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Assessment of Groundwater Quality with Respect to Fluoride

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Abstract The study was conducted in the summer season (April–May 2007). The fluoride concentration along with physico-chemical parameters in ground water samples was determined in various villages of Kadi tehsil at Mehsana district of Gujarat state (India), since in most of the villages it is the only source of drinking water. The fluoride concentrations in these villages varied from 0.94 to 2.81 mg/L (1.37 ± 0.56) with highest fluoride level at Visalpur (2.08 mg/L) and lowest at Adaraj (0.91 mg/L). There was found a positive correlation of pH with fluoride and a negative relationship of fluoride with bicarbonate which is generally observed in deep ground water.

Keywords Fluoride · pH · Correlation · Groundwater chemistry

The problem of excessive fluoride in ground water in India was first reported in 1937 in the state of Andhra Pradesh (Short et al. 1937). In India, approximately 62 million people including 6 million children suffer from fluorosis because of consumption of water with high fluoride concentrations (Susheela 1999a, b). Seventeen states in India have been identified as endemic for fluorosis. Gujarat is one of the most severely affected states in the country considered to be endemic to fluorosis, where about 18 out of 19 districts are prone to fluorosis due to high fluoride content in drinking water (Barot 1998). Mehsana district located in North Gujarat is considered to be the most affected part of the state. Though fluoride enters the body through food, water, industrial exposure, drugs, cosmetics, etc., drinking water is the major contributor (75–90% of daily intake) (Sarala and Rao 1993). The studies carried out by various researchers on groundwater quality with respect to fluoride across India, including Gujarat, are reported elsewhere (Shaji et al. 2007; Asadi et al. 2007; Misra et al. 2006; Sujatha 2003; Rao and Devadas 2003; Sarma and Rao 1997; Madhnure et al. 2007; Kaushik et al. 2004; Gupta et al. 2006; Kundu et al. 2001; Barot 1998; Gupta et al. 1999) and are presented in Table 1.

Considering the grim scenario, the Kadi tehsil in Mehsana district (Gujarat, India), which is situated between the latitudes 23°02′ to 24°09′ N and longitudes 71°26′ to 72°51′ E, was selected for the study to assess its ground water quality with particular reference to fluoride. 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 and the conditions affecting the ground water quality. While assessing the

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Table 1 Distribution of fluoride in groundwater across India

Location	Ranges (mg/L)	References
Kerala (Palghat district)	1.51–5.75	Shaji et al. (2007)
Andhra Pradesh Hyderabad (MCH)	0.34–3.12	Asadi et al. (2007)
Maharashtra (Yavatmal district)	0.30–13.41	Madhnure et al. (2007)
West Bengal (Birbhum district)	0.006–1.95	Gupta et al. (2006)
Haryana (Rohtak)	0.4–4.8	Kaushik et al. (2004)
Andhra Pradesh (Reddy district)	0.70–4.80	Sujatha (2003)
Andhra Pradesh (Anantpur)	0.56–5.80	Rao and Devadas (2003)
Orissa (Nayagarh district)	0.16–10.10	Kundu et al. (2001)
Gujarat (Ahmedabad)	0.50–0.72	Barot (1998)
Uttar Pradesh Agra (Kheragarh)	0.11–12.80	Gupta et al. (1999)
Andhra Pradesh (Vishakapatnam)	0.35–8.35	Sarma and Rao (1997)

ground water quality, the following aspects were also taken into consideration, such as the district is underlain by alluvium having good porosity, and high groundwater storage potential. It has quaternary alluvium deposit in the Cambay Graben on its flanks. The geological evolution is controlled by the Precambrian orogenies—the Aravalli. The structural set-up of rocks is controlled by Precambrian orogenic trends, i.e. NE-SW Aravalli trend. Hydrochemically, the fresh water is overlain by saline ground water (Gupta et al. 2005; Merh 1995; Dinesh kumar 2002). Fluoride in natural waters may originate from the solution of fluorite or apatite and more commonly from the solution of fluoride-bearing micas and amphiboles. A common sink for fluoride is adsorption by kaolinite. Fluoride is common in semi-arid climate with crystalline igneous rocks and alkaline soils (Handa 1975).

