7 Appraisal of Fluoride Contamination of Groundwater through Multivariate Analysis: Case Study

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CONTENTS

ABSTRACT

Groundwater in the surrounding area of a hot spring in the Nayagarh district of Orissa, India, is enriched in fluoride. Although the hot-spring water has higher pH and bicarbonate concentration but is depleted in Mg, the concentrations of other species are more or less similar to the uncontaminated groundwater. The temperature and pH of the hot spring water mostly rules out any abnormal input of heat and addition of species from deeper crustal origin other than the expected exchange of components between the circulating meteoric water and the surrounding rock. Principal component analysis on measured parameters in the hot spring water, contaminated and uncontaminated groundwater from the area, confirmed mixing of water from the hot spring with that in the subsurface, causing fluoride enrichment in the latter. Furthermore, R-mode factor analysis on selected hydrochemical parameters explains the interrelationships among pH, fluoride, and bicarbonate concentrations; the scores of the two principal factors discriminate the water types. The hydrochemical parameters were classified into two groups by cluster analysis. The first group comprised pH, F^-, Na, and Fe ascribed to the process operating within the hot spring and the second, consisting of Ca, Mg, and HCO_3^-, is related to the host rock.

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7.1 INTRODUCTION

The hydrosphere chemistry in general is influenced by a multitude of anthropogenic factors besides natural causes — namely, mineralogy and chemistry of the country rock through which water flows and the interactions among them in a given environment. The residence time of water in any reservoir (host aquifer rock), the soil through which the water seeps, and phenomena like melting of ice and discharge of geothermal fluids are additional factors affecting the constitution of hydrochemical species of any water.

Various anthropogenic activities generate many chemical species that mix and interact with the surface and groundwater reservoirs through a series of processes. The general chemical makeup of the water, particularly anomalous concentrations of chemical species that pose serious threats to life, are the results of such processes. It is generally not possible to work out the cause and effect relationship in all cases deterministically. In an attempt to understand the process, many chemical parameters in the water are analyzed, landing up in a multivariate system; the objective then is to transform the dataset to an easily understandable form.

Several multivariate statistical techniques have been adopted for this purpose and results are quite encouraging [1–10]. Among the multivariate techniques, principal component analysis, factor analysis, and cluster analysis have been quite effective in understanding the processes controlling the chemistry of natural waters [1,11–15] and contaminated waters, in particular [16].

Fluoride enrichment of surface and groundwater is a frequent phenomenon and health problems arising out of excess intake of the anion are quite widespread as indicated by the statistics on the regions and populations facing the problem all over the world [17–20]. Fluoride enrichment of water and resultant health problems are reported from many parts of India [21–23].

7.2 STUDY AREA

The study area comprises a cluster of villages (Figure 7.1) in the Nayagarh district of Orissa, India, where enrichment of fluoride in ground and surface water was reported earlier [24]. The population of the area is affected by dental and skeletal fluorisis due to intake of fluoride-enriched water. The area spreads over approximately 100 km^2 (Figure 7.1) and experiences subtropical climate with maximum temperature rising up to 42°C during the month of May. The southwest monsoon is the principal source of rainfall; it breaks in the middle of June and continues till early October. The average annual rainfall recorded over the period of the last 12 years is 1145.35 mm. The area is a part of the Eastern Ghats geological province, comprising mainly granite gneisses and more Al-rich quartzofeldspathic gneisses (khondalites) with Fe–Mg-rich charnockites and mafic granulites. Among the structural elements, joints/fractures and foliations (trending NE–SW with gentle easterly dips) form the prominent conduits for subsurface fluid movement.

In the area, groundwater generally occurs under unconfined conditions. The area is also characterized by the presence of a hot spring, one among many such occurrences in the Eastern Ghats province of Orissa over a linear tract of 200 km. The surface temperature of the hot spring water varies from 40 to 60°C. The hot spring is located near the topographic low of the area with a steeper slope in the northern, western, and southwestern parts compared to that of the eastern and southeastern parts. The soil cover varies in thickness from 2 to 4 m and is thinner over elevated ground. The fluoride-enriched zones in the study were earlier delineated by employing geoelectrical resistivity sounding in conjunction with hydrogeochemical study [13]. The present work has attempted a more detailed analysis of the hydrogeochemical parameters employing multivariate geostatistics to signify the observed variability in the data physically in terms of natural processes giving rise to fluoride enrichment in water.

