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Hydrochemical Status of Groundwater in District Ajmer (NW India) with Reference to Fluoride Distribution

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Abstract: High fluoride in groundwater has been reported from many parts of India. However, a systematic study is required to understand the behaviour of fluoride in natural water in terms of local hydrogeological setting, climatic conditions and agricultural practices. Present study is an attempt to assess hydrogeochemistry of groundwater in Ajmer district in Rajasthan to understand the fluoride abundance in groundwater and to deduce the chemical parameters responsible for the dissolution activity of fluoride. Ajmer district falls in the semi-arid tract of central Rajasthan and is geologically occupied by Precambrian rocks (granites, pegmatites, gneisses, schists etc) where groundwater occurs under unconfined condition. A total of 153 well-water samples, representing an area of 8481 km^2 (further subdivided into eight blocks), were collected and chemically analyzed. The results of chemical analyses (pre-monsoon 2004) show fluoride abundance in the range of 0.12 to 16.9 mg/l with 66% of the samples in excess of permissible limit of 1.5 mg/l.

Presence of fluoride bearing minerals in the host rock, the chemical properties like decomposition, dissociation and dissolution and their interaction with water is considered to be the main cause for fluoride in groundwater. Chemical weathering under arid to semi-arid conditions with relatively high alkalinity favours high concentration of fluoride in groundwater. Dental and skeletal fluorosis are prevalent in the study area which can be related to the usage of high fluoride groundwater for drinking. The suggested remedial measures to reduce fluoride pollution in groundwater include dilution by blending, artificial recharge, efficient irrigation practices and well construction.

Keywords: Groundwater, Fluoride, Dissolution, Alkalinity, Fluorosis, Ajmer district, Rajasthan.

INTRODUCTION

Rajasthan State (Fig.1) is unique as all the 32 districts have been reported to have variable fluoride contamination in groundwater. However, the fluoride abundance levels are generally controlled by local geological parameters and hydrogeological regime. Excessive fluoride in the domestic water supply is reported in at least 10% villages in Rajasthan (Jacks et al. 2005). Most of the fluoride related groundwater studies in Rajasthan have been focused on the western and southern parts of the state which are conventionally described as ‘high fluoride’ areas (Maithani et al. 1998; Choubisa et al. 2001; Muralidharan et al. 2002). The Central Ground Water Board and State Ground Water Department have reported high fluoride contents in groundwater in some parts of Ajmer district in the course of district-wise hydrogeological and hydrochemical studies. Prevalence of fluorosis in parts of Ajmer district was reported by Mathur et al. (1976). Madhavan and Subramanian (2002) analyzed soil samples in Ajmer district and correlated high fluoride in clay-rich fractions to fluoride variation in groundwater. These authors have also provided an outline of the fluoride problem in Ajmer district (Madhavan and Subramanian, 2003). Datta et al. (1999) carried out ^{18}O-isotopic studies on water samples from Pushkar Lake area.

Water born fluorosis, a crippling disease, is prevalent in parts of Ajmer district in central Rajasthan (Fig.1) which can be correlated to excessive concentration of the toxic F^- ion in drinking water. The authors have carried out detailed hydrochemical studies in Ajmer district with a focus on fluoride occurrence and the findings are presented here. Besides offering a comprehensive status of fluoride concentration in groundwater in Ajmer district, this paper also discusses fluoride distribution in relation to