Materials and Methods

The study area includes Kadi tehsil of Mehsana district (Gujarat, India). The sampling locations were fixed by Global Positioning System (GPS) and are reported in Universal Transverse Mercator (UTM) coordinates. Fifteen ground water samples were collected from hand-pumps during the summer season (April–May 2007). This season was selected because in this season often contamination increases due to low dilution and this tends to the accumulation of ions. 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 2 L capacity. The samples were taken by holding the bottle at the bottom to avoid any contamination. The ground water samples were analyzed to assess various chemical water quality parameters such as Na, K, Ca, Mg, Cl, bicarbonate and sulfate. The ground water samples were also analyzed to assess various physico-chemical parameters, according to APHA–AWWA–WPCF (1995). The pH and electrical conductivity of the water samples were measured by using a portable pH meter (Model-Cyberscan Eutech pH 510) and EC meter (Systronic, Model 306), respectively. The cations like Na and K were determined by flame photometer, Ca were assessed by titrimetric method, whereas anions like Cl and SO_4 were determined by argentometric method and turbidity method respectively. The fluoride concentration was measured by using the following SPADNS (sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate) method., 500 mL of sample aliquot was taken in a round bottom flask, then concentrated H_2SO_4, glass beads and Ag_2SO_4 (at a rate of 5 mg/mg Cl if concentration is greater than 7000 mg/L) were added to it. The flask was attached to distillation unit. Then the flask was heated until the temperature of the flask content reached exactly 180°C. In the SPADNS method, fluoride reacts with the dye lake, dissociating a proportion into a colorless complex anion (ZrF_6^{2-}) and the dye. As the amount of fluoride increases, the colour produced becomes progressively lighter. A calibration standard ranging from 0–1.4 mg/L fluoride was prepared by diluting an appropriate volume of standard fluoride solution. To 50 mL of standard solution, 10 mL of SPADNS reagent was added and mixed well. The spectrophotometer was set to 570 nm and calibration graph was prepared from different standard fluoride concentrations. When the graph gave a straight line, the instrument was ready for measurement of fluoride concentrations. The detection limit and analytical range of fluoride were 0.02 and 0–2.0 mg/L respectively. AR grade chemicals were used throughout the study. To prepare all the reagents and calibration standards, double distilled water was used. A statistical method adopted to evaluate the correlation between various ground water quality parameters.

Table 2 One-way ANOVA test for specific parameters

Ions	Variation	Sum of squares	df	Mean square	F
SO_4	Between groups	1.200	1	1.200	0.002
	Within groups	17427.6	28	622.3	
	Total	17425.8	29		
Na	Between groups	116.0	1	116.0	0.005
	Within groups	704448.9	28	25158.8	
	Total	704564.9	29		
K	Between groups	3.333	1	1.333	1.207
	Within groups	77.33	28	2.762	
	Total	80.66	29		
F	Between groups	8.3×10^{-5}	1	8.3×10^{-5}	0.001
	Within groups	4.276	28	0.153	
	Total		29		

The analytical precision for the measurement of cations and anions, indicated by the ionic balance error (IBE), was computed on the basis of ions measured. The value of IBE was found within a standard limit of ±5%. The minimum, maximum, average and standard deviation (SD) were determined for all data sets. A fortified sample recovery was performed by adding a known amount of analyte to a minimum of 10% of the routine samples. The analyte concentration was high enough to detect the original sample and was not less than four times the method detection limit. The mean percentage recovery and standard deviation were observed in the range of 95 ± 0.07 respectively. The correlation analysis was performed for measured parameters to determine the relationship between these variables. The significance level reported ($p < 0.05$) is based on the Pearson's coefficients. The statistical analysis, Oneway ANOVA was applied to estimate the measurement uncertainty in analysis. The analytical variance for the data was not more than 20% of the total variance. The statistics were performed within and between batches using SPSS software and F test results, and are presented in Table 2. The F test statistic was applied to test the null hypothesis and found true for specific parameters. The calculated F_{value} were observed in the range of 0.001–1.207 which were less than $F_{critical}$ of 3.328 for a stated level of confidence (typically 95%), which means that the difference being tested is statistically significant at 95% confidence level (Ramsey et al. 1992).