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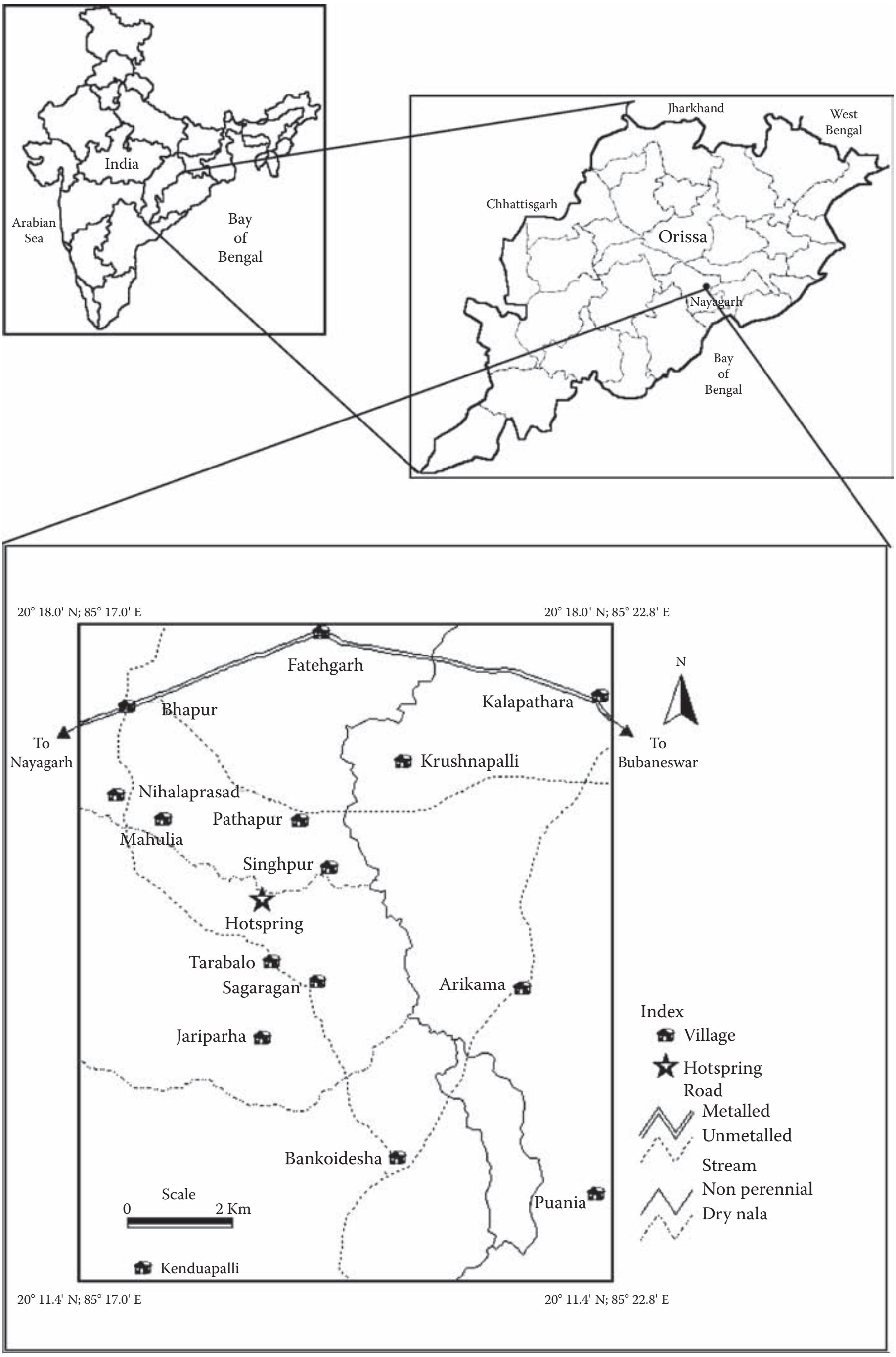

FIGURE 7.1 Location map of the study area around the hot spring in the Nayagarh district of Orissa, India.

7.3 MATERIALS AND METHODS

Water samples in duplicate from various potable sources comprising bore wells and open wells in 55 villages in the study area were collected during the postmonsoon period. In addition, premonsoon water samples collected from selected locations were used to study the temporal variations of

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different parameters. In addition, water samples from the hot spring were also collected in the pre- and postmonsoon periods. One set of samples was filtered and acidified with 2 ml of 35% HNO_3 and stored in air-tight polyethylene bottles for use in the determination of pertinent cations; the unfiltered and nonacidified ones were used to determine the concentrations of anions, pH, electrical conductivity (EC), and total dissolved solids (TDS).

Water samples collected from the hot spring and potable sources were analyzed for fluoride, chloride, EC, and pH by Orion ion selective electrode model 1260. The instrument was calibrated using E-MERCK buffers of pH 4, 7, and 9, respectively. For fluoride measurement, the instrument was calibrated using 0.1 *M* standard sodium fluoride (NaF) solution; for chloride, 1 *M* chloride solution was used. Blank solutions made up from MILLI-Q water (resistivity: 10 to 15 MΩcm; conductivity: <0.2 µs/cm; TOC: <30 ppb) were also analyzed. To each 50-ml sample, including the blank before analysis for fluoride, 2 ml of total ionic strength adjustment buffer (TISAB IV) was added. Similarly, 2 ml of ionic strength adjuster (ISA) was added to 50 ml of each sample and the blank, during chloride measurement. The buffer solutions helped in minimizing complex formation and buffered the solution pH to 5.2. The samples were continuously stirred using a magnetic stirrer during measurement.

The concentrations of Na, Ca, K, Mg, Al, and Fe were determined by analyzing the acidified water samples employing the Perkin–Elmer Model 3300 inductively coupled plasma optical emission spectroscopy (ICP-OES) at the Department of Earth Sciences, University of Western Ontario, Canada. Standard wet chemical methods [25] were employed in the determination of carbonate and bicarbonate concentrations in water samples. Sulphate and silica were determined by CINTRA-5 UV-VIS spectrophotometer. Results of analyses are presented in Table 7.1.

7.4 SALIENT HYDROCHEMICAL FEATURES

The pH of hot spring water ranges from 7.9 to 8.9, with a mean of 8.2, and the fluoride concentration varies from 12 to 14.2 ppm, with a mean of 13 ppm; the temperature of the surface discharge varies from 40 to 60°C, with a mean of 53°C. The thermal waters are soft and more alkaline in nature than the groundwater. The hot spring water is mostly depleted in Mg and low in Ca and K; however, Na content is considerably higher and the bicarbonate content is marginally higher than the groundwater. The inverse relationship of fluoride concentration in water with Ca and Mg is reported quite often [26,27].