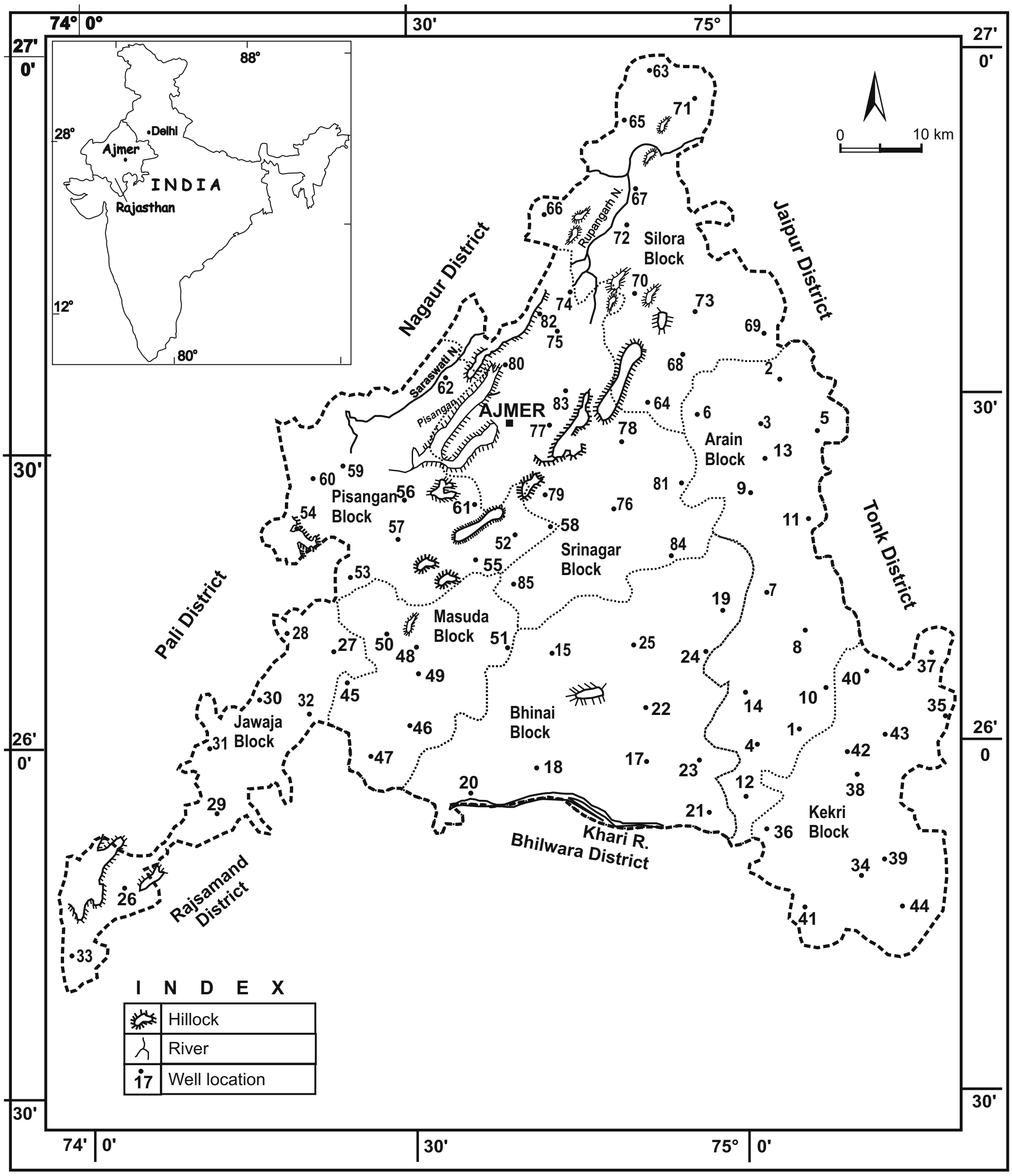

Fig.1. Outline map of Ajmer district showing location of groundwater samples.

geological setting, and fluorine geochemistry. The present study pertains to the fluoride in phreatic groundwater (the top aquifer system) and it is in this regimen that hand pumps, dug and bore wells have been constructed.

GEOMORPHOLOGICAL FEATURES

Ajmer district (25°38'-26°58' N: 73°54'- 75°22' E) covers an area of 8481 km^2 (Fig.1). The entire district has been divided into eight blocks and we have retained the nomenclature in this study for consistency and to avoid any ambiguity.

The main geomorphic features in the district are alluvial plains, linear ridges, pediment, denudation hill, buried pediment and structural valleys. The NE–SW trending Aravalli range is the most distinguishing geomorphic feature that occupies the western part of the district and acts as a major groundwater divide. The Banas is the most important river, and in addition, the region is drained by its tributaries and few other ephemeral rivers like Khari, Sagarmati, Saraswati and Dei. The district lies in the semiarid region of the state with an average mean annual rainfall of 480 mm.