Results and Discussion

Table 3 Physico-chemical characteristics of groundwater samples

Location	UTM coordinates		pH	EC µS/cm	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	F (mg/L)
	Long.	Lat.	–									
Anandpura	235051	2582092	8.68	2780	352	61	335	711	25	58	51	0.94
Movan	228059	2585876	8.48	2430	322	64	167	532	27	79	36	1.21
Dhangarva	234787	2578772	8.73	2430	262	60	378	674	25	55	33	1.06
Vishalpur	224739	2583389	9.31	1900	143	46	310	568	25	32	18	2.08
Sarsav	222296	2578669	9.31	1850	99	49	420	652	26	20	15	1.26
Rajpur	222273	2588311	8.85	2500	289	82	316	749	25	39	42	1.81
Indrad	231894	2588577	8.97	3310	457	78	372	961	25	40	35	0.94
Laxmanpura	230542	2581730	9.34	2780	326	48	344	727	25	20	40	1.67
Asjol	227902	2582887	8.56	3350	456	109	207	771	26	93	65	1.11
Babajipura	218706	2578293	9.12	2270	222	110	209	530	26	52	35	1.89
Kaswa	221219	2581238	8.83	1850	151	42	248	494	26	47	31	1.68
Adaraj	230806	2568095	8.84	1670	144	75	209	256	26	62	22	0.91
Vinayakpura	236425	2584506	8.99	2320	265	99	198	665	25	27	31	1.02
Khanderavpura	228252	2579667	8.69	2130	243	110	175	535	27	68	21	1.78
Jasvantpura	218209	2579079	8.96	2160	271	90	200	730	26	58	20	1.04
Min			8.48	1670	99	42	167	256	25	20	15	0.91
Max			9.34	3350	457	110	420	961	27	93	65	2.08
Avg			8.91	2382	267	75	273	637	26	50	33	1.36
SD			0.27	505	107	24	84	161	1	21	13	0.41
%			–	–	20	5	20	47	2	4	2	0.10

The values obtained for various physico-chemical parameters after carrying out the analysis of the ground water samples are presented in Table 3. The abundance of major ions in groundwater was found in the following order:

EC > Na > HCO_3 > Cl > SO_4 > Ca > Mg = K > F. The pH values varied from 8.48–9.34 (8.91 ± 0.27) indicating alkaline nature. The sodium and bicarbonate values varied from 256 to 961 and 167 to 420 mg/L respectively. The fluoride concentration varied from 0.94–2.81 (1.37 ± 0.56) with highest fluoride level at Visalpur (2.08 mg/L) and lowest at Adaraj (0.91 mg/L). In terms of % contribution, the fluoride level <1 mg/L was observed as 20% at three locations (Anandpura, Indrad and Adraj), between 1 and 1.5 mg/L it was 40% at six locations (Movan, Dhangarva, Sarsav, Asjol, Vinayakpura and Jasvantpura) and at the fluoride level >1.5 mg/L, it was 40% at six locations (Visalpur, Rajpur, Laxmanpura, Babajipura, Kaswa and Khanderavpura). The concentration of fluoride found in the ground water samples was higher compared to the Indian Drinking Water Standard of maximum permissible limit of 1 mg/L. Whereas the values of fluoride were lower than the maximum tolerance limit (1.5 mg/L) recommended by World Health Organization (WHO) (BIS 2003; WHO 2004). Ingestion of water with fluoride concentration above >1.5 mg/L causes fluorosis (Madhnure et al. 2007). The major source of fluoride is the fluorite mineral which may be found in granite, gneiss and pegmatite. The process of weathering of rock releases fluoride in soil and ground water. The alkaline water can mobilize fluoride from fluorite with precipitation of calcium carbonate because the solubility of CaF_2 increases with an increase in $NaHCO_3$ rather than with other salts (Handa 1975; Saxena and Ahmed 2001). In ground water, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature, the action of other chemical elements, and the depth of wells. The aqueous ionic concentrations of ground water may influence the fluoride solubility behavior in the presence of excessive sodium bicarbonates and the dissociation activity of fluoride will be high (Tirumalesh et al. 2007). In acidic form, fluoride is absorbed in clay and in alkaline form, it is desorbed, hence, alkaline pH is more favorable for fluoride dissolution activity and can be represented as:

Table 4 Ratio and correlation values of different water quality variables

S. no.	Possible combinations	Ratio values (range, average and SD)
1	HCO_3/Cl	0.45–4.24 (1.27 ± 0.94)
2	Na/Cl	1.65–6.59 (2.68 ± 1.24)
3	Na/Ca	4.13–36.3 (15.9 ± 9.6)
4	HCO_3/Ca	0.69–6.90 (2.37 ± 1.80)
5	F vs [Ca + Mg]	Coefficient of F = 0.0143 (Ca + Mg); $R^2 = -1.82$

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$$

In order to identify possible combinations, ratio values of different variables were studied, which are presented in Table 4. The ratio of HCO_3/Cl was found in the range of 0.45–4.24 (1.27 ± 0.94). The average ratio value of 1.27 indicates dominance of carbonate ions, whereas values less than one indicate that chloride ion is prevalent in the region. The Na/Cl ratio was observed in the range of 1.65–6.59 (2.68 ± 1.24). The decrease in ratio indicates modification of sodium carbonate water by dissolution or mixing with sodium chloride, whereas increase in chloride may be due to local recharge (Dhiman and Kesari 2006). The ratio value of Na/Ca was observed in the range of 4.13–36.3 (15.9 ± 9.6). The increase in ratio value may be due to lowering calcium activity whereby high sodium activates the dissolution of fluoride bearing minerals at higher pH in groundwater system (Shaji et al. 2007).The HCO_3/Ca ratio observed in the range of 0.69–6.90 (2.37 ± 1.80) (values in meq), which indicate favorable chemical condition during fluoride dissolution process (Saxena and Ahmad 2003). The correlation coefficient values [F = 0.0143 (Ca + Mg) $R^2 = -1.82$)] of Ca + Mg and fluoride are negative, which indicate low solubility of fluoride with these ions (Das et al. 2003).

An attempt was made to correlate the fluoride with various parameters, as indicated in Table 5. Correlation coefficient of fluoride was observed relatively not

Table 5 Correlation matrix of different parameters in groundwater

	pH	EC	SO_4	HCO_3	Na	K	Ca	Mg	Cl	F
pH	1.0									
EC	−0.23	1.0								
SO_4	−0.22	0.22	1.0							
HCO_3	0.41	0.14	−0.56	1.0						
Na	0.04	0.78	0.16	0.32	1.0					
K	−0.41	−0.41	0.31	−0.61	−0.51	1.0				
Ca	−0.86	0.10	0.43	−0.58	−0.13	0.60	1.0			
Mg	−0.41	0.84	0.17	0.03	0.44	−0.24	0.25	1.0		
Cl	−0.35	0.93	0.26	−0.03	0.73	−0.62	0.25	0.79	1.0	
F	0.28	−0.17	−0.48	−0.04	−0.04	−0.04	−0.41	−0.08	−0.33	1.0

dependent on other water soluble components, except correlation between fluoride and pH values. There was found a positive correlation between pH and fluoride, which indicates that high alkaline nature of the water promotes leaching of fluoride and thus, affects the concentration of fluoride in ground water. The ionic radius of fluoride (0.136 nm) was same as that of hydroxyl ion which can be easily substituted for one another from water at high pH (Sreedevi et al. 2006; Gupta et al. 2006). A negative relationship was observed between fluoride and bicarbonate which is generally observed in deep ground water at pH range of 8.3–9.2, however, a positive relationship was observed in shallow ground water (Muralidharan et al. 2002). The correlation of Ca and Mg indicates a possible ion-exchange process in the ground water system. The HCO_3, Cl, Na, SO_4 ions constitute 92% of major ions indicating the active secondary geochemical process controlling the ground water chemistry.

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