Fluoride Quantification in Groundwater of Rural Habitations of Faridabad, Haryana, India

Bhupinder Singh[1], V.K. Garg*[2]

[1]BPS Mahila Vishwavidayalaya Khanpur-Kalan, Sonepat, Haryana, India

*[2]Department of Environmental Science and Engineering, Guru Jambheshwar University of Science and Technology, Hisar-125001, Haryana, India

[1]bhupindersinghmehta@gmail.com; *[2]vinodkgarg@yahoo.com

Abstract— **High concentration of fluoride in the groundwater of different parts of the world is responsible for widespread fluorosis. Haryana State in India is one such region where groundwater is laden with higher fluoride concentration. Since there are no major studies in the recent past, the present study was carried out to quantify the present status of groundwater quality in some rural habitations of Haryana State and also to assess the possible causes for high concentration of fluoride in groundwater. The fluoride concentration in underground water was quantified in five villages of Hodal block, Faridabad district of Haryana state (India) where it is the only source of drinking water. Various other water quality parameters namely pH, electrical conductivity, total dissolved salts, total hardness, total alkalinity, sodium, potassium, calcium, magnesium, carbonate, bicarbonate, chloride, phosphate, nitrate-nitrogen and sulphate 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 study area varied from 1.0 to 40.0 mg/l, Overall water quality was unsuitable for drinking purposes without any prior treatment. The results indicated that weathering of rocks and anthropogenic activities were responsible for high fluoride concentration in groundwater of this area.**

Keywords— **Fluoride; Groundwater; Ion selective electrode; Fluorosis; Rocks**

I. INTRODUCTION

Excessive fluoride concentration in the groundwater of different parts of the world is responsible for widespread fluorosis. High groundwater fluoride concentrations, associated with igneous and metamorphic rocks such as granites and gneisses, have been reported from India, Pakistan, West Africa, Thailand, China, Sri Lanka and Southern Africa (WHO 2006). It is estimated that nearly 29 countries in the world suffering from excessive fluoride in the groundwater and India is one of them. According to an estimate, in India about 80% of domestic water requirements in rural areas and 50% in urban areas are fulfilled by groundwater and it is under threat from natural pollutants i.e. fluoride, arsenic, iron, etc. The excessive extraction of groundwater in comparison to recharge has not only limited the fresh water resource but also influenced the water quality. The dissolution of fluorite, apatite and topaz from local bedrocks leads to high fluoride content in groundwater. It is estimated that India has 14.1% of total fluoride deposits on earth's crust and about 70 million people in 20 States and Union Territories are under fluorosis risk. The most seriously affected areas in India include Andhra Pradesh, Bihar, Madhya Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Utter Pradesh (Kumaran *et al.* 1971; Teotia *et al.* 1984; Ayoob and Gupta 2006; Sharma *et al.* 2007; Singh et al. 2007 and *Hussain et al. 2002).*

Fluoride is naturally occurring element that is found in groundwater of various regions of the world. Ingestion of excessive fluoride through drinking water can result in a disease known as fluorosis. Table I summarizes the harmful effects of inappropriate fluoride content in drinking water on human health.

TABLE I FLUORIDE CONTENT IN DRINKING WATER AND VARIOUS EFFECTS ON HUMAN HEALTH

Fluoride content in mg/l	Corresponding effects on human health
≤ 1.0	Safe limit
1.0-3.0	Dental fluorosis
3.0-4.0	Stiff and brittle joints/bones
≥ 4.0	Deformities in knees; crippling fluorosis; bones finally paralyzed resulting inability to walk or stand straight

There are five major routes of fluoride exposure in human beings e.g. drinking water, food, drugs, cosmetics & dental products and industrial activities. But drinking water is major contributor i.e. up to 75-90% (Sarala and Rao 1993). The fluoride is highly electronegative and does not occur in free State, it reacts with other elements to produce ionic compounds like HF and NaF in water and upon dissociation form negatively charged fluoride ion. The occurrence of fluoride in groundwater is mainly due to natural or geogenic contamination and the source of contamination is often unknown (Saxena and Ahmad 2003). The presence of excessive concentrations of fluoride in the groundwater may persists for years, decades or even centauries and can reach the food system (Todd, 1980). Probably the main source of fluoride in soil is the parent rock itself. The various minerals which contain fluoride are Fluorite, Apatite, amphiboles, pegmatite, hornblende, muscovite, biotite, micas, certain types of clays and villiaumite also contain fluorine.

As fluoride in drinking water does not change its colour, smell or taste, normally there is no way to detect it unless tested. In recent years, there has been an increased interest in fluoride research because excess concentration of fluoride in drinking water causes adverse impacts on human health. In order to mitigate the excess fluoride in groundwater, it is essential to determine and monitor the causal factors of enrichment of fluoride concentration. Therefore, a systematic assessment of fluoride in groundwater is required for the better management of the fluoride toxicity.