HYDROGEOLOGY

The main lithological units include gneisses, schists, granites, quartzites, phyllites, and limestones belonging to the Bhilwara and Delhi Supergroup of rocks of Archaean and Proterozoic ages, respectively. Quaternary and Recent alluvium occurs as thin veneer on the older consolidated rocks. Although groundwater occurs mainly under water table condition in all the formations, the Quaternary alluvium forms good aquifers in parts of Ajmer district. In hard rock terrain, the occurrence and movement of groundwater is controlled by secondary porosity such as fractures, fissures, joints, foliation etc. The weathered mantle of hard rocks yields copious water. Depth to water level, in general, varies from10 m to 25 m bgl during pre-monsoon period (May, 2004), while during post-monsoon period (Nov., 2004) it ranges from 5 to 20 m bgl. The water table elevation in the area ranges from 310 m in the southeastern part to more than 660 m amsl in the southwestern part.The groundwater flow direction, is towards east, south, southeast and north.

MATERIALS AND METHODS

Block wise water samples were collected (Fig. 1) during pre-monsoon of 2004, and were analyzed at the chemical lab of Central Ground Water Board, Jaipur for pH, Electrical conductivity (EC), Total Hardness (TH), major anions and cations along with fluoride, following the procedures described in APHA (1995) and the results of selected wells are presented in Table 1.

RESULTS AND DATA PRESENTATION

There are remarkable differences in the water chemistry between deeper and shallow aquifers. The water samples exhibit a wide range of pH (4.63 to 9.2) in shallow aquifers, while deeper aquifers show a narrow range between 7.05 and 8.06. The EC varies from 245 to 13560 mmhos/cm at 25° C (Mean - 2846 mmhos/cm) in shallow aquifer samples, while deeper water samples are characterized by higher EC values of 670 -12320 mmhos/cm at 25° C (Mean - 3692 mmhos/cm). The anion and cation concentrations, except fluoride, are within the desirable limits (BIS, 1991). The analysis results indicate that the water is generally alkaline in nature. The total hardness in the groundwater ranges from 9.6 to 2775 mg/l and is due to the presence of alkaline earths such as calcium and magnesium. Ca concentration varies from 9 to 548 mg/l and Mg concentration ranges from 2.4 to 492 mg/l in the analyzed samples. The concentration of bicarbonate ranges from 104 to 1586 mg/l (Mean - 493 mg/l). The abundance of major ions is as follows: $Na^+ > Ca^{2+} > Mg^{2+} > K^+ = Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > CO_3^{2-}$. Bicarbonate and Na/K type waters dominate in the area with lesser proportion of Cl and mixed type waters as per Piper classification. A positive correlation between alkalis (Na + K) and chlorides clearly depicts that at low concentrations, the data distribution approaches a 1:1 trend characterizing a pure evaporite source. Similarly, the plots of the weight ratios of Na / (Na + Ca) and Cl / (Cl+ HCO_3), as a function of TDS, show that most of the data distribution falls in the field of evaporation dominance (Fig.2). Groundwater in the area is generally fresh to brackish, hard to very hard, alkaline and medium to high saline type.

Fluoride concentration in shallow aquifer samples ranges between 0.12 (Makarwali village in Srinagar block) and 16.9 mg/l (Almas village in Arain block) with an average value of 2.96 mg/l. Deeper aquifer samples are characterized by relatively lower F^- concentrations, ranging from 1 to 7.96 mg/l (mean - 2.54 mg/l). In the case of open wells (OW),

