GROUNDWATER QUALITY ASSESSMENT OF TEHSIL KHERAGARH, AGRA (INDIA) WITH SPECIAL REFERENCE TO FLUORIDE

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Abstract. Fluoride concentration and other parameters in groundwater from 261 villages in Tehsil Kheragarh of District Agra were assessed and attempts were made to observe the relationship between fluoride and other water quality parameters. Of 658 groundwater samples (collected from separate sources) analysed for fluoride, 27% were in the range of 0–1.0 mg/L, 25% in 1.0–1.5 mg/L, 32% in 1.5–3.0 mg/L and 16% above 3.0 mg/L. The highest fluoride concentration recorded was 12.80 mg/L. Significant correlation of fluoride with pH, alkalinity, Na, SiO_2 and PO_4 were observed. Factor analysis was also attempted in order to identify the contributing sources.

Keywords: correlation, district Agra, factor analysis, fluoride, groundwater, irrigation

1. Introduction

The effect of fluoride on humans has been extensively studied (WHO, 1970; WHO, 1984 and Slooff *et al.*, 1989) and fluoride related health and environmental concerns have reached an alarming proportion in many regions of the world. The occurrence and development of endemic fluorosis has its roots to the high fluoride content in air, soil, and water, of which water is perhaps the major contributor. The significance of fluoride in water has always been a subject of debate. Whereas an intake of fluoride in controlled quantities (less than 1 ppm) is known to be beneficial for human health in preventing dental caries, high fluoride concentration in water causes dental and skeletal fluorosis. Caries-preventing aspects of fluoride, however, have been challenged recently by several workers, who urge a scientific re-examination of the alleged dental benefits of fluoridation (Diesendorf, 1986; Smith, 1988a-b; Sutton *et al.*, 1988). Many studies have found fluorosis to be invariably associated with high concentrations of fluoride in drinking water (Desai *et al.*, 1988; Samal *et al.*, 1988; Dwarakanath *et al.*, 1991). The recent implications, though not universally accepted, of involvement of fluoride as a carcinogen and mutagen have added yet another dimension to the unresolved role of fluoride in human health (Mahoney *et al.*, 1991; Hamilton, 1992; Yiamouyiannis, 1993). The U.S. Environmental Protection Agencies maximum contamination level of 4 mg/L of fluoride in drinking water has been found to be an appropriate interim standard

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by a sub-committee, constituted by National Research Council (NRC), in 1993 (NRC, 1993), which also reported that 'the available laboratory data are insufficient to demonstrate a carcinogenic effect of fluoride in animals'. The report however, created controversy among fluoride researchers (Hirzy, 1993; Carton, 1993).

The fluoride concentration in groundwater is largely governed by presence of Ca, Mg, Na, SiO_2, PO_4, pH and alkalinity. Nanyaro *et al.* (1984) have attributed high fluoride content of waters in Northern Tanzania to their exceptionally low Ca and Mg concentrations. Citing Eriksson (1981), Nanyaro *et al.* (1984) explained this relationship on the basis of low solubility of Ca and Mg fluorides. Maina and Gaciri (1984) have found, in a study of 47 boreholes, that low Ca and negligible Mg concentrations corresponded to relatively high fluoride values. Chandra *et al.* (1981) and Teotia *et al.* (1981) have reported that water with low hardness, i.e. low Ca and Mg contents, and high alkalinity present the highest risk of fluorosis. Ca and Mg were found to be low, as they are largely precipitated as carbonates. Only limited incorporation of F is permitted in the $CaCO_3$ structure, such that there is always a net balance of F in solution. Gaumat *et al.* (1992), in their study on F levels in shallow groundwater of Uttar Pradesh, India, found negative correlation between fluoride and calcium.

About 80% population in the Agra District of Uttar Pradesh use groundwater for drinking and other purposes. Evidences of dental and skeletal fluorosis in many areas of this district led us to perform an extensive survey of groundwater quality in Tehsil Kheragarh (approximately 799 km^2 area comprising 0.4 million population, mainly agrarian, within the Agra District) with special emphasis on fluoride. Besides fluoride, pH, electrical conductance (EC), chloride (Cl), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), phosphate (PO_4), silica (SiO_2), total hardness (TH) and total alkalinity (TA) were determined with the objectives a) assessment of water quality with respect to its suitability for drinking and irrigation uses, and b) determination of potential sources of fluoride in groundwater on the basis of statistical analysis of the data.