The subsurface temperature of the hot spring is about 100 to 125°C on the basis of Na–K–Mg triangular plot and its chemistry indicates partial equilibrium with rocks of average continental crust [28]. Because the area is a part of a stable continental shield with a normal geothermal gradient, input of additional heat for sustaining a geothermal system at this temperature is required. Crustal radiogenic heat is a strong possibility. The temperature, along with the alkaline pH of the hot spring, also would rule out any additional input of volatile component from the deeper part and the chemistry of the hot spring is a result of exchange of components with the near-surface rocks.

Water samples with more than 1.5 ppm fluoride fall into "sodium" or "potassium" type in cation facies and include samples from the hot spring. About 60% of these are the chloride type in anion facies. Among the samples containing less than 1.5 ppm fluoride, 50% fall in "no dominant type," and approximately 25% are sodium type or potassium type; the remainder is "calcium" type. Concurrently, nearly half of these samples fall into the "bicarbonate" type and the rest into the "chloride" type in anionic facies [12].

Spatial distribution of fluoride concentration of groundwater (Figure 7.2) was obtained from the analytical data using SURFER 6.04. The semicircular area around the hot spring, including the villages of Singhpur and Sagargaon, shows high concentrations of fluoride in groundwater above the permissible limit; in other words, a delineation of the contaminated zone in the area is revealed.

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TABLE 7.1
Results of Analysis of the Ground Water and Hot Spring Water of the Study Area

No.	pH	EC	TDS	TH	HCO_3^-	CO_3^{2-}	F^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al^{3-}	Fe^{3-}
1	7.7	428	257	86	162	7.8	0.28	28.5	42.0	15	11.7	97.8	1.3	0.96	0.97
2	7.5	1037	622	738	198	2.3	0.38	181	0.8	183	68.3	175.2	2.1	0.52	4.69
3	7.6	1341	805	96	301	4.7	1.06	202	4.3	1.9	22.2	143.5	1.7	0.46	0.02
4	7.7	1382	829	95	301	20.3	0.85	219	12.3	1.8	22.1	109.6	1.4	0.72	0.47
5	7.6	2273	1364	168	368	12.5	0.65	464	11.6	2.3	39.4	114.0	10.2	0.82	2.65
6	7.7	1226	736	220	257	7.8	0.64	204	12.9	76.5	7.0	76.9	3.9	0.28	0.51
7	7.5	2000	1547	44	285	6.2	0.55	543	16.5	4.4	7.9	10.7	15.8	0.16	3.93
8	7.5	550	352	249	160	0.9	0.67	26.5	0.1	49.1	18.0	19.0	1.6	0.40	0.37
9	7.2	2054	1232	197	273	9.4	0.47	385	0.5	2.3	46.5	18.6	11.0	0.92	0.98
10	7.7	2000	1800	48	371	14.0	0.33	712	12.3	6.8	7.6	100.8	56.2	0.71	0.72
11	7.9	2634	1580	35	582	17.9	1.11	411	17.4	2.2	7.3	96.7	94.3	0.14	0.32
12	7.6	620	397	128	130	0.3	0.39	9.2	1.4	35.3	9.6	15.6	2.0	0.55	1.10
13	7.6	617	370	468	222	7.8	0.49	37.9	8.9	46.5	85.6	17.8	3.2	0.99	0.41
14	6.8	1453	930	515	170	0.6	0.53	228	26.8	159.6	28.6	35.5	3.2	0.86	0.45
15	7.1	415	249	92	105	0.0	0.21	64.3	14.1	14	13.9	35.9	2.8	0.77	29.2
16	7.9	976	586	87	523	15.6	0.69	32.3	9.5	1.4	20.4	53.6	1.2	0.59	0.24
17	7.7	106	68	268	150	0.5	1.15	16.3	4.8	46.4	37.0	28.9	2.8	0.37	0.22
18	7.0	271	163	58	86	0.0	0.27	27.7	8.1	10	8.0	16.6	5.2	0.56	1.38
19	7.7	2481	1489	233	514	15.6	1.60	441	12.3	2.2	55.2	108.6	17.0	0.38	0.23
20	7.7	216	138	71	120	0.3	0.28	36.3	0.1	22.7	3.6	13.9	3.0	0.35	1.56
21	6.8	1259	755	80	127	0.0	0.36	303	8.3	1.9	18.3	14.7	2.2	0.67	17.70
22	7.8	945	567	484	377	10.9	0.38	69.9	13.4	93.5	60.9	190.9	28.5	0.12	1.36
23	7.3	254	152	31	67	3.1	0.17	35	19.3	9	2.1	91.3	17.4	0.38	0.31
24	7.7	886	532	486	209	1.6	1.17	157	1.4	47.5	89.2	86.4	1.6	0.94	1.97
25	8.0	844	506	433	320	12.5	1.46	45.1	14.1	35.5	83.6	80.6	1.9	0.21	0.42
26	7.9	1114	668	884	428	14.0	0.62	92.3	1.3	342	7.3	33.1	1.5	0.25	0.30
27	7.8	1572	943	454	301	7.8	0.41	252	6.0	169.5	7.5	15.4	1.7	0.73	0.21
28	7.6	100	64	432	110	0.3	0.29	247	12.9	144.4	17.6	38.5	2.9	0.39	0.70
29	7.6	1127	676	34	374	14.0	0.43	137	116.5	2.2	6.9	27.1	2.6	0.70	0.41
30	7.4	332	199	46	111	4.7	0.61	18.9	13.6	6	7.6	66.5	1.1	0.16	1.07
31	6.6	159	102	27	58	0.0	0.16	16.7	4.8	6.3	2.9	14.1	1.5	0.04	15.8
32	7.7	452	271	126	216	7.8	1.07	5.58	34.8	19.5	18.9	67.5	1.1	0.46	0.27
33	7.5	488	293	161	243	7.8	1.18	5.11	15.3	23.5	24.8	42.9	1.0	0.53	0.41
34	7.2	106	68	40	84	0.1	0.25	7.52	1.5	11.5	2.7	10.8	2.0	0.46	0.57
35	7.3	327	196	89	106	3.1	0.36	32.6	50.7	10.5	15.2	43.5	2.4	0.89	0.32
36	7.7	456	274	163	198	8.6	0.48	15.4	0.1	24	25.0	16.4	2.0	0.46	0.34
37	7.1	862	552	768	86	0.1	0.30	552	34.2	190.1	71.3	117.7	2.6	0.40	0.22
38	7.6	2719	1631	271	374	9.4	0.48	562	21.3	2.4	64.3	160.8	1.9	0.28	0.99
39	8.6	427	256	147	193	0.8	1.19	17.8	21.5	31.7	16.5	19.0	0.9	0.21	0.59
40	7.9	1363	818	149	336	7.8	1.10	198	1.5	2.1	35.0	102.3	0.9	0.65	0.29
41	7.6	1427	856	37	374	12.5	0.32	226	15.2	2.4	7.5	32.6	1.3	0.35	0.36
42	6.6	377	241	92	100	0.0	0.30	47.9	15.6	24.2	7.7	19.5	2.0	0.07	1.44
43	7.8	650	390	239	263	3.1	2.51	37.1	7.5	75.6	12.2	203.2	1.1	0.41	0.24