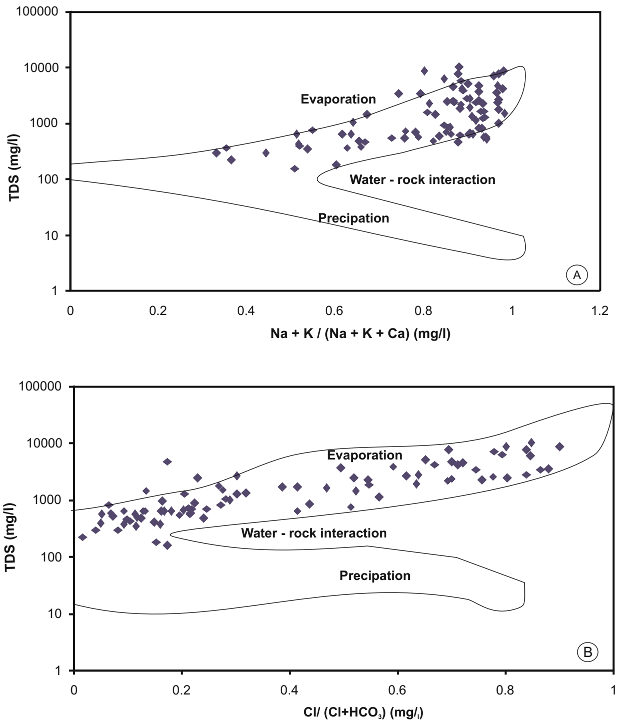

Fig.2. Hydrochemical parameters of groundwater in Ajmer district, Rajasthan showing variations in weight ratios. (**A**) Na+K / (Na+ K+Ca) and (B) Cl / (Cl + HCO_3), as functions of TDS.

Table 1. Analytical Data for the Groundwater Samples from District Ajmer. (The anion and cation values shown in mg/l and EC in micromhos per cm at 25^{0}C)

Well No.	Location	Block	EC	TDS	pH	Na	K	Ca	Mg	Cl	HCO_3	F	TH
1	Ajgara	Arain	3100	1875	8.30	570	7.0	60	66	702	403	2.16	423
2	Almas	Arain	13005	8427	8.60	2897	5.0	50	192	3936	976	16.90	913
3	Arain	Arain	9840	7009	8.50	1839	626.0	100	182	2447	690	1.66	1000
4	Arain	Arain	640	379	7.70	72	1.5	38	29	21	397	0.76	215
5	Bhamolav	Arain	13560	9956	8.20	2747	39.0	370	316	3617	647	1.40	2225
6	Borada	Arain	2560	1571	7.70	410	9.0	98	69	539	610	0.76	530
7	Chandolai	Arain	6940	4650	8.60	1600	6.0	52	51	1603	683	8.10	340
8	Fatehgarh	Arain	5790	4136	7.80	800	579.0	174	102	1163	574	1.80	855
9	Gordhanpura	Arain	1110	721.5	8.05	160	5.0	52	12	149	549	1.90	180
10	Hingonia	Arain	3890	2584	8.20	899	2.3	26	51	624	1440	13.90	275
11	Pandarwara	Arain	2580	1647	8.20	549	11.0	41	35	472	744	2.54	245
12	Sampla	Arain	2360	1494	9.00	549	4.6	9	30	277	726	14.70	145
13	Sandolia	Arain	1120	693	7.50	195	6.6	35	29	156	476	1.54	205
14	Sarwar	Arain	5220	3366	7.80	731	184.0	236	90	1113	378	4.00	9.6
15	Bandanwara	Bhinai	1055	685.75	7.81	156	3.7	44	38	106	378	0.87	210
16	Bhinai	Bhinai	2150	1427	7.65	245	55.0	62	63	142	915	2.34	415
17	Champaneri	Bhinai	3740	2419	8.05	445	219.0	112	131	780	720	0.72	820
18	Ekalsingha	Bhinai	775	510	8.10	180	5.8	11	6	39	488	5.00	53
19	Goyala	Bhinai	1060	657	8.45	210	5.0	22	16	106	415	3.10	120
20	Jaliya	Bhinai	450	292.5	8.10	24	4.7	36	19	21	476	1.10	170
21	Kairot	Bhinai	3920	2563	8.30	720	9.0	110	71	688	427	2.00	565
22	Nagola	Bhinai	970	638	8.50	180	3.0	29	33	71	464	1.62	208