Fluoride has long been recognised as one of the most significant natural groundwater-quality problems affecting arid and semi-arid regions of India including Haryana. Suitability of groundwater with reference to drinking purpose has been investigated in some parts of Haryana including Panipat (Bishnoi and Malik 2008), Hisar (Khaiwal and Garg 2006, 2007), Jind region (Mor *et al.* 2003; Meenakshi *et al*. 2004), Bhiwani region (Garg *et al.* 2008) and Gurgaon region (Singh *et al.* 2007). Singh *et al.* (2007) has reported the fluoride content in the groundwater of Pataudi block of Gurgaon district in the range of 0.95 and 5.20 mg/l. Garg *et al.* (2008) reported up to 86.0 mg/l fluoride content in the groundwater of rural habitations of Bhiwani district i.e. highest fluoride content ever recorded for Haryana state including India. A bibliographic survey has shown that however several studies are available showing fluoride concentration in the groundwater of some areas of Haryana state. Still there is lack of studies from Hodal block of Faridabad region regarding the fluoride content of groundwater. So the objective of this study was to investigate the quality of drinking water (underground water) with special reference to fluoride from some habitations of Hodal block of Faridabad district of Haryana state (Fig. 1). The ground water quality was investigated by analyzing various chemical parameters, with special focus on fluoride concentration, which are responsible for affecting the ground water quality. In the present study, an attempt has also been made to statistically correlate the concentrations of fluoride with the other measured parameters.

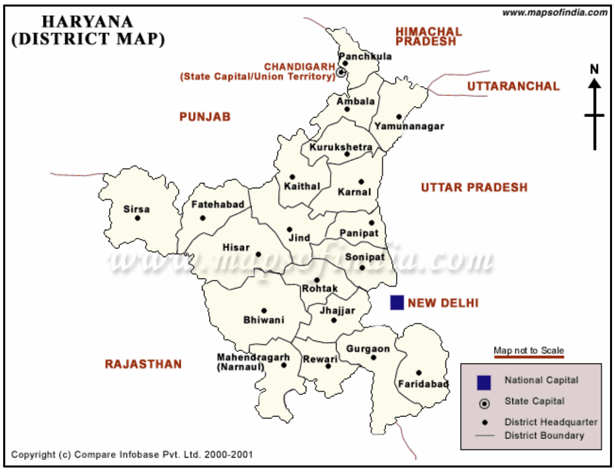

Fig. 1 Study area in the map of Haryana state

II. MATERIALS AND METHODS

A. Study Area

The study area is situated in Faridabad district in Southern-Eastpart of Haryana state (Fig. 1). Lying at the southern fringe of the urban Delhi, Faridabad district is a hub of industrialization of Haryana state in India. The negative impacts of industrialization, increase in population and agriculture, have put the surface water sources under the pressure of pollution and therefore the demand on the use of groundwater has increased. The southern part of the State is semi-arid with low and erratic precipitation. The area is characterized by extreme temperature in winter and summer and high wind velocity during summer. Summer spans over April to July and October have moderate temperature conditions. Groundwater is the main source of drinking water for this region. The subsoil water is stored in sand and gravel beds. Hand-pumps and bore-wells are used to pump out the groundwater. The depth of water table is 7– 30 m. Therefore, manually operated hand-pumps can be easily installed in this region. The study area included six villages namely, Hodal, Bhandoli, Bhiduki, Bhirwi, Bhanshwa and Berapatti of Faridabad district (Haryana), India.

B. Sampling

All water sources sampled for this assessment were in use as drinking water supply sources at the time of sampling. The samples were collected either from hand-pumps or from electricity operated pumps. First, 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 and then water samples were collected in pre-cleaned, sterilized polyethylene bottles of 2L capacity. Some samples were also obtained from the public water supply system. Public supply samples were generally collected from a tap at the water treatment plant itself, during a visit that included a brief inspection of the treatment system and interviews with staff and management. Each sample’s physical properties were measured in the field using portable meters (colour, odour, taste, electrical conductivity and pH) at the time of sampling. Samples were placed in clean containers and immediately placed in ice box. The analyses of various physico-chemical parameters were performed according to APHA–AWWA–WPCF (1995) and ASTM (1972). The ground water samples were analyzed to assess various chemical water quality parameters, viz., pH, electrical conductivity, total dissolved salts, total alkalinity, total hardness, sodium, potassium, calcium, magnesium, carbonate, bicarbonate, chloride, sulphate, phosphate, nitrate-nitrogen and fluoride concentrations.