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TABLE 7.1
Results of Analysis of the Ground Water and Hot Spring Water of the Study Area (continued)

No.	pH	EC	TDS	TH	HCO_3^-	CO_3^{2-}	F^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	Al^{3-}	Fe^{3-}
44	7.4	201	129	255	137	0.2	0.62	44.6	6.0	62.4	23.9	82.9	2.4	0.72	0.24
45	7.9	692	415	1081	330	18.7	0.52	17.2	22.8	356.5	46.3	15.2	1.1	0.23	0.11
46	8.0	1835	1101	836	416	17.2	0.91	301	1.5	322.5	7.4	24.4	1.8	0.35	0.75
47	7.1	262	157	61	89	0.0	0.21	26.1	7.5	9.4	9.1	18.6	0.9	0.89	9.54
48	7.6	1678	1007	36	200	4.7	0.61	364	31.4	2.6	7.3	31.2	10.8	0.61	0.29
49	7.7	905	579	123	366	1.1	3.06	42.1	5.0	37.5	7.0	124.0	1.9	0.07	0.20
50	7.7	85	54	126	366	1.1	2.71	45.3	4.8	38.5	7.2	130.6	2.1	0.42	0.30
51	8.2	914	548	50	397	9.4	3.12	37.7	5.8	1.1	11.5	132.9	1.1	0.33	0.34
52	7.8	416	250	163	168	3.1	0.56	17.1	18.3	50	9.3	29.5	1.9	0.93	0.07
53	7.7	1637	948	51	232	0.7	4.64	33.3	2.2	14.1	3.7	137.6	1.6	0.05	0.90
54	7.9	96	61	132	285	1.4	8.07	184	16.5	30.1	13.8	152.3	1.7	0.43	0.20
55	8.1	652	417	54	315	2.4	5.35	37.1	1.0	15.2	3.9	144.4	1.7	0.68	1.80
56	7.8	1454	872	156	374	9.4	1.39	203	16.5	2	36.7	153.9	1.0	0.55	0.20
57	7.4	1537	922	34	270	7.8	0.32	272	33.7	2.2	6.9	29.9	3.3	1.32	0.52
58	8.0	829	531	13	167	1.5	12	180	16.1	5.1	0.1	125.5	3.3	0.11	0.15
59	8.9	853	546	15	382	28.5	12.7	192	17.0	5.9	0.2	132.4	4.4	0.13	0.14
60	7.9	1524	975	13	409	3.0	13.1	176	16.6	5	0.1	130.9	4.1	0.36	0.21
61	7.9	485	310	9	329	1.6	14.2	173	22.8	3.5	0.2	128.2	3.2	0.58	0.22
62	8.1	621	397	14	311	3.6	13.1	171	17.4	5.2	0.1	132.8	3.5	0.46	0.13

Note: Analyses # 58 to 62 are for the hot-spring water.

7.5 MULTIVARIATE ANALYSIS OF HYDROCHEMICAL DATA

The various hydrochemical parameters analyzed for all the types of water from the area represent a set of multivariate data. Three different types of multivariate statistical analyses were attempted in order to reduce the dimensionality of the dataset for meaningful interpretation in terms of the processes responsible for the variability of the data. Principal component analysis was attempted in order to resolve the variance into mutually orthogonal axes for identification of different fluid components in the study area. Results of similar analysis on a fewer number of analytical data were reported earlier [12].

Because of the three distinct components — thermal spring, groundwater with high fluoride concentration, and groundwater with low fluoride concentration, it is necessary to determine the actual number of end member components. The permissible limit of 1.5 ppm was taken as the dividing line between the contaminated and uncontaminated groundwater. The present statistical analysis is based on 49 water samples from the uncontaminated zone, 7 samples from the inner zone of contamination, and 5 samples from the thermal spring, as shown in Figure 7.2. A robust principal component analysis program (ROPCA) was used for the Q-mode principal component analysis [29] and the first two components were chosen for plotting the principal component scores.