23	Nandsi	Bhinai	635	459	8.15	128	4.7	18	30	43	391	1.62	170
24	Santola	Bhinai	3320	2172	8.05	609	11.0	80	73	702	311	3.24	500
25	Sarana	Bhinai	1335	857	7.75	249	5.4	42	25	152	525	2.78	208
26	Barakhan	Jawaja	985	569	8.30	143	7.0	40	24	85	305	1.72	200
27	Beawar	Jawaja	7200	4680	7.20	1220	52.0	100	173	54	256	5.00	960
28	Beawarkhas	Jawaja	950	617.5	8.09	181	3.8	24	12	113	512	1.07	110
29	Jawaja	Jawaja	2530	1644.5	7.77	473	8.2	32	41	390	549	1.84	250
30	Kalaliya	Jawaja	2820	1833	8.24	520	1.0	68	36	341	281	2.50	320
31	Naikalan	Jawaja	1140	752	8.00	108	12.0	98	26	206	195	2.64	753
32	Shahpura	Jawaja	4660	2767	8.20	779	16.0	88	102	1220	232	1.44	640
33	Tadgarh	Jawaja	890	549	7.95	137	3.9	52	18	64	500	2.04	205
34	Aloli	Kekri	3500	2200	8.28	609	59.0	46	89	610	506	7.08	480
35	Baghera	Kekri	840	537	8.10	60	75.0	43	26	82	336	0.88	215
36	Bhimrawas	Kekri	8640	6233	8.20	1462	109.0	282	288	2156	555	3.52	1885
37	Deogaon	Kekri	7600	5034	7.75	1407	5.4	152	187	1397	744	3.52	1150
38	Farkiya	Kekri	8840	5792	7.85	1642	11.0	212	185	2213	397	2.68	1290
39	Ghatiyali	Kekri	755	462	8.70	67	5.8	36	40	74	232	1.16	255
40	Joonia	Kekri	980	637	7.58	59	0.1	56	58	121	171	0.25	380
41	Kadera	Kekri	1790	1113	8.45	300	43.0	30	33	319	244	1.16	210
42	Kekri	Kekri	960	624	7.65	76	1.0	44	51	64	329	0.80	320
43	Mevda Kalan	Kekri	990	625	865.0	195	3.9	19	23	74	366	2.64	143
44	Motiala	Kekri	5540	3434	8.50	1099	5.8	38	91	1347	183	4.08	470
45	Andharidevri	Masuda	1250	812.5	8.30	220	4.0	16	27	92	244	4.00	150
46	Daulatpura	Masuda	2000	1300	7.84	385	19.0	40	27	184	390	8.60	210
47	Jiwana	Masuda	515	340	8.30	47	9.0	48	16	35	268	1.44	188
48	Kirap	Masuda	5250	3835	8.05	379	759.0	138	111	851	586	0.88	800
49	Masuda	Masuda	6980	4423	7.60	1140	29.0	176	220	1844	708	0.88	1345
50	Piplaj	Masuda	720	468	7.88	83	8.6	48	12	35	244	2.08	170
51	Shergarh	Masuda	985	632	7.90	195	3.9	21	22	82	555	4.40	142