2. Materials and Methods

Agra, located in the north central India at the end of the chain of Aravalli hills, (27° 10′N and 78° 05′E, 168 m above sea level) is a semi-arid area bounded by Thar desert on its south-west, west, and north-west peripheries. The temperature and relative humidity in the area lie, respectively, in the range 38–48°C and 18–48% (during summers) and 2–10°C and 60–73% (during winters). Average annual rainfall is 760 mm with 90% of the rainfall being received during the period June–October. The soil of Agra is loose, sandy and calcareous. Hydrogeology of this region is characterised by unconfined and semi-confined aquifers at a depth of 2.3 to 23.3 m below ground level. The perennial river Yamuna, touches the city on its north and north east borders. Agra is represented by alluvium, which is an admixture of gravel, sand, silt and clay in various proportions, deposited during the Quaternary period (Rai, 1996). The land is predominantly used for agriculture.

Water samples were collected, in precleaned one litre polyethylene containers in the month of August 1992 from 658 groundwater sources (handpump, openwell and tubewell) scattered in the entire area of Tehsil Kheragarh (Figure 1). The depth of the source of samples ranged between 5 to 70 meters. Collected samples were preserved at low temperature ($\approx 4°C$) and analysed within 48 hrs. Fluoride concentration was measured with Orion ion analyser EA 940 using fluoride ion selective electrode. The pH was measured using pH meter (CD instruments, Bangalore, India). EC was measured using Systronics conductivity bridge. Cl, TH and TA were analysed using argentometric, complexometric and acid-base titrations, respectively. PO_4 and SiO_2 were determined spectrophotometrically using ascorbic acid and molybdosilicate method, respectively as per Standard Methods (APHA, 1985). Ca, Mg, Na and K were determined using atomic absorption spectrophotometer (Perkin Elmer 2380).

The concept of residual sodium carbonate (RSC), as introduced by Eaton (1950), deals with precipitation of Mg and Ca present in the soil as carbonates (due to the presence of carbonate and bicarbonate ions in water). Similarly, the relative proportion of sodium, calcium and magnesium is expressed as SAR (sodium adsorption ratio). The values of RSC and SAR were computed by employing equation 1 (suggested by Eaton (1950)) and the equation 2 (which is a standard equation (Biswas *et al.*, 1987)), respectively.

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (1)$$

$$SAR = Na^+/[(Ca^{2+} \times Mg^{2+})/2]^{1/2} \quad (2)$$

where, concentrations are in me/L.

Correlation and factor analysis (Harman, 1968) of the data were performed using a SPSS PC^+ statistical software package (SPSS, 1983).

3. Results and Discussion

The fluoride concentration in groundwater ranged from 0.11 to 12.80 mg/L with a mean value of 2.06. In 658 samples analysed, the fluoride concentration (mg/L) ranged from 0–1.0 mg/L in 178 (27%), 1.0–1.5 in 165 (25%), 1.5–3.0 in 210 (32%) and > 3.0 in 105 (16%) samples. Observed values of other parameters are given in Table I.

On comparing the results with the limits prescribed by the Bureau of Indian Standards (1990) for drinking water, it was observed that about 73%, 80%, 82%, 88%, 48%, 64% and 99% of samples did not fall under the prescribed safe limits for F, pH, TH, TA, Cl, Ca and Mg respectively.