The data collected during the study are well posed, as revealed from the first two eigenvalues extracted from the dispersion matrix accounting for more than 55% of the total variance. Principal factor analysis was also attempted on the data presented in Table 7.1. Eigenvalues were extracted from the dataset and the corresponding factor loadings for variables and factor scores for each case were calculated using STATISTICA 4.0. Only nine variables with significant correlation

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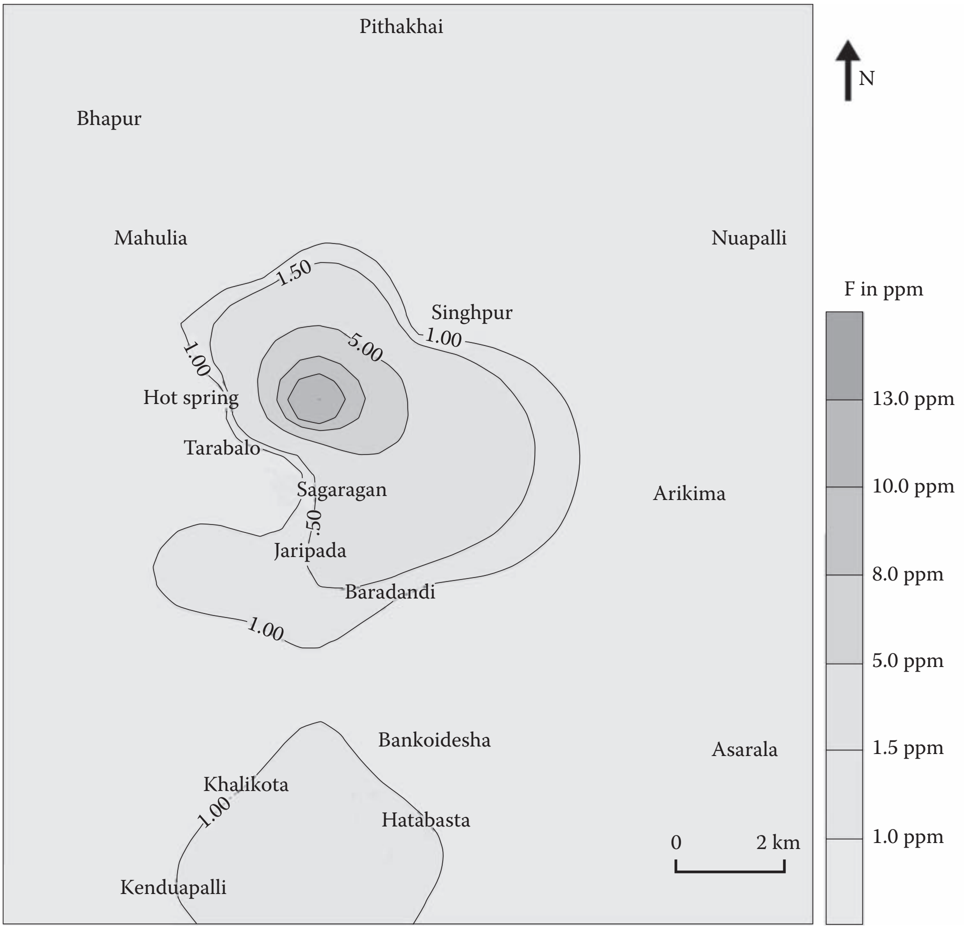

FIGURE 7.2 Spatial distributions of fluoride concentrations in ground water in the study area (see text for details).

coefficient ($r > 0.5$) were considered for the analysis. Cluster analysis of 15 chemical parameters was also done on the same dataset using Ward's method and Euclidean distance measure for the clustering.

7.6 RESULTS AND DISCUSSION

7.6.1 PCA

Principal component analysis has been quite useful in deducing the end-member components of groundwater [1]. Plots of the first two principal components in the present case as shown in Figure 7.3 reveal an interesting mixing trend between the hot spring water and the uncontaminated groundwater, resulting in enriched fluoride content in the latter. The colinearity of the plots necessarily rules out the involvement of any other water type. The cause of fluoride enrichment in the groundwater is thus discernible.

7.6.2 Factor Analysis

The parameters presented in Table 7.1 lack good correlation and therefore the resolvability of the total variance of the system is not satisfactory. Out of the various combinations that were tried,

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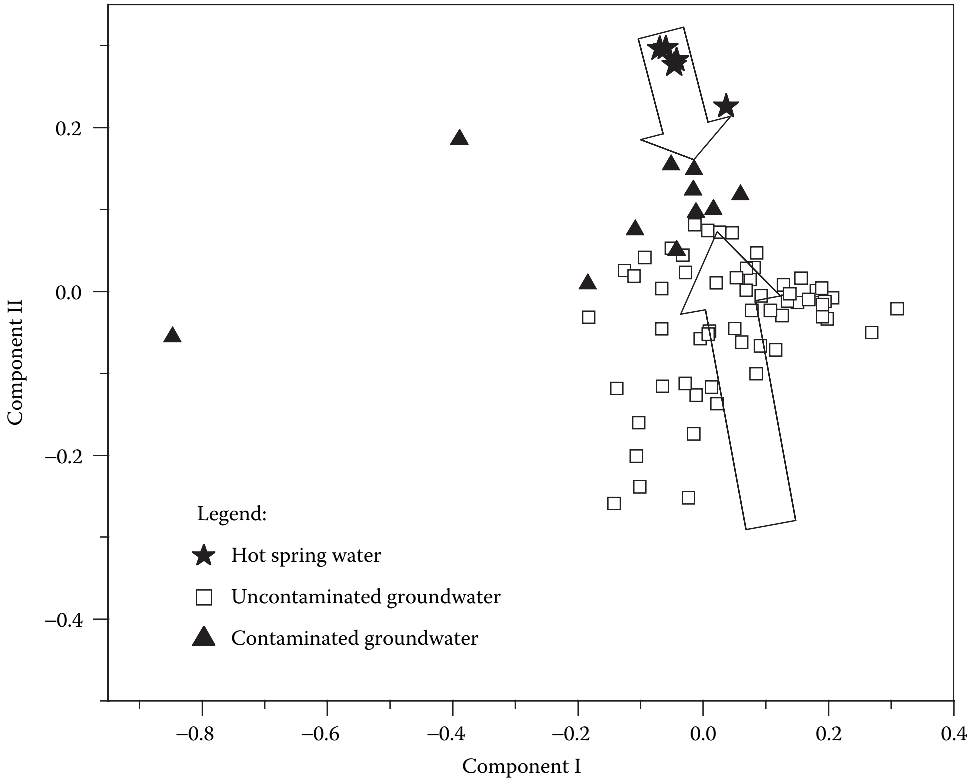