Table 1. Contd....

Well No.	Location	Block	EC	TDS	pH	Na	K	Ca	Mg	Cl	HCO_3	F	TH
52	Bhawanikhera	Pisangan	520	362	8.5	50	31	48	17	35	183	2.18	190
53	Gola	Pisangan	1965	1277.25	8.04	440	5.0	28	22	121	464	4.45	160.0
54	Govindgarh	Pisangan	900	585	7.87	145	20.0	32	19	28	378	3.19	160
55	Jethana	Pisangan	1250	813	7.89	250	3.1	20	9.7	50	708	4.85	90
56	Kalesara	Pisangan	10950	7459	7.85	2598	20.0	75	131	3067	1336	5.00	725
57	Nagelao	Pisangan	5830	3379	8.00	720	11.0	249	219	1886	293	0.88	1520
58	Nasorabad	Pisangan	4140	2720	8.05	761	7.0	80	105	950	537	1.16	630
59	Pisangan	Pisangan	1935	1238	8.25	370	9.0	26	46	234	537	2.92	253
60	Richmalia	Pisangan	1310	838	8.20	245	2.0	40	24	238	305	3.80	200
61	Tabiji	Pisangan	450	292.5	8.20	15	5.0	40	22	21	232	0.45	190
62	Tilora	Pisangan	650	422.5	7.85	30	43.0	68	9.7	43	366	0.66	210
63	Bhairwaj	Silora	980	637	7.80	95	2.0	60	34	50	488	0.70	290
64	Godiana	Silora	1410	929	7.95	266	3.0	48	37	142	720	4.00	273
65	Jhak	Silora	340	221	4.63	16	2.5	32	12	14	781	1.17	130
66	Karkeri	Silora	1505	973	8.60	300	5.0	9	54	206	506	1.72	243
67	Kathoda	Silora	2530	1763	8.05	651	5.0	19	22	386	1050	8.60	140
68	Kishangarh	Silora	3400	2210	8.00	620	8.0	144	5	880	281	1.89	380
69	Mundoti	Silora	560	364	7.90	27	6.0	60	32	35	342	1.44	283
70	Salemabad	Silora	4060	2328	8.60	651	5.0	20	163	1113	476	2.32	720
71	Sanodia	Silora	4100	2379	8.05	779	7.0	68	51	1206	293	2.32	380
72	Sursura	Silora	865	561	8.85	175	5.0	12	19	85	311	2.64	108
73	Tiloniya	Silora	1580	1034	7.80	157	29.0	104	64	209	531	5.00	523
74	Babayacha	Srinagar	730	485	8.30	125	5.0	28	18	43	323	2.64	145
75	Bubani	Srinagar	2230	1415	8.10	165	77.0	117	98	401	366	1.44	698
76	Dhal	Srinagar	600	394	8.60	60	3.0	58	16	43	244	3.52	213
77	Ghooghra	Srinagar	870	553	8.85	195	5.0	12	9	21	384	4.08	65
78	Kanpura	Srinagar	6580	4047	9.00	1462	6.0	28	47	1730	696	6.76	265
79	Kayampura	Srinagar	2830	2379	7.65	520	40.0	83	65	347	1159	4.68	475
80	Makarwali	Srinagar	325	179	8.65	28	1	19	21	21	116	0.12	135
81	Nabab	Srinagar	4160	2527	8.30	609	184.0	62	106	979	281	1.44	590
82	Narwar	Srinagar	5700	3639	7.90	1140	26.0	92	102	1213	1233	4.00	650
83	Ramner Dhani	Srinagar	11880	7560	7.65	1899	16.0	260	492	3918	744	1.72	2675
84	Sanod	Srinagar	12000	8420	8.25	2000	16.0	496	374	3670	403	2.92	2775
85	Balwanta	Srinagar	245	154	8.40	22	4.0	25	7	22	104	1.44	90

only 35% of wells record F^- concentration values within permissible limit. i.e. 1.5 mg/l (BIS, 1991; WHO, 1984). However, only 26% of borewell (BW) samples recorded F^- concentration values within the maximum permissible limit.

Fluoride concentration in shallow aquifers has been depicted in an isofluor map (Fig. 3) for a better understanding of the distribution and behaviour. Occurrence of fluoride is quite sporadic and marked differences in concentrations occur even at very short distances. A perusal of pre-Monsoon (May 2004) fluoride distribution shows that F^- concentration below the maximum permissible limit (1.5 mg/l) is restricted only to some linear stretches and isolated pockets, while higher concentrations are observed in Masuda, Pisangan, Kekri, Arain, Jawaja blocks and in isolated pockets in Bhinai, Srinagar and Silora blocks. Similarly, F^- concentration between 1.5 mg/l and 3.0 mg/l is observed in all the blocks of the district. Higher concentrations have been noticed in Silora, Arain, Srinagar, Masuda and Jawaja blocks, while lower concentration in Kekri, Bhinai and Pisangan blocks. The F^- concentration above 3.0 mg/l has been noticed in and around Srinagar, Silora, Masuda and Jawaja blocks. Very high F^- concentrations (>6 mg/l) have been observed in isolated pockets in Kekri, Bhinai, Arain, Srinagar, Pisangan, and Silora blocks. These high values are mostly confined to the eastern and southeastern parts of the district, which form the discharge areas having weathered schistose and gneissose rocks. Those blocks showing F^- concentration above 3.0 mg/l in groundwaters can be considered as highly problematic for drinking water.