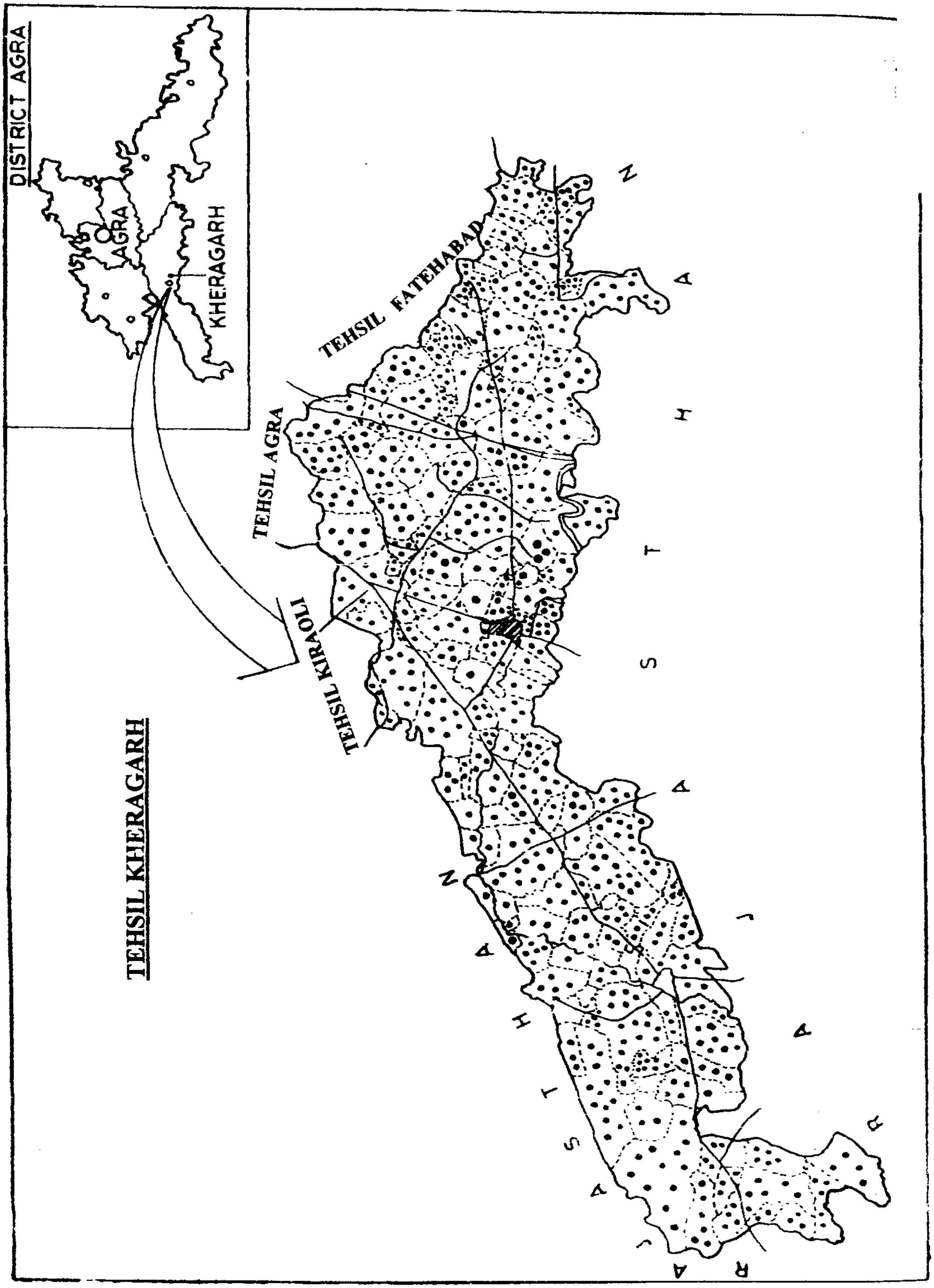
DISTRICT AGRA
AGRA
KHERAGARH
TEHSIL FATEHABAD
TEHSIL AGRA
TEHSIL KIRAOLI
TEHSIL KHERAGARH
RAJASTHAN

TABLE I

Statistical characterization of groundwater of Tehsil Kheragarh

Parameters	Minimum	Maximum	SD ±	Mean
Depth (metres)	5.00	70.00	5.85	19.40
F (mg/L)	0.11	12.80	1.78	2.06
pH	7.61	9.50	0.33	8.80
EC (mmhos/cm)	0.17	9.80	1.85	3.00
TH (mg/L as $CaCO_3$)	88.50	7684.00	1219.00	1269.00
TA (mg/L as $CaCO_3$)	44.00	1648.00	229.04	410.33
Cl (mg/L)	18.00	2705.00	331.35	350.05
Ca (mg/L)	4.58	1794.00	148.55	128.24
Mg (mg/L)	1.60	1840.00	282.93	230.14
Na (mg/L)	0.00	4600.00	374.24	357.57
K (mg/L)	0.00	800.20	131.09	62.36
PO_4 (mg/L)	0.00	0.67	0.06	0.03
SiO_2 (mg/L)	1.87	20.87	2.98	10.40
RSC (mg/L)	–96.71	24.14	25.85	–12.31
SAR	0.00	55.01	4.65	4.77