FIGURE 7.3 Plots of the first two principal component scores computed on the hydrochemical parameters of ground water and hot-spring water of the study area. The arrows indicate the mixing trend.

TABLE 7.2
Eigenvalues Extracted by Principal Factor Analysis

	Eigenvalue	% Total variance	Cumulative eigenvalue	Cumulative %
1	2.619194	29.10216	2.619194	29.10216
2	2.321811	25.79790	4.941005	54.90006
3	1.125874	12.50971	6.066879	67.40977

only the combination of the nine parameters (pH; total hardness (TH); HCO_3; F; Ca; Mg; Na; Al; and Fe) yielded satisfactory results. The three eigenvalues extracted account for 67% of the total variance (Table 7.2).

The first three principal factors extracted from the dataset and the raw loadings of the parameters on these factors are presented in Table 7.3. Only factor loadings exceeding absolute value of 0.6 are considered. As seen from the table, pH, HCO_3, F, and Na are significantly loaded on the first factor, and TH, Ca, and Mg are loaded significantly on the second factor. The third factor is apparently insignificant, so the system can be visualized as being controlled by two factors. The first factor indicates strong mutual influences of F, HCO_3, Na, and pH.

As explained earlier on the basis of the equilibrium governing calcite, fluorite, bicarbonate, and fluoride ions, at a constant pH, an increase in the bicarbonate concentration would increase the fluoride concentration in the water. Figure 7.4(a–c) shows the plots of fluoride concentration

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TABLE 7.3
Factor Loadings (Unrotated) on Three Principal Factors

	Factor 1	Factor 2	Factor 3
PH	–0.825[a]	0.156	0.016
TH	0.116	0.972[a]	–0.105
HCO3	–0.7010[a]	0.229	0.170
F	–0.703[a]	–0.314	–0.150
CA	0.080	0.860[a]	–0.403
MG	0.118	0.619[a]	0.600[a]
NA	–0.690[a]	0.019	0.287
AL	0.381	–0.066	0.669
FE	0.546	–0.270	–0.103
Expl. var	2.619	2.322	1.126
Prp. totl	0.291	0.258	0.125

[a] Significant loadings (>0.6).

vs. pH, HCO_3, and Na and reveals an interesting commonality — i.e., there is a high in the fluoride concentration at restricted ranges of variation of the other three parameters. In other words, the hot spring and the contaminated groundwater correspond to a restricted range of pH (7.5 to 8.5), HCO_3^- (200 to 400 ppm), and Na (between 100 to 150 ppm). This possibly needs to be resolved further from speciation study of the water and aqueous equilibria considerations. The principal factor analysis only indicates the interplay of the two factors. The plot of the first two principal factors' scores for all the samples (Figure 7.5) very clearly separates the three types of water in the area.

7.6.3 CLUSTER ANALYSIS

R-mode cluster analysis was carried out on the same set of variables used for factor analysis and the tree diagram (Figure 7.6) using Ward's method, and Euclidian distance measures are obtained. The figure shows three different clusters of chemical species in the water: pH, F^-, Al, Fe, and Mg make up one; Ca and Na constitute the second; and HCO_3^- and TH comprise the third. It may be noted that, though pH, Na, and HCO_3^- were associated with the first factor obtained in the factor analysis, these species are now separated into different clusters. However, pH and F^- fall into the same cluster and are in accordance with their strong association with the first factor and therefore establish the strong control of pH on the fluoride.

As was noted earlier [12,13,30], the hot spring represents a hydrothermal convection cell operating by percolation of meteoric water through the fracture network in the rock — acquiring higher temperature at deeper levels and the chemical species by interaction with the rock and, finally, venting the hot water through the major fractures/fissures. Such evolved waters in the up-flow zones are characterized by higher pH [17] mostly in the stability fields of HCO_3^-/CO_3^{-2} and K-feldspar. The close relationship of fluoride, bicarbonate, and pH is thus explainable.

However, the presence of a separate cluster for bicarbonates suggests that its concentration in the water is not related to the hot spring activity; rather, bicarbonate, along with Ca, Mg, and Na, is basically controlled by the chemical and mineralogical composition of the surrounding country rocks. It is generally observed that pH of water in land-based geothermal systems is mostly independent from the dominance of anionic species [31]. In summary, the cluster analysis brings out a classification of the chemical species in the water in the area; pH, fluoride, and, to some extent, Fe and Al are associated with the hot spring; Ca, Mg, and HCO_3^- are controlled by the surrounding rocks.