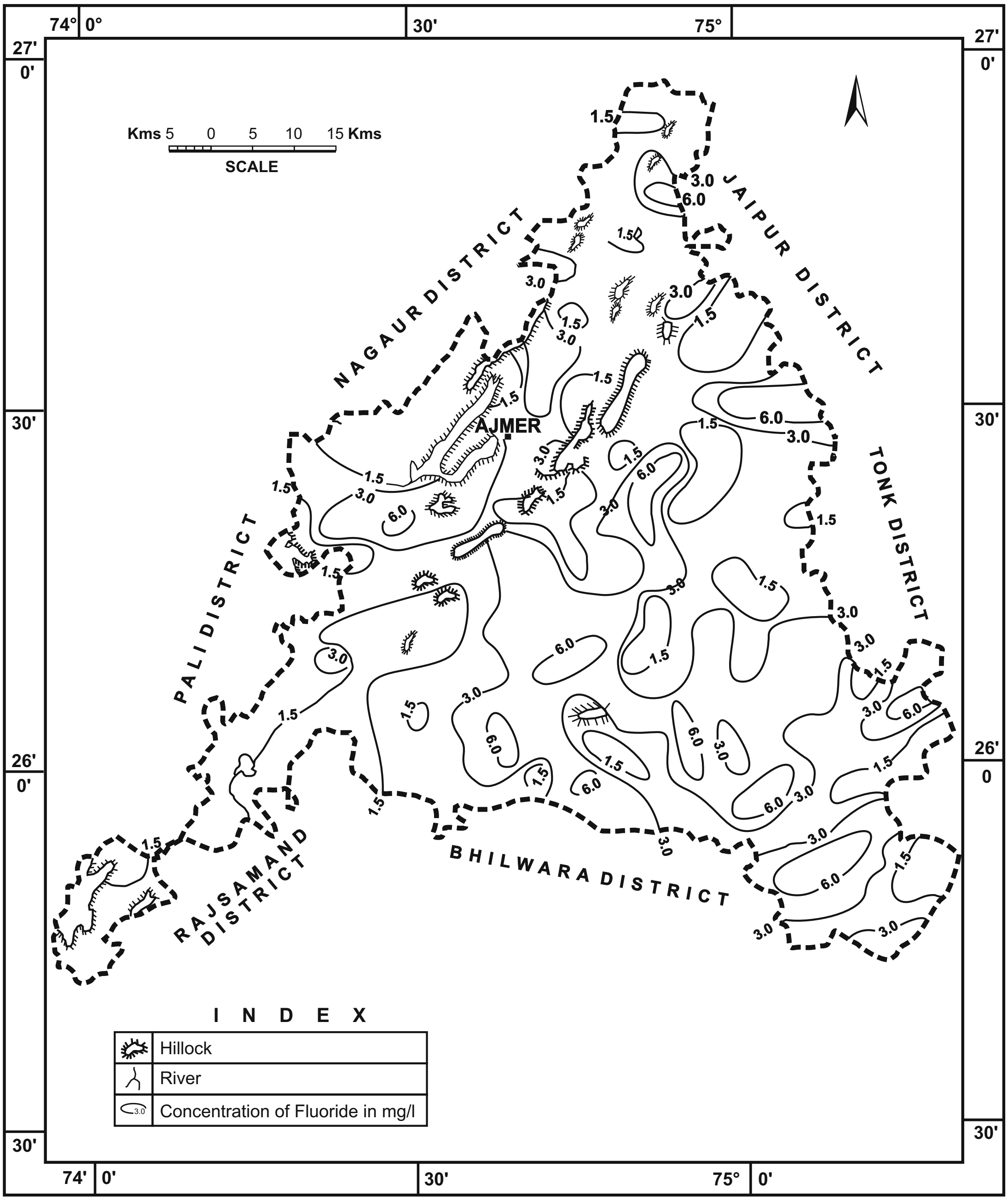

Fig.3. Isofluor map (pre-monsoon, 2004) of groundwater in Ajmer district.

This is in agreement with the observations made by Gupta et al. (1993).

The area where groundwater is enriched in fluoride is underlain by different types of rocks. The main rock formations include schists, gneisses, granites and quartzites with alluvial formations confined to the western and southeastern parts of the district. Majority of the samples are from aquifers in weathered and fractured zones occurring in the unconfined/semi-confined conditions. The concentration of F^- in groundwater depends on the abundance of fluoride bearing minerals in the rock types and their decomposition, dissociation and dissolution activities along with residence time of the chemical reaction.