C. Physico-Chemical Analysis

Analytical grade chemicals were used throughout the study without further purification. To prepare all the reagents and calibration standards, double distilled water was used. The glassware were washed with dilute nitric acid (1.15) followed by several portions to distilled water.

The pH of water samples was analyzed on the sampling site itself. The pH of the samples was estimated using a ‘CHAMP Model pH Scan Meter from HANNA Instruments’. The pH meter was first calibrated with buffer solutions of pH 4.0, 7.0 and 9.2 and then pH of sample was determined. The conductivity of the water samples was estimated on the spot by using a ‘DIST Model TDS SAN Meter from HANNA Instruments’. The conductivity meter was calibrated with standard KCl solution (0.1 M). The TDS were calculated using a formula from the United States Salinity Laboratory, 1954. Total alkalinity and total hardness were measured by titrimetric method using standard sulphuric acid and standard EDTA solutions, respectively. Sodium, potassium and calcium concentrations were determined using ELICO CL-220 Flame photometer. Chloride was determined by argentometric titration method. Sulphate was determined nephelometrically. Phosphate was determined in the samples by molybdenum blue method, and nitrate-nitrogen was estimated by spectrophotometrically with brucine sulphate method. For all spectrophotometric determinations, a Systronics-118, UV–Vis spectrophotometer was used. The fluoride concentration in water was determined by the method adopted by Singh *et al.* (2007). The electrode used was an Orion 96-09 fluoride electrode, coupled to an Orion 420 A electrometer. Standards fluoride solutions (0.1–10 mg/l) were prepared from a stock solution (100 mg/l) of sodium fluoride. To estimate the concentration in the water, 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. Statistical analysis was carried out using Statistical Package for Social Sciences (SPSS) 11.5. All the experiments were carried out in triplicate. The results were reproducible within ±3% error limit.

III. RESULTS AND DISCUSSION

Haryana is a relatively small 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.

Analytical data for the water samples are presented in Table 2. In Table 3, 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 respect to their chemical composition. The drinking water samples were free from colour, odour and turbidity. The taste was slightly to moderately saline at some of sampling sites.

TABLE II PHYSICO-CHEMICAL CHARACTERISCTICS OF GROUNDWATER IN THE STUDY AREA

Sample	pH	EC	TDS	TA	TH	Na^+	K^+	Ca^{2+}	Mg^{2+}	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	PO_4^{3-}	F^-	NO_3^-–N
H-1	8.1	1.09	700	580	520	170	01	112	58	0	760	405	196	0.07	1.00	22
H-2	8.2	1.71	1100	580	500	120	00	84	119	0	719	611	225	0.09	1.15	24
H-3	8.0	2.65	1700	590	700	160	00	118	62	0	640	433	315	0.19	1.60	20
H-4	8.1	2.50	1600	620	980	230	00	180	129	0	648	234	400	0.18	1.55	15
H-5	8.2	1.56	1000	460	740	200	00	132	100	0	585	156	388	0.25	1.45	08
H-6	8.3	2.03	1300	510	560	160	01	100	75	0	610	213	249	0.26	1.49	10
H-7	8.1	1.25	800	620	720	190	01	124	100	0	745	202	300	0.38	1.56	09
H-8	8.0	1.40	900	740	620	110	00	100	90	0	833	372	289	0.39	1.80	10
H-9	8.1	2.18	1400	720	740	110	00	90	125	0	799	362	310	0.40	1.75	08
H-10	7.9	2.34	1500	600	520	220	02	130	47	0	685	185	251	0.50	1.57	09
H-11	7.9	3.12	2000	620	560	210	01	136	53	0	705	469	287	0.56	1.90	10
H-12	8.0	3.12	2000	540	240	180	01	44	32	0	680	334	110	0.40	1.91	05
H-13	8.3	3.90	2500	500	200	240	00	56	15	0	599	369	185	0.39	2.50	06

Sample	pH	EC	TDS	TA	TH	Na^+	K^+	Ca^{2+}	Mg^{2+}	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	PO_4^{3-}	F^-	NO_3^-–N
H-14	8.3	1.25	800	350	360	280	00	52	56	0	495	99	211	0.38	1.56	08
H-15	7.9	1.87	1200	390	320	292	00	60	41	0	480	383	280	0.09	1.68	10
H-16	7.5	1.56	1000	400	560	150	00	84	85	0	506	142	250	0.08	1.52	15
H-17	7.6	1.09	700	380	340	200	00	110	16	0	480	85	196	0.07	1.51	09
H-18	7.7	1.56	1000	540	360	174	01	104	24	0	690	121	187	0.10	3.50	10
H-19	7.8	1.87	1100	600	200	160	01	40	24	0	698	156	119	0.19	3.00	22
H-20	7.6	2.18	1400	620	360	190	01	104	24	0	711	341	188	0.18	8.00	25
H-21	7.5	1.87	1200	740	300	200	01	110	06	0	885	177	110	0.16	3.12	28
H-22	7.3	4.84	3100	580	760	230	02	122	111	0	685	745	298	0.18	40.00	30
H-23	7.2	5.00	3200	420	360	210	02	116	17	0	496	802	150	0.28	35.00	29
H-24	7.1	4.35	2900	610	540	296	21	120	58	0	733	816	301	0.27	14.00	35
H-25	7.0	2.34	1500	290	800	298	09	186	81	0	385	163	100	0.26	5.50	30
H-26	7.4	4.37	2800	880	980	340	09	190	103	0	996	887	395	0.08	5.60	19
H-27	7.9	4.53	2900	740	990	236	02	128	160	0	833	781	400	0.38	3.35	20
H-28	8.0	8.75	5600	1800	3660	306	03	190	774	0	2000	2499	1600	0.39	4.00	19
H-29	8.1	5.78	3700	1400	2210	300	05	180	428	0	1615	1526	1385	0.40	2.00	35
H-30	7.6	2.50	1600	1310	1670	420	30	291	229	0	1495	483	1400	0.41	1.50	29
H-31	7.4	2.50	1600	980	1040	300	07	210	125	0	1098	603	525	0.39	1.48	25
H-32	7.3	3.43	2200	1680	2160	180	04	130	446	0	1885	2307	1805	0.28	1.90	30
H-33	7.6	9.21	5900	490	440	240	06	110	40	0	585	128	200	0.29	3.85	35
H-34	7.5	1.09	700	280	300	640	07	084	22	0	386	99	185	0.23	1.50	29
H-35	7.8	0.78	500	250	280	124	05	100	07	0	390	92	100	0.15	1.40	21
H-36	7.9	0.62	400	540	650	124	02	72	114	0	698	845	315	0.18	1.35	18
H-37	8.0	4.37	2800	720	830	90	10	60	165	0	878	376	425	0.19	2.56	33
H-38	8.1	2.03	1300	390	400	304	44	102	35	0	476	376	196	0.20	1.50	05
H-39	7.9	2.18	1400	440	420	160	25	108	36	0	555	177	220	0.21	1.49	35
H-40	7.6	1.56	1000	420	360	190	20	94	30	0	535	170	185	0.28	1.52	15
H-41	7.5	1.40	900	400	340	150	03	94	26	0	496	192	200	0.29	1.50	18
H-42	7.4	1.40	900	390	310	150	03	96	17	0	480	241	198	0.30	1.50	20
H-43	7.1	1.87	1200	520	430	102	03	100	44	0	619	240	226	0.13	1.50	25
H-44	7.2	5.93	3800	1350	1510	190	02	116	296	0	1505	1540	1000	0.14	1.80	17
H-45	7.3	4.84	3100	1490	1400	352	06	220	208	0	1601	1171	1115	0.15	3.00	19
H-46	7.4	7.03	4500	1150	1120	290	29	204	148	0	1305	1739	999	0.09	8.40	58
H-47	7.4	7.18	4600	490	580	420	10	136	58	0	585	1633	305	0.08	2.80	56
H-48	7.4	1.87	1200	400	380	386	185	104	29	0	501	234	210	0.16	1.18	22
H-49	7.5	1.87	1200	880	900	164	07	288	184	0	999	291	495	0.18	1.80	28
H-50	7.9	2.50	1600	960	1060	182	03	104	194	0	1106	547	885	0.20	2.80	35

All parameters have been express as mg/L except pH and EC. Units of EC are mS.

TABLE III STATISTICAL ANALYSIS AND COMPARISON OF GROUNDWATER OF HODAL BLOCK WITH DRINKING WATER STANDARDS (INDIAN AND WHO)

Parameters	Range of Samples				ISI Standards		WHO Limit
	Min.	Max.	Mean	S.D.	Accept. Limit	Max. Limit	
pH	7.00	8.30	7.71	0.35	7.0-8.5	6.5-9.2	8.0-8.5
EC	0.62	9.21	2.96	2.02	-	-	-
TDS	400	5900	1900	1296	500	1500	500
TA	250	1800	679	363	200	600	-
TH	200	3660	745	620	200	600	100
Na^+	90	640	226	101	50	-	-
K^+	00	185	9.5	27	-	-	-
Ca^{2+}	40	291	122	54	75	200	75
Mg^{2+}	06	774	109	135	200	400	50
CO_3^{2-}	00	00	00	00	75	200	75
HCO_3^-	385	2000	797	387	30	-	150
Cl^-	85	2499	551	567	200	1000	200
SO_4^{2-}	100	1805	417	408	200	400	200
PO_4^{3-}-P	0.07	0.56	0.24	0.12	-	-	-
F^-	1.00	40.00	4.01	7.28	1	1.5	1
NO_3^--N	05	58.00	21.00	11.70		-	-

All parameters have been expressed as mg/L except pH and EC. The units of EC are mS.

The pH value of groundwater in the study area varies from 7.0 to 8.3. The average pH was 7.71 ± 0.35 and pH of all the water samples was within the safe limits.

Electrical conductivity, measures how well the water conducts an electrical current, a property that is proportional to the concentration of ions in solution. The electrical conductivity varied from 0.62 to 9.21 mS. EC has a wide applicability with respect to agricultural use, but for the drinking use high value of EC denotes proportionately high value of calcium, magnesium, sodium and potassium. TDS values ranged from 400-5900 mg/l. Water containing less than 500 mg/l of dissolved solids is suitable for domestic use. In our study, 44% water samples were above the specified limit (500 mg/l) for TDS. Water containing more than 1,000 mg/l of dissolved solids is likely to contain enough of certain constituents to cause noticeable taste or make the water unsuitable for drinking. A high concentration of salts of sodium, calcium, and magnesium is responsible for high amounts of total dissolved solids. Rabinove *et al.* (1958) have classified the drinking water on the basis of TDS contents and according to that ten samples were non saline, thirty one samples were slightly saline and nine samples were under the category of moderately saline (Table II). The sources of dissolved solids are natural as minerals in soils and anthropogenic as agrochemicals. The average EC and TDS content were 2.96 ± 2.02 mS and 1900 ± 1296 mg/L respectively.

Alkalinity is a related concept that is commonly used to indicate a system’s capacity to buffer against acid impacts. Buffering capacity is the ability of a body of water to resist or dampen changes in pH. Alkaline compounds in water such as bicarbonates, carbonates, and hydroxides remove H^+ ions and lower the acidity of the water (i.e., increase pH). Alkalinity (as $CaCO_3$) ranged from 250 to 1800 mg/l with a mean value of 679 ± 363 mg/l. The WHO acceptable limit for alkalinity in drinking water is 200 mg/l. The results reveal that at 21 locations, TA was higher than acceptable limits. Carbonate was either absent or present in negligible amounts. Bicarbonate ranged from 385 to 2000 mg/l with a mean of 797 ± 387 mg/l and this high value indicates intense chemical weathering of the parent granite rock.

Hardness is the sum of polyvalent metallic ions in water. Calcium and magnesium are the principal components, and hard waters are most common in groundwater, especially when derived from limestone, dolomite or chalk aquifers. The total hardness ranged from 200 to 3660 mg/l with a mean value of 745 ± 620 mg/l. Soft waters are those with a hardness of less than 60 mg/l; moderately hard waters are those with a hardness range from 61 to 120 mg/l; hard waters are those which have hardness in the range of 121 to 180 mg/l and very hard waters are those which have hardness in excess of 180 mg/l. The results indicate that none of the water samples had hardness lesser than 200 mg/l. Twenty two samples had hardness higher than 600 mg/l. Hard water can be unacceptable to consumers. Hard water requires more soap to produce lather, and can form scale deposits on pipes, basins, pots and hot water heaters. The hardness may also be advantageous in certain conditions; it prevents the corrosion in the pipes by forming a thin layer of scale, and reduces the entry of heavy metals from the pipe to the water and this is known as plumbosolvency. On the basis of Durfor and Becker (1964) classification water was very hard at all the studied locations. Calcium content ranged from 40 to 291 mg/l. The average calcium content was 122±54 mg/l and five samples had calcium content higher than permissible limit. Magnesium content ranged from 6 to 774 mg/l. The average Mg^{2+} content was 109 ± 135 mg/l. All samples were within acceptable limit except three which were from Bhiduki village. A very high concentration of calcium and magnesium can be attributed to the geologic characteristic of the study area.

Although, sodium and potassium ions are naturally occurring ions in groundwater, but industrial and domestic wastes also add ions to groundwater. In this study, sodium content varied from 90-640 mg/l with an average of 226 ± 101 mg/l. All samples had higher Na^+ content and concentration more than 50 mg/l makes the water unsuitable for domestic use and cause severe health problems. The potassium content varied from nil to 185 mg/l. The average potassium content was 9.5 ± 27 mg/l.

The chloride content ranged from 85 to 2499 mg/l. with an average of 551 ± 567 mg/l. Maximum permissible limit of chloride in potable water is 200 mg/l which may be further relaxed up to 1,000 mg/l for Indian conditions. Water containing more than 250 mg/l of chloride ion has salty taste. Excessive chlorides impart bitter taste to water, corrode steel and may cause cardio-vascular problems (Karthikeyan *et al.* 2010). The greater concentration of chloride in groundwater could be associated with chloride rich minerals or likely to originate from pollution sources, e.g., domestic effluents, fertilizers and septic tanks. At seven locations, chloride content was higher than acceptable limit.

Sulphate is a naturally occurring ion in almost all kinds of water bodies and is a major contributor to total hardness. The sulphate content ranged from 100 to 1805 mg/l with an average of 417 ± 408 mg/l. At eleven locations, sulphate content was higher than acceptable limit. Sulphate content more than 200 mg/L is objectionable for domestic purposes. Beyond this limit, SO_4^{2-} causes gastro-intestinal irritation particularly when Mg^{2+} and Na^+ are also present in groundwater. This permissible limit of 200 mg/l may be extended up to 400 mg/l of SO_4^{2-} provided Mg^{2+} does not exceed 30 mg/l. Waters containing SO_4^{2-} beyond 1000 mg/l have purgative effects. The main source of sulphate in water may be rainfall, fertilizers and dissolutions of surface minerals present in granites (Khaiwal and Garg, 2007).

The phosphate content in the ranged from 0.07 to 0.56 mg/l with an average of 0.24 ± 0.12 mg/l. Sewage effluents, including septic tanks discharged to unsaturated aquifers, fertilisers, animal excreta and rainfall, are expected to be important sources for phosphate in the groundwater.

Nitrate contamination in drinking water is an emerging global concern that has harmful effects on human health, livestock, environment, and economy. High N fertilization in intensively cultivated areas is the most common anthropogenic source of NO_3 contamination in groundwater (Kaown *et al.* 2009). Nitrate is the end product of aerobic stabilization of organic nitrogen and occurs generally in trace quantities in surface water supplies but may attain higher levels in some ground waters. Application of fertilizers to land and leaching from cesspools contribute nitrate to ground waters. The nitrate-nitrogen content ranged from 5 to 58 mg/l with an average of 21.00 ± 11.70 mg/l i.e. significantly higher than the maximum permissible limit of 10 mg/l. At 36 locations NO_3^-–N content was higher than permissible limit. Nitrate pollution of water is a potential health hazard because consumption of NO_3^- N in water can lead to methemoglobinemia or blue baby syndrome in infants and gastrointestinal cancer in adults (McDonald and Kay 1988). The functioning of the central nervous system and cardiovascular system may also be affected by nitrate rich water. Human and animal wastes, industrial effluents, application of fertilizers and chemicals, seepage and silage through drainage system are the main sources of nitrate contamination of groundwater (Agrawal 1999). Many investigators have reported that the contribution of nitrate from the fertilizer to the groundwater can vary from as little as 3 mg/l to as much as 1,800 mg/l (Mehta *et al.* 1990; Kolpin *et al.* 1994)

Fluoride is one of the most serious chemical contaminants that occur naturally in drinking water. Fluoride is a fairly common element, with an average concentration of 300 mg/kg in the earth's crust. Granite, granite gneisses and pegmatite can contain significant amounts of fluorite (CaF_2). Fluoride can also be concentrated in coal or evaporite deposits such as gypsum and fluorite. In present study the fluoride content ranged from 1.00 to 40.00 mg/l. Figure 2 shows the frequency distribution of fluoride content in the groundwater of study area. The desirable range of fluoride concentration in drinking water is from 0.6 to 1.2 mg/l according to the Indian standard specifications (BIS, 1992). Thus, if the concentration of fluoride is below 0.6 and above 1.2 mg/l, the water is not suitable for drinking purposes. However, it is suggested that the maximum limit can be extended up to 1.5 mg/l (BIS, 1992). The average content was 4.01 ± 7.28 mg/L, i.e. significantly higher and this shows that F^- is an alarming pollutant in this region. Authors did not obtain even a single sample of water which had fluoride concentration lesser than 1.0 mg/l. However, only 30% of the total collected water samples had the fluoride content within the prescribed range of 1.0 to 1.5 mg/l. In this study nearly 68% samples exceeded maximum permissible limit of 1.5 mg/l. Based on the concentration of fluoride, the groundwater samples obtained from the study area have been classified into four groups as safe (up to 1.0 mg/l), partially problematic (1.0 to 1.5 mg/l), problematic (1.5 to 3 mg/l) and highly problematic (>3.0 mg/l) (Figure 3). World Health Organization has set the maximum permissible limit at 1.5 mg/l of fluoride

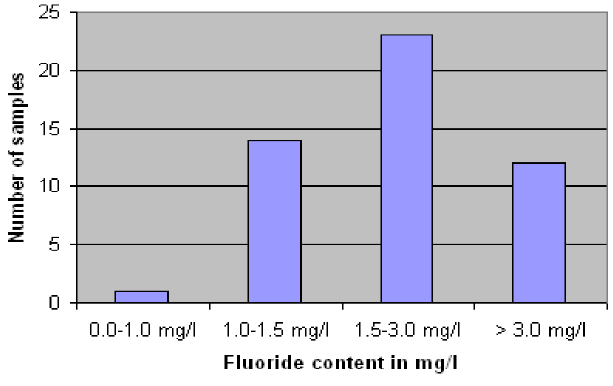

Fig. 2 Frequency distribution of fluoride content in the groundwater of study area

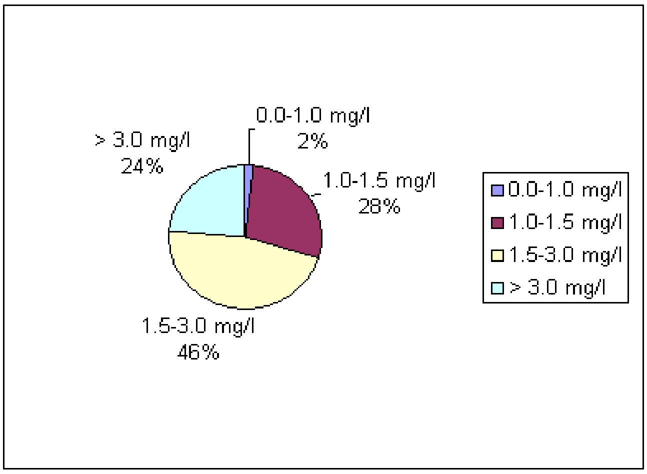

Fig. 3 Numbers of samples with different fluoride ranges in Hodal region, Faridabad

in drinking water if alternative source of water is not available globally. But in tropical regions like India where 5-7 litres water is consumed by the people daily, this limit seems to more (Khaiwal and Garg (2007); Suthar *et al.* 2008). Under such conditions, the consumption of water is high and so is the fluoride exposure and ingestion. Therefore the high concentration of fluoride in most of the sources of water is a cause of concern for health. At this stage, even low concentration offluoride in drinking water may cause risks of dentalfluorosis. Ibrahim et al.1995, have reported the prevalence of dental fluorosis to the extent of 91% in a study of Sudanese children consuming water with 0.25 mg/l of fluoride. Hence, the acceptable fluoride concentration in drinking water should be less under tropical conditions (Galagan and Vermillion, 1957). USPHS (1962) has set a range of allowable concentration 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 determined by the air temperature in that region (Table IV).

TABLE IV RANGE OF MAXIMUM ALLOWABLE FLUORIDE CONTENT IN DRINKING WATER (AFTER USPHS 1987)

Annual average maximum daily air temp. (^{0}C)	Recommended F^- concentration mg/l			Maximum allowable F^- conc. mg/l
	Lower	**Optimum**	**Upper**	
≤ 12	0.9	1.2	1.7	2.4
12.1-14.6	0.9	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	0.6	0.7	0.8	1.4

The maximum F^- content (35.00 and 40.00 mg/L) was recorded in two samples from village Bhandoli. Hence it is evident from the results that the people in the study area are chronically exposed to higher levels offluoride from drinking water as the residents rely on this source for potable purpose.

High fluoride levels in groundwater are primarily caused by interactions with rock and sediments, and can occur in a wide range of geological environments, characterized by a semi-arid climate, crystalline igneous rocks (e.g., granite), and alkaline soils. Fluoride concentrations have been observed to increase along groundwater flow lengths, due to rock-water interactions. Alkaline waters (pH >7.5) and the presence of other anions (e.g., bicarbonate) increase fluoride mobility by displacing fluoride from clay and other mineral surfaces.

In present study there was large variation in the fluoride content. Further calcium concentrations were lower than the sodium concentrations (Table 2), which indicates the higher fluoride content in the groundwater of the study area. This is in agreement with Raju *et al*. (2009). Generally, high concentration of sodium will increase the solubility of fluoride- bearing minerals in the waters. This is the cause for the higher levels of fluoride in the groundwater of the study area. Under the prevailing semi-arid climatic conditions, during weathering of granite gneissic rocks, fluorine may release from apatite and biotite to the circulating alkaline groundwater. Hence fluoride could have originated fromfluoride bearing minerals such as fluorite, apatite and micas. In the study area fluoride contamination is mainly a natural process, i.e., leaching of fluorine-bearing minerals. Beside the natural sources, anthropogenic activities may also contribute to the fluoride content of groundwater as indicated by higher nitrate content. People doing agricultural practice in the surrounding area having applied nitrogenous and phosphate fertilizers which may be leached down to groundwater and hence increase the fluoride as well as nitrate content. But, their contribution may be in negligible amounts only, as these activities are not practiced on a large scale over the entire study area when compared to contribution by weathering of rocks. Further, our results are in agreement with Saxena and Ahmed (2003), according to them alkaline pH ranging from 7.6 to 8.6 with high bicarbonate concentration (350–450 mg/l) and moderate EC are the favourable conditions for CaF_2 dissolution in the ground waters and can be represented as:

$$CaF_2 + 2\,NaHCO_3 = CaCO_3 + 2Na + 2F + H_2O + CO_2$$

Moreover, Nash and McCall (1995) concluded that availability and solubility of F minerals, velocity offlowing water, temperature, pH, concentration of calcium and bicarbonate in water, etc., also influence the level of fluoride in water. Overexploitation of groundwater for domestic and agriculture purposes also altar the availability offluoride in groundwater (Khaiwal and Garg 2006). It is also suggested that deeper groundwater from older bore-wells are most likely to contain high concentration offluoride, be cause of differences in geo-chemical conditions in aquifers and differences between contact period between groundwater and F bearing rocks.

To establish the relationship of fluoride with other water quality parameters, correlation analysis was performed (Table V). Correlation of fluoride with other ions was observed relatively not dependent except fluoride and pH. A positive correlation between pH and fluoride indicates, high alkaline nature of water promotes leaching of fluoride and thus, increases fluoride in ground water. The ionic radius of fluoride (0.136 nm) is same as that of hydroxyl ion which can be easily substituted for one another from water at high pH (Gupta *et al.* 2006). In acidic medium (acidic pH), fluoride is adsorbed in clay; however, in alkaline medium, it is desorbed, and thus alkaline pH is more favourable for fluoride dissolution activity (Saxena and Ahmed, 2001). Hence acidity/alkalinity of the groundwater is the factor that controls the leaching of F from the fluoride bearing minerals. The correlation analysis indicated that F^- is positively correlated with pH (r = 0.374, $p < 0.01$) which in agreement with earlier studies (Gupta *et al.* 1986; Jha *et al.* 2010). The positive correlation of pH with F suggests that pH is important in determiningfluoride in the ground water. Our findings were also in agreement with earlier observations (Handa 1975) that elevatedfluoride i n the groundwater was generally associated with low calcium, high amount of bicarbonates and in some cases with high nitrate ions as in present study.

TABLE V CORRELATION COEFFICIENTS AMONG DIFFERENT WATER QUALITY PARAMETERS OF GROUND WATER OF HODAL BLOCK

	pH	TDS	TA	TH	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	F^-	NO_3^-
pH	1.00											
EC	-0.215											
TA	-0.110	0.512**	1.00									
TH	-0.028	0.534**	0.890**	1.00								
Na^+	-0.255	0.274	0.127	0.191	1.00							
K^+	-0.181	-0.021	-0.075	-0.056	0.330*	1.00						
Ca^{2+}	-0.314*	0.294*	0.565**	0.562**	0.349*	0.064	1.00					
Mg^{2+}	0.040	0.506**	0.864**	0.980**	0.107	-0.081	0.548**	1.00				
Cl^-	-0.208	0.681**	0.793**	0.796**	0.215	-0.036	0.348*	0.793**	1.00			
SO_4^{2-}	-0.098	0.467**	0.935**	0.909**	0.219	-0.010	0.549**	0.882**	0.793**	1.00		
F^-	0.374**	0.311*	-0.052	-0.030	0.045	-0.052	0.038	-0.051	0.155	-0.071	1.00	
NO_3^-	-0.487**	0.499**	0.241	0.205	0.277	0.124	0.335*	0.161	0.423**	0.288*	0.264	1.00

**Significant at 0.01 level
* Significant at 0.05 level

IV. CONCLUSION

The quality of groundwater in parts of Hodal region of Faridabad district, Haryana was assessed with special reference to fluoride. In this study very high concentration of fluoride in groundwater of up to 40.0 mg/l was measured. About 68% samples exceeded maximum permissible limit of 1.5 mg/l, set by World Health Organization and Indian drinking water standard. Moreover, it is also important to note that only one sample has fluoride content up to 1.0 mg/l. General population using groundwater for drinking purpose without any defluoridation technique may exposed to very high fluoride content through drinking water and may suffer from fluorosis. It is a deadly disease with no cure so far. Hence defluorination of groundwater before using it for consumption is essential. Weathering of rocks and leaching of fluoride bearing minerals are the major reasons which contribute to elevated concentration of fluoride in groundwater. Suitable measures such as defluoridating the groundwater before use and recharging the groundwater by rainwater harvesting need to be practiced to improve the groundwater quality in this area. Besides this, reducing the use of chemical fertilizers for agriculture, and adopting organic farming also restore the groundwater quality of the area. The present study was limited to a small area in the Hodal region of Faridabad district, Haryana, India. A more detailed study is necessary for better understanding of the source and effects of fluoride problems in other parts of the Faridabad district.

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