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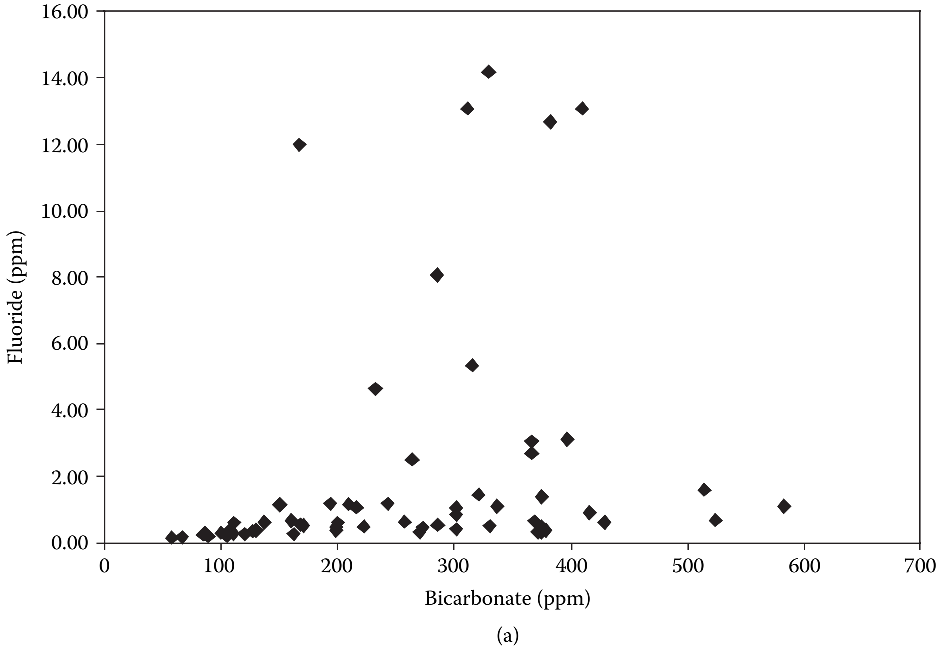
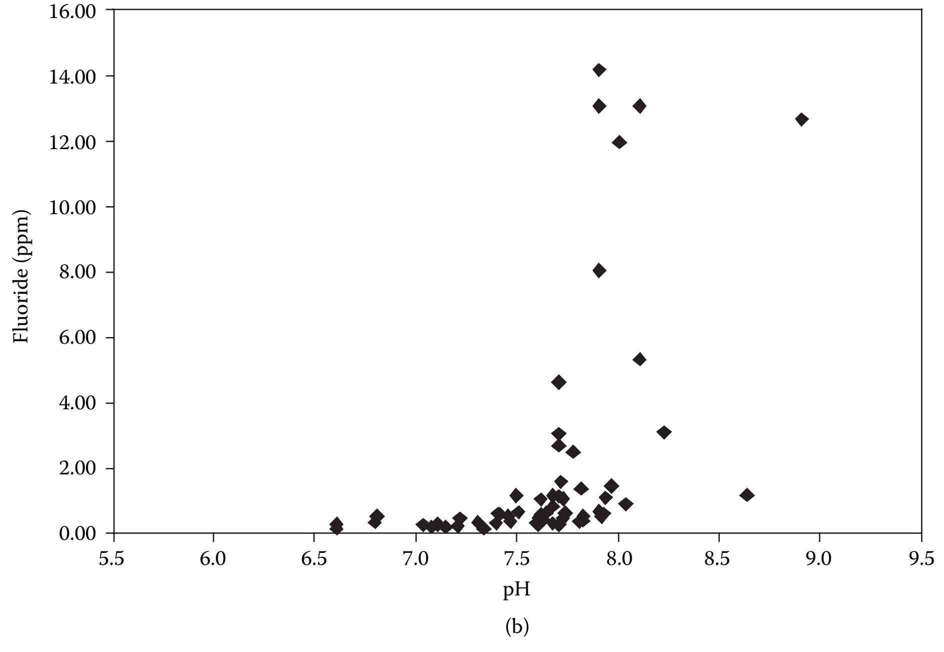


(a)



(b)

FIGURE 7.4 Variation of fluoride concentration with (a) HCO_3^-; (b) pH; and (c) Na. These parameters constitute the first and the most important factor that underlies the data examined (see text).

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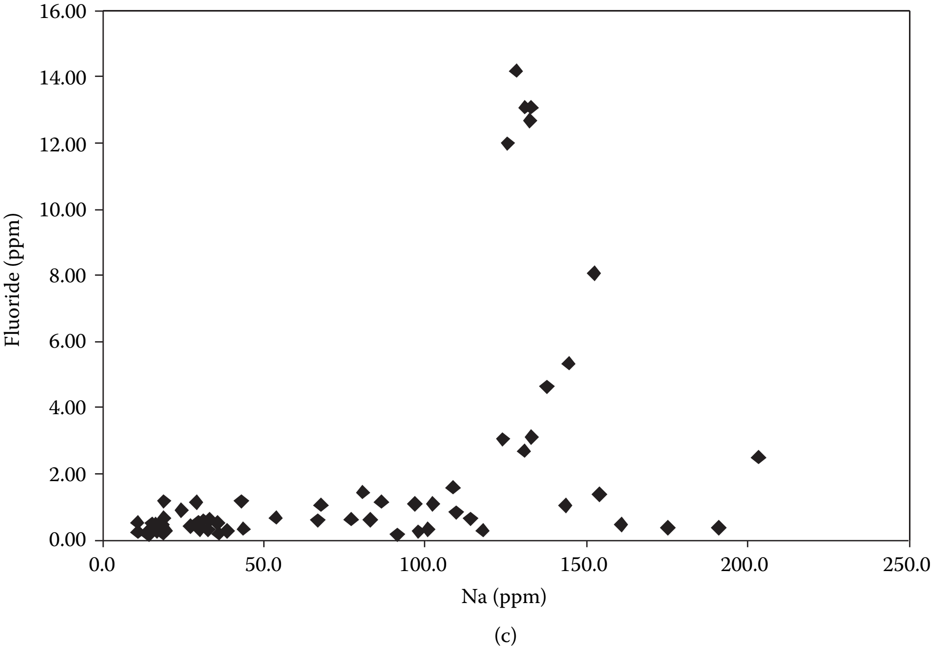

FIGURE 7.4 (continued)

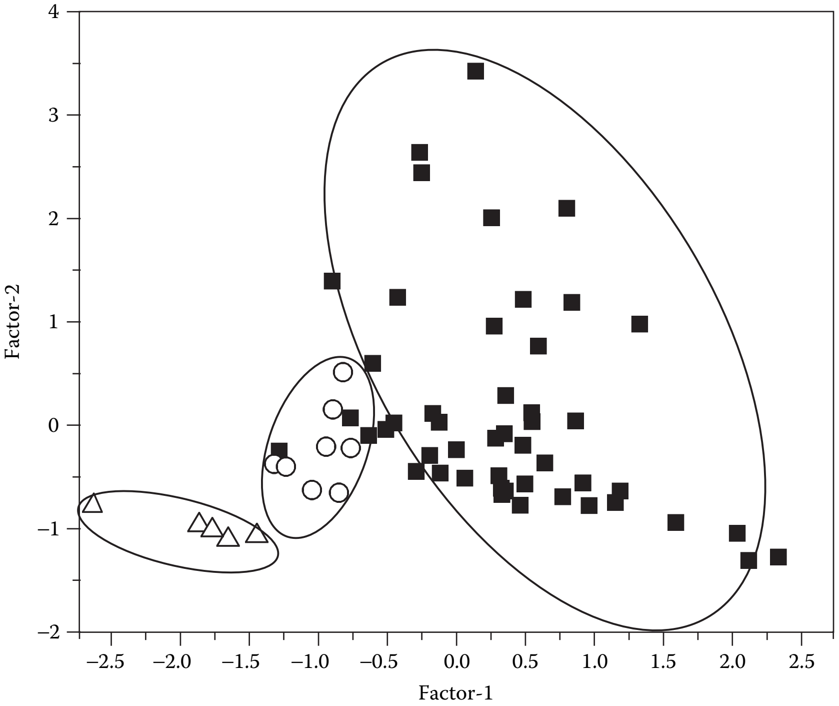

FIGURE 7.5 Plots of scores of the first two factors extracted from a subset of the data (see text for details). The three types of waters are well discriminated on the plot with their respective fields shown.

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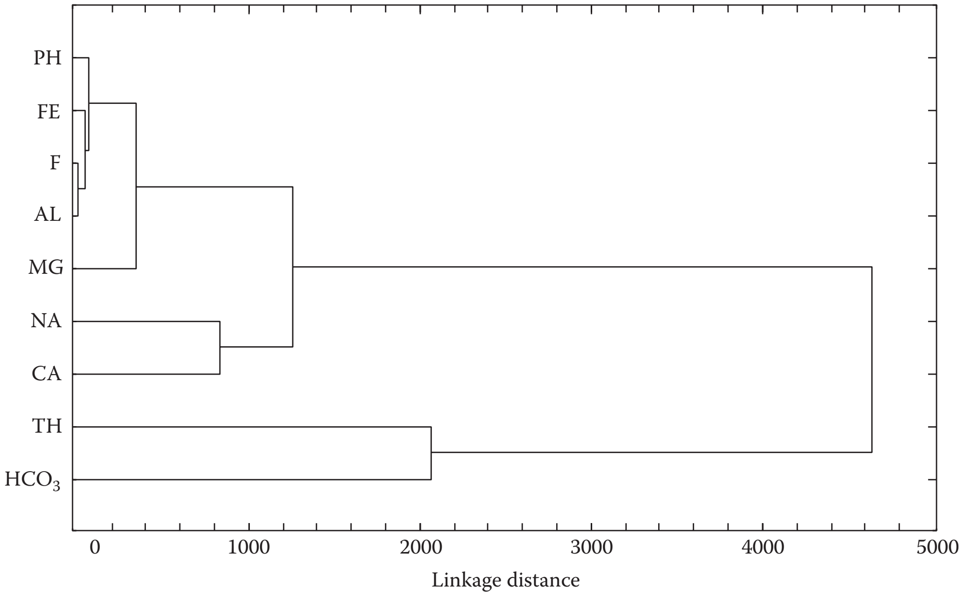

FIGURE 7.6 Dendogram of the ten important chemical species considered for cluster analysis using Ward's method and Euclidean distance measures.

7.7 CONCLUSION

The fluoride-enriched groundwater in the study area is a result of mixing the hot-spring water and normal groundwater as revealed from the principal component analysis. Two major factors that control the water chemistry are identified; the one associated with F^-, HCO_3^-, and pH is the major one. Furthermore, cluster analysis classified the hydrochemical species into two identifiable categories: fluoride and pH with or without Na, Al, and Fe are related to the hot-spring activity; calcium, magnesium, and bicarbonate contents in the water are mainly governed by the chemistry of the rocks.

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