DISCUSSION

Fluoride in Groundwater

High fluoride concentration in groundwater is common in areas where rocks contain fluoride-bearing minerals (Handa, 1975; Wenzel and Blum, 1992). The subsurface rocks in an area control the zones in which weathering affects the host rocks in minerals (Perez and Sanz, 1999). High concentration of fluoride in water is common in pegmatite-rich fractured hard rock terrains, which contain minerals like fluorite, topaz, fluorite, fluor-apatite, villuamite, cryolite and fluoride-replaceable hydroxyl ions in ferromagnesium silicates (Ramesham and Rajagopalan, 1985). Fluoride ions from these minerals leach into the groundwater and contribute to high fluoride concentrations. In some cases, micas (muscovite and biotite) also contribute to fluoride content (Handa, 1975). Fractions of soil in a high F^- area in Rajasthan have been found to contain about 10 (sand) to 130 (clay) mg/kg of fluoride (Madhavan and Subramanian, 2002). Fluorospar (fluorite – CaF_2) occurs in structurally weak planes like shear fractures, joints and host rock – vein quartz interface. Chemical weathering (hydrolysis) of minerals results in formation of Ca- and Mg-carbonates which serve as good sinks for fluoride ions (Jacks et al. 1980). However, it is the leachable state of fluoride ions that determines the water fluoride levels which is mainly governed by (i) pH of the draining solutions and (ii) dissolved carbon dioxide in the soil.

Presence of dissolved fluoride in groundwater is possible only under favourable physicochemical conditions and with a sufficient residence time (Kullenberg and Sen, 1973; Handa, 1975). In the present case, the area is underlain by crystalline rocks like calc-gneiss, schist (calc-schist and biotite schist), granite, quartzite, phyllite, and limestone which are potential sources of fluoride. Major fluoride bearing minerals present in the igneous and metamorphic rocks are fluorapatite, fluorite, cryolite, muscovite, biotite, lepidolite, hornblende, tourmaline, asbestos etc. Sedimentary horizons also have apatite as an assessory mineral and fluorite also often occurs as cement in some sandstones. Among the fluorine bearing minerals fluorapatite ($Ca_3(PO_4)_2$) and fluorite (CaF_2) are most significant. A minor occurrence of fluorspar is noticed at Khairot and Barla in Ajmer district. Fluorite seems to be the most likely source along with minor contributions from hornblende gneisses and schists. In Rajasthan, sepiolite and palygorskite are the Mg-hydroxy-silicates that form the probable sources and sinks for F^- in the hydroxyl positions. However, under high pH conditions, sepiolite may turn into a source due to replacement of F^- by OH^- ions (Jacks et al. 2005). Apart from natural sources, a considerable amount of fluoride may be contributed through anthropogenic activities. Phosphatic fertilizers, which are extensively used in agriculture, often contain fluoride as an impurity that can leach down to the saturated zone.

The arid to semiarid climatic conditions are quite conducive for chemical weathering, which results in enhanced salinity and fluoride abundances in phreatic water system. High fluoride groundwater is concentrated mostly in the discharge areas (i.e. towards the east and southeast of the study area) than in the recharge areas with a trend of fluoride enrichment along the direction of flow (Fig. 3). These findings also corroborate the results obtained by Gaciri and Davies (1993). In the present case a positive correlation between F and HCO_3 ($r = 0.737$) is observed in bore well samples (Fig. 4A). Coupled with high Na content, these correlations can be interpreted in terms of weathering, to be the major factor for enhanced fluoride concentration in groundwater. It has been observed that waters with relatively high pH have a tendency to displace fluoride ions from the mineral surface (Gupta et al. 1994). From the above, it is evident that relatively high alkalinity has played an important role in the enrichment of fluoride in groundwater of the study area.

The arid climate with low rainfall and high evapo-transpiration and insignificant natural recharge cumulatively lead to salinisation of groundwater and precipitation of calcite. Soils become more alkaline with very high pH which affects the solubility of calcite (Ramasesha et al. 2002). These conditions lower the activity of Ca and increase the Na/Ca ratios thus allowing fluoride to concentrate in the groundwater environment. Datta et al. (1999) used $\delta^{18}O$ values of water as supporting evidence to explain a positive correlation between high evapotranspiration and F^- concentration in Ajmer district. Physiography, geology, