the aquifers of this city. Weathering of sodium bearing minerals, cation exchange process and industrial activities may be responsible for the dominance of sodium ion.

Cl^- and SO_4^{2-} are major inorganic components, which may deteriorate the quality of groundwater for drinking. Health concerns regarding SO_4^{2-} in drinking water have been raised because of the reports that diarrhea may be associated with the ingestion of water containing higher levels of SO_4^{2-}. SO_4^{2-} concentration ranged from 80 (Barwali Dhani) to 733 mg l^{-1} (Mini Secretariat). The concentration of SO_4^{2-} in most of the samples was higher than the statutory limit (200 mg l^{-1}) accepted for drinking waters. Sources of SO_4^{2-} may include rainfall, fertilizers, and dissolution of sulphide minerals present in granite. If higher concentrations of SO_4^{2-} are ingested, the main health impacts include catharsis, dehydration, and gastro-intestinal irritation. Cl^- concentration in groundwater ranged from 4 (Kunjlal Garden) to 839 mg l^{-1} (Government Colony) and a significant number of samples contained higher concentration than maximum permissible limits (250 mg l^{-1}) for drinking water. Cl^- concentrations higher than 200 mg l^{-1} are considered to be at risk for human health and may cause unpleasant taste of water. High consumption of Cl^- may be crucial for the development of essential hypertension, risk for stroke, left ventricular hypertrophy, osteoporosis, renal stones and asthma (McCarthy 2004). Considering that Cl^- rich minerals are not found in the Hisar city, high Cl^- content of groundwater is likely to originate from pollution sources such as domestic effluents, fertilizers, and septic tanks, and from natural sources such as rainfall, the dissolution of fluid inclusions.

3.2 Fluoride and fluorosis in Haryana

The dominant controls on F^- build-up in water are geology, contact times with F^- minerals, groundwater chemical composition, and climate. F^- in water derives mainly from dissolution of natural minerals in the rocks and soils with which water interacts. The most common F^- bearing minerals are fluorite, apatite and micas and hence the problems consequently occur in the area, where the element is most abundant in the host rocks (Gupta et al. 1999). In addition to the availability and solubility of F^- minerals, velocity of flowing water, temperature, pH, concentration of Ca^{2+}, HCO_3^- in water, etc. also influence the levels of F^- in water (Nash and McCall 1995). Another factors contributing to excess F^- is the over-exploitation of groundwater resources for agricultural and drinking water purposes. Deeper groundwater from old bore-wells are most likely to contain high concentrations of F^-. Because of differences in geo-chemical conditions in aquifers and differences in contact period between groundwater and F^- bearing rocks, the F^- content in groundwater of Indian aquifers varies from <1 to >25 mg l^{-1} (Gupta et al. 1999).

F^- concentration and the severity of fluorosis are directly related to the alkalinity of water which may be one of the deciding factors for the high incidence of fluorosis in area (Chatterjee and Mohabey 1998). Positive correlation of F^- with pH and alkalinity on the basis of high bicarbonate concentration in waters has been reported by Gupta et al. (1986). Shukla et al. (1993) have reported a positive correlation of F^- with phosphate which was attributed to contribution of phosphatic fertilizers, which are being used extensively in this area. It has been reported elsewhere that phosphatic fertilizers can provide as high as 25,670 mg kg^{-1} F^- to the soils.

A comparative account of F^- levels in various cities and town of Haryana is shown in Table 4. Susheela et al. (1993) has reported that F^- content in the underground water of Faridabad district was in the range of 0.25–8.0 mg l^{-1}. A study conducted by Yadav and Lata (2003) in the Jhajjar district of Haryana have reported that F^- content was higher than 2.00 mg l^{-1} in all the blocks of this district. This study also revealed that more than 50% population was affected by dental fluorosis. Mor et al. (2003) found a maximum concentration of 2 mg l^{-1} of F^- in Jind city, whereas Meenakshi et al. (2004) have also reported a range of 0.30–6.90 mg l^{-1} of F^- in the rural areas of Jind districts where handpums are the main source of drinking water.

Table 4 Levels of fluoride in various cities and villages of Haryana state

City/Town	Number	Concentration of F^- (mg l^{-1})						References
		Range	Average±SD	$n^{F=1-1.5}$	$n^{F=1.5-3}$	$n^{F=3-6}$	$n^{F>6}$	
Hisar City	22	0.1–3.4	1.33±1.3		5	1		Kaushik et al. (2002)
Hisar city	127	0.03–16.6	1.51±2.0	30	26	7	5	Ravindra and Garg (2006)
Jind city	23	0.4–2.0	1.14±0.44	7	6	0	0	Mor et al. (2003)
Jind (Butani)	15	2.0–4.56	3.03±0.81	0	8	7	0	
Jind (Karkhana)	15	0.88–5.08	2.86±1.24	0	9	5	0	Meenakshi et al. (2004)
Jind (Malar)	15	0.30–6.90	2.51±1.93	3	6	2	2	
Jind (Rojala)	15	0.84–5.90	3.68±1.48	0	5	9	0	
Faridabad	78	0.25–8.0						Susheela et al. (1993)
Faridabad	25	0.04–1.5	0.57±0.35	2	1	–	–	Kaushik et al. (2004)
Jhajjar (rural)	100	1.78–2.62	2.05					Yadav and Lata (2003)
Beri (rural)	100	1.56–3.05	2.14					
Bahadurgarh (rural)	100	1.6–3.52	2.05					
Rohtak	27	0.4–4.8	2.5±3.5					Kaushik et al. (2004)

The average F^- concentration in groundwater samples of Hisar city ranged from 0.1 (Rishi Nagar) to 9.2 mg l^{-1} (Industrial area) and more than one of three of the total samples exceeded the permissible limit (Ravindra and Garg 2006). The data also revealed that there is no uniform distribution of F^- in the groundwater of Hisar city (Table 3). Samples collected from east and south of Hisar city have highest average F^- concentration i.e. 2.34±3.6 and 2.37±2.2 mg l^{-1}, respectively, whereas the minimum levels of F^- were observed in west of Hisar (0.51±0.4 mg l^{-1}). Further it has been observed that in most of the studied localities, in one or two sample(s) the F^- content was with in the permissible limits whereas in other samples it was much higher or lower than recommended limit. This uneven distribution of F^- in groundwater can be attributed to uneven distribution of F^- containing minerals in the rocks (Ravindra and Garg 2006).

The study of groundwater contour map of the Haryana State shows that the groundwater flows predominantly from north to south in to the central region except some flow taking place from north-east to north-west direction. Surface contours also indicate that the central region of the state is like bowl and surface water accumulate in the area. Owing to such phenomena of surface and groundwater flows; the groundwater quality, distribution and water table fluctuations are inter-dependent.

The WHO has set the maximum permissible limit at 1.5 mg l^{-1} of F^- in drinking water, but mild dental fluorosis may appear at lower levels. Prolonged intake of drinking water having F^- higher than 1.5 mg l^{-1} can cause dental fluorosis; 3–6 mg l^{-1}, skeletal fluorosis; and more than 6 mg l^{-1}, crippling skeletal fluorosis (Brouwer et al. 1988; WHO 1997). Considering these evidence, the higher level F^- in groundwater of Haryana may pose a threat to the public health. Furthermore the public health and economic importance of fluorosis also seeks attention in Haryana as reported by WHO (1997) that the crippling skeletal fluorosis is confined to tropical and subtropical areas. As many studies have reported the development of dental fluorosis from the consumption of water with F^- concentrations as low as 0.8 mg l^{-1} (Brouwer et al. 1988). The maximum allowable F^- concentration of 1.5 mg l^{-1} set by BIS seems to be higher as more water intake of water in hot tropical areas increases fluorosis risk.

3.3 Control and prevention of fluoride and fluorosis

The lack of resources and low-cost efficient technology acceptable to the affected populations restricts the development of an effective F^- and fluorosis control and prevention programme 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

Table 5 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^-	Non-specific	–	Established process	Sludge produced, treated water is acidic, residual Al present	Med–high
	Lime	30 mg/mg F^-	Non-specific	–	Established process	Sludge produced, treated water is alkaline	Med–high
	Alum+Lime (Nalgonda)	150 mg alum+7 mg lime/ mg F^-	Non-specific, optimum 6.5	–	Low-tech., Established process	Sludge produced, high chemical dose, residual Al present	Med–high
	Gypsum+fluorite	5 mg gypsum+<2 mgfluorite/ mg F	Non-specific	–	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	Non-specific	–		Poor capacity	High
	Defluoron 2	360 g F^-/m^3	Non-specific	Alkalinity		Disposal of chemicals used in resin regeneration	Medium
	Clay pots	80 mg F^-/kg	Non-specific	–	Locally available	Low capacity, slow	Low
	Activated alumina	1200 g F^-/m^3	5.5	Alkalinity	Effective, well-established	Needs trained operators, chemicals not always available	Medium
	Bone	900 g F^-/m^3	>7	Arsenic	Locally available	May give taste; degenerates Not universally accepted	Low
	Bone char	1000 g F^-/m^3	>7	Arsenic	Locally available, High Capacity	Not culturally accepted	Low
Other	Electrodialysis	High	Non-specific	Turbidity	Can remove other ions. Used for high salinity	Skilled operators High cost. Not much used	Very high
	Reverse osmosis	High	Non-specific	Turbidity	Can remove other ions. Used for high salinity	Skilled operators High cost	Very high

have been summarized in Table 5, many of these method are discussed in detail by Heidweiller (1990) and references with in. Nalgonda technique of community defluoridation is the most common available method in India, which is based on precipitation process. Although it is a very efficient and cost effective technique but the main limitations of this technique are daily additions of chemicals, large amount of sludge production, least effective with water having high TDS and high hardness (Apparao et al. 1990). Further it converts a large portion of ionic F^- (67–87%) in to soluble aluminum complex and practically removes only a small portion of F^- 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 5). 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), burn clay (Karthikeyan et al. 1999) and other low cost adsorbents. Although the low-cost defluoridation methods have been received increasing attention but are not yet technically feasible or culturally acceptable. If successfully developed, these simple methods could benefit especially rural communities that are least likely to obtain piped water supplies in the near future. Although based on the field test, economical evaluation and religious consideration clay pot chip, activated alumina adsorption and Nalgonda methods seems more promising for defluoridation in India.

Provisions of alternative water sources such as the delivery of water from low F^- sources have also been considered for fluorosis prevention strategies. A major problem in the delivery of water from low F^- sources and defluoridated water is the scarcity of piped distribution systems in rural communities and the reliance of households on individual wells, springs and/or surface sources. This situation requires that the defluoridation methods should be developed in a way that they can be applied at individual well and spring sites or household storage tanks, and can run without technical supervision at household and community levels for a month or more. Construction of piped networks for the purpose of distributing

Table 6 Correlation matrix for different water quality parameters in Hisar city

	pH	EC	TDS	TH	TA	Na^+	K^+	Ca^{2+}	Mg^{2+}	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	F^-
pH	1.000	−0.179	−0.104	−0.613**	0.042	0.056	−0.422**	−0.505**	−0.340*	0.370*	−0.126	0.215	0.048	0.145
EC		1.000	0.926**	0.539**	0.131	0.525**	0.491**	0.403**	0.355*	−0.240	0.220	0.499**	0.784**	−0.153
TDS			1.000	0.524**	0.048	0.318*	0.418**	0.437**	0.336*	−0.197	0.124	0.348*	0.722**	−0.204
TH				1.000	−0.233	0.062	0.576**	0.841**	0.594**	−0.259	−0.128	0.045	0.311*	−0.173
TA					1.000	0.278	−0.092	−0.350*	−0.112	0.115	0.962**	0.186	0.083	0.095
Na^+						1.000	0.282	−0.033	0.071	−0.066	0.288*	0.747**	0.527**	0.049
K^+							1.000	0.333*	0.389**	−0.046	−0.024	0.017	0.110	0.096
Ca^{2+}								1.000	0.380**	−0.203	−0.262	0.038	0.412**	−0.166
Mg^{2+}									1.000	−0.220	−0.066	0.083	0.182	−0.169
CO_3^{2-}										1.000	−0.065	−0.132	−0.262	0.408**
HCO_3^-											1.000	0.162	0.111	−0.027
Cl^-												1.000	0.690**	0.206
SO_4^{2-}													1.000	−0.040
F^-														1.000

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

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. Further it is suggested that the sources of municipal water supply must be established in a region where an adequate levels of F^- has been observed (Ravindra and Grag 2006).

Community participation has been identified as an important factor in the success and sustainability of community water programmes. 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 programmes.

Information on the geographic distribution and hydrology of F^- is extremely important in the development of water resources. F^- levels tend to vary considerably in different groundwater and surface water sources as well as aquifers within the same communities as we have seen in Haryana state. This information can form the basis for developing alternative water sources. For example, transporting or mixing water from low F^- aquifers with higher F^- sources can reduce exposure risk. In the absence of adequate hydrogeological surveys of water sources, high F^- levels may result in the abandonment of wells and entire water supply programmes.

4 Statistical Analysis

Correlations matrixes between various water quality parameters were also studied and it was noticed that most of the parameters bear statistically significant correlation and indicates towards close association of these parameter with each other (Table 6). EC shows a very strong correlation with TDS (r=0.93, p<0.01). Further TDS show a strong correlation with Na (r=0.32, p<0.05), K (r=0.42, p<0.01), Ca (r=0.44, p<0.01), Mg (r=0.34, p<0.05), Cl^- (r=0.35, p<0.05) and SO_4^{2-} (r=0.72, p<0.01). Total hardness also shows a very strong correlation with K^+ (r=0.58, p<0.01), Ca^{2+} (r=0.84, p<0.01) and Mg^{2+} (r=0.59, p<0.01), and proves the interdependence of these ions. Na^+ also shows a well correlation with Cl (r=0.75, p<0.01) and SO_4^{2-} (r=0.53, p<0.01). In general most of these parameters also shows strong correlation in between and hence TDS or EC can be used as an indicator of these parameters, other study also supports TDS as a marker of water quality (Ravindra et al. 2003). Based on correlation matrix, F^- and EC are suggested as a marker of groundwater quality of Hisar city, prior to its use for domestic and especially for drinking purposes.

5 Conclusions

Present study shows that groundwater of Hisar city is rich in natural salts which makes this water not to be consumed directly for drinking purposes without proper treatment. The higher concentrations of F^- also seek some attention, which is responsible for fluorosis. Concentration of some pollutants like Cl^- and Mg^{2+} indicate towards the anthropogenic source of pollution. Statistical analysis of groundwater quality shows that TDS can be usd as a single parameter to calculate the approximation of other ion concentration but it does not shows any relation to F^- content. Groundwater of Hisar city can be used for drinking, if there is no other source of drinking water, but it required prior treatment before consumption. The evaluation of various defluoridation methods on the basis of social and economical structure of India revels that the clay pot chip, activated alumina adsorption and Nalgonda techniques are the most promising.

References

APHA–AWWA–WPCF (1994). *Standard methods for the examination of water and wastewater* (15th edn.). Washington, DC: American Public Health Association.

Apparao, B. V., Meenakshi, S., & Karthikayan, G. (1990). Nalgonada technique of defluoridation of water. *Indian Journal of Environmental Protection, 10*, 292–298.

Arulanantham, A. J., Ram Krishna T., & Balasubramaniam, N. (1992). Studies on fluoride removal by coconut shell carbon. *Indian Journal of Environmental Health, 13*, 531–536.

Brouwer, I. D., De Bruin, A., Dirks, O. A., & Hautvast, J. (1988). Unsuitability of WHO guidelines for fluoride concentration in drinking water in Senegal. *Lancet, 1*, 223–225.

Bureau of Indian Standards (BIS) (1991). Indian standard specification for drinking water. IS, 10500, pp. 2–4.

Chatterjee, M. K., & Mohabey, N. K. (1998). Potential fluorosis problems around Chandidongri, Madhya Pradesh, India. *Environmental Geochemistry and Health, 20*, 1–4.

Durfor, C. N., & Becker, E. (1964). Public water supplies of the 100 largest cities in the US. *US-Geological Survey Water Supply Paper, 1812*, 364.

Foster, S. S. D. (1995). Groundwater for development – An overview of quality constraints. In H. Nash & G. J. H. McCall (Eds.), *Groundwater quality. 17th Special Report* (pp. 1–3). London United: Chapman and Hall.

Gupta, M. K., Singh, V., Rajwanshi, P., Agarwal, M., Rai, K., Srivastava, S., et al. (1999). Groundwater quality assessment of Tehsil Kheragarh, Agra (India) with special reference to fluoride. *Environmental Monitoring and Assessment, 59*, 275–285.

Gupta, S. C., Doshi, C. S., & Paliwal, B. L. (1986). Occurrence and chemistry of high fluoride groundwater in Jalore District of Western Rajasthan. *Annals of Arid Zone, 25*(4), 255–264.

Heidweiller, V. M. L. (1990). Fluoride removal methods. In J. E. Frencken (Ed.), *Proc. symposium on endemic fluorosis in developing countries: Causes, effects and possible solutions* (Chapter 6) (pp. 51–85). Leiden: NIPG–TNO.

Hoko, Z. (2005). An assessment of the water quality of drinking water in rural districts in Zimbabwe. The case of Gokwe South, Nkayi, Lupane, and Mwenezi districts. *Physics and Chemistry of the Earth, 30*, 859–866.

Hudak, P. F., & Sanmanee, S. (2003). Spatial patterns of nitrate, chloride, sulfate, and fluoride concentrations in the woodbine aquifer of North-Central Texas. *Environmental Monitoring and Assessment, 82*, 311–320.

Kaminsky, L. S., Mahoney, M. C., Leach, J., Melius, J., & Miller, M. J. (1990). Fluoride: Benefits and risks of exposure. *Critical Reviews in Oral Biology and Medicine, 1*, 261–281.

Karthikeyan, G., Andal, M. N., & Sundar, S. G. (1999). Defluoridation property of burnt clay. *Journal of Indian Water Works Association, 31*, 291.

Kaushik, A. Kumar, K., Kanchan, Taruna, & Sharma, H. R. (2002). Water quality index and suitability assessment of urban groundwater of Hisar and Panipat in Haryana. *Journal of Environmental Biology, 23,* 325–333.

Kaushik, A., Kumar, K., Sharma, I. S., & Sharma, H. R. (2004). Groundwater quality assessment in different landuse areas of Faridabad and Rohtak cities of Haryana using deviation Index. *Journal of Environmental Biology, 25*, 173–180.

Killedar, D. J., & Bhargava, D. S. (1993). Effect of stirring rate and temperature on fluoride removal by fishbone charcoal. *Indian Journal of Environmental Health, 35*, 81–87.

Kruawal, K., Sacher, F., Werner, K., Mqller, J., & Knepper, T. P. (2005). Chemical water quality in Thailand and its impacts on the drinking water production in Thailand. *Science of the Total Environment, 340*, 57–70.

Kumar, S. (1995). Studies on desorption of fluoride from activated alumina. *Indian Journal of Environmental Protection, 12*, 50–53.

McCarthy, M. F. (2004). Should we restrict chloride rather than sodium? *Medical Hypotheses, 63*, 138–148.

Meenakshi, Garg, V. K., Kavita, Renuka, & Malik, A. (2004). Groundwater quality in some villages of Haryana, India: Focus on fluoride and fluorosis. *Journal of Hazardous Material, 106*, 85–93.

Mor, S., Bishnoi, M., & Bishnoi, N. R. (2003). Assessment of groundwater quality of Jind City. *Indian Journal of Environmental Protection, 23*, 673–679.

Mor, S., Ravindra, K., Dahiya, R. P., & Chandra, A. (2006). Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. *Environmental Monitoring and Assessment, 118*, 435–456.

Muthukumaran, V., Balasubramaniam, N., & Ramkrishna, T. V. (1995). Removal of fluoride by chemically activated carbon. *Indian Journal of Environmental Protection, 12*, 514–517.

Nash, H., & McCall, G. J. H. (1995). *Groundwater quality. 17th Special Report*. London, UK: Chapman and Hall.

Office of the Technology Assessment (OTA) (1984). *Protecting the nation's groundwater from contamination, vol. II*. US Congress, OTA-0-276.

Rabinove, C. J., Long Ford, R. H., & BrookHart, J. W. (1958). Saline water resource of North Dakota. *U.S. Geological Survey Water-Supply Paper, 1428*, 72.

Ravindra, K., Ameena, Meenakshi, S., Rani, M., & Kaushik, A. (2003). Seasonal variation in physico-chemical characteristics of river Yamuna in Haryana and its ecological best-designated use. *Journal of Environmental Monitoring, 5*, 419–426.

Ravindra, K., & Garg, V. K. (2006). Distribution of fluoride in groundwater and its suitability assessment for drinking purpose. *International Journal of Environmental Health Research, 16*, 163–166.

Robins, N. S. (2002). Groundwater quality in Scotland: Major ion chemistry of the key groundwater bodies. *Science of the Total Environment, 294*, 41–56.

Sanchez-Perez, J. M., & Tremolieres, M. (2003). Change in groundwater chemistry as a consequence of suppression of floods: The case of the Rhine floodplain. *Journal of Hydrology, 270*, 89–104.

Shrivastava, P. K., & Deshmukh, A. (1994). Defluoridation of water with natural zeolite. *Journal of the Institute of Public Health Engineers (India), 14*, 11–14.

Shukla, S., Singh, P., Rajwanshi, P., Singh, V., Gupta, M. K., Srivastava, S. et al. (1993). Fluoride content of commonly used chemical fertilizers. *Proceedings of Indo-German conference on impact of modern agriculture on environment, vol. 111*. (pp. 59–62). Hisar, India: Hisar Agriculture University.

Susheela, A. K., Kumar, A., Bhatnagar, M., & Bahadur, R. (1993). Prevalence of endemic fluorosis with gastrointestinal manifestations in people living in some North-Indian villages. *Fluoride, 26*(2), 97–104.

United Nations Environment Program (UNEP) (1999). *Global environment outlook 2000*. UK: Earthscan.

Virkutyte, J., & Sillanpa, M. (2006). Chemical evaluation of potable water in Eastern Qinghai Province, China: Human health aspects. *Environment International, 32*, 80–86.

WHO (World Health Organization) (1997). *Guideline for drinking water quality*, vol. 2 (2nd edn.) Health criteria and other supporting information (pp. 940–949). Geneva: World Health Organization.

Yadav, J. P., & Lata, S. (2003). Urinary fluoride levels and prevalence of dental fluorosis in children of Jhajjar district, Haryana. *Indian Journal of Medical Sciences, 57*(9), 394–399.