The correlation matrix of fluoride with other constituents is shown in Table II. Positive correlation of fluoride with pH (r = 0.40) and alkalinity (r = 0.56) may be explained on the basis that the high bicarbonate concentration in waters, at relatively high pH, can replace fluoride from mineral surfaces. This is also in agreement with the findings of Gupta *et al.* (1986). Significant correlation of fluoride with sodium (r = 0.19) may be due to the fact that solubility of fluoride is more in high sodium waters. Similar results have been observed in other Districts of Uttar Pradesh (Gaumat *et al.*, 1992). Significant negative correlation of fluoride with silica (r = –0.34) possibly reveals that fluoride is not only a product of mineral weathering but some other sources may also be contributing fluoride to groundwater. Positive correlation of fluoride with phosphate (r = 0.18) may be 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 fluoride to the soils (Shukla *et al.*, 1993).

In order to further identify contributing sources on the basis of their chemical signatures, factor analysis of the data was attempted, employing varimax rotation method, which led to the extraction of three principal components (PCs) with 57.8% of the total variance (Table III).

PC1 (27% variance) is significantly correlated with fluoride, pH and alkalinity and reveals that high fluoride concentration in groundwater of study area is

TABLE II

Coefficient of correlation 'r' among various water quality parameters

Parameters	Depth	F	pH	EC	TH	TA	Cl	Ca	Mg	Na	K	PO_4	SiO_2
Depth	1.00												
F	–0.12[a]	1.00											
pH	0.01	0.40[b]	1.00										
EC	–0.03	0.07	–0.12[b]	–1.00									
TH	0.03	–0.21[a]	–0.27[b]	0.47[b]	1.00								
TA	–0.12[a]	0.56[b]	0.73[b]	0.20[b]	–0.23[b]	1.00							
Cl	–0.03	–0.09[a]	–0.31[b]	0.86[b]	0.50[b]	–0.05	1.00						
Ca	–0.07	–0.08	–0.20[b]	0.05	0.30[b]	–0.10[a]	0.08	1.00					
Mg	0.05	–0.20[b]	–0.23[b]	0.47[b]	0.95[b]	–0.21[b]	0.50[b]	–0.01	1.00				
Na	–0.04	0.19[b]	0.05	0.61[b]	0.20[b]	0.27[b]	0.48[b]	0.07	0.19[b]	1.00			
K	–0.08	–0.07	0.15[b]	0.28[b]	0.11[a]	0.12[a]	0.22[b]	–0.06	0.14[b]	–0.01	1.00		
PO_4	–0.08	0.18[b]	0.09[a]	0.05	–0.07	0.16[b]	–0.01	0.02	–0.08	0.09[a]	0.01	1.00	
SiO_2	0.02	–0.34[b]	–0.53[b]	–0.21[b]	–0.03	–0.54[b]	–0.07	0.02	–0.04	- 0.20[b]	–0.12[a]	–0.13[b]	1.00

1 - Tailed significance. [a] = 0.01; [b] = 0.001

TABLE III

Factor analysis

Parameters	PC 1	PC 2	PC 3
F	0.6532		
Depth			–0.7361
TA	0.8630		
pH	0.8484		
EC		0.9269	
Na		0.6949	
Mg		0.6411	
Ca			0.4884
Cl		0.9060	
PO_4			0.4645
SiO_2	–0.6979		
% of variance	27.0	21.2	9.6

* Values above 0.4 are reported here.

favoured by high pH and high alkalinity (i.e. the carbonate and bicarbonate concentration). Handa (1975) took a thermodynamic approach to study the occurrence of fluoride ions in the presence of calcite equilibrium, and correlated high fluoride concentration with increase in bicarbonate ions in groundwaters of nearly constant pH. Handa (1975) used a combined mass law equation relating both the solute species as given below

$$CaCO_3\,(S) + H^+ + 2F^- \longrightarrow CaF_2\,(S) + HCO_3^- \qquad \text{(I)}$$

$$\text{Hence, K Cal flour.} = \frac{a_{HCO_3^-}}{a_{H^+} \cdot a_{F^-}^2} \qquad (3)$$

where symbol ‘a’ represents the equilibrium activities of the corresponding species written as suffix.

The increase in $[F^-]$ with increasing pH (i.e. decreasing $[H^+]$) and increasing bicarbonate ion concentration is quite readily explained by the application of LeChatelier’s principle to the Reaction I or by examination of the expression for the equilibrium constant of this reaction (Equation 3).

Gupta *et al.*, 1986 have also concluded, from a study of high fluoride groundwater of Rajasthan (India), that high bicarbonate containing groundwaters, in general, have relatively high pH, and have a tendency to displace fluoride ions from mineral surface into the solution. The PC1, also shows a negative correlation with silica, indicating that groundwater fluoride is derived from other sources besides weathering of rocks. A possible source could be phosphatic fertilizers which are extensively used in this area and are known contributor of fluoride. We have earlier estimated total F in diammonium phosphate (DAP) as high as 25,670 mg/kg (Shukla *et al.*, 1993). Excessive use of phosphatic fertilizers may, therefore, be responsible for the increase in fluoride concentration in groundwater.

PC 2 (21.2% variance) is strongly associated with EC, sodium, chloride and magnesium. The strong electrolytic nature of both $MgCl_2$ and NaCl, along with the saline nature of the water in the study area, might explain the grouping of sodium, chloride and magnesium with EC. The effect of this on $[F^-]$ can be understood on the basis of the general tendency for solubilities of slightly soluble ionic compounds to increase in solutions of higher ionic strength, as predicted by Debye-Huckel theory. Generally, ionic activity coefficients decrease with increasing ionic strength in dilute solutions. The expression for K Cal fluor (equation 3) indicates that, an increase in ionic strength will result in similar decrease in the ionic activity coefficients of bicarbonate, fluoride, and hydrogen ion. This in turn, possibly shifts the reaction equilibrium to the right decreasing the fluoride concentration as is also evident from the obtained data.

PC 3, with 9.6% of the variance, bears a negative loading with depth and positive loadings with Ca and PO_4, both of which are present in phosphate rock. Phosphate rock which is primarily tricalcium phosphate, $[Ca_3(PO_4)_2]$ and apatite, $[CaF_2.\ 3Ca_3(PO_4)_2]$ is sparingly soluble in water. However, it gets converted to calcium dihydrogen phosphate $[CaH_2(PO_4)_2]$, which is relatively more soluble. A mixture of $CaH_2(PO_4)_2$ and gypsum, marketed under the name of superphosphate of lime, is used as phosphatic fertilizer. The significant association of Ca and PO_4 with this PC and a negative loading with depth may be attributed to fertilizer addition and slow leaching of these species with respect to depth in the soils of the study area.

The categorization of groundwater quality for irrigation purposes has been described on the basis of the values of electrical conductivity (EC), residual sodium carbonate (RSC) and sodium adsorption ration (Table IV).

According to the limit of EC for irrigation water, proposed by Bhumbla and Abrol (1972), only 41% of sources within the study area provide water suitable for irrigation.

The high value of RSC in irrigation water tends to increase adsorption of sodium in soil. According to Bishnoi *et al.* (1984), an RSC value above 5 mg/L in irrigation waters is harmful to soil properties and crop growth (Bhumbla *et al.*, 1972). On the basis of this, it is clear that 96% of groundwater sources in the study area provide water fit for irrigation purposes.

According to the classification proposed by Richards (1954) for sodium adsorption ratio, water from 92% of sources is satisfactory for irrigational purposes, in Tehsil Kheragarh.

TABLE IV

Categorization of water quality for irrigation purposes

EC range mmho/cm	Quality[a]	RSC range me/L	Quality[b]	SAR range	Quality[c]
0–1	Very Good	< 0	Very Good	0–10	Fit
1–2	Good	0–2.5	Fit	10–18	Marginal
2–4	Marginal	2.5–5.0	Marginal	18–26	Poor
4–6	Harmful	5.0–7.5	Poor	>26	Unfit
> 6	Very harmful	> 7.5	Unfit		

[a] Bhumbla and Abrol, 1972
[b] Bishnoi *et al.*, 1984
[c] Richards, 1954

4. Conclusion

The study reveals that water of nearly 50% of sources within the study area has fluoride concentration more than 1.5 mg/L and people residing in this area are vulnerable to fluoride toxicity. It is recommended therefore, that piped water should be provided to the residents for drinking and cooking purposes after proper analysis only. Besides, the use of existing handpump and tubewells, having high fluoride sources, may be restircted for washing, bathing and other such purposes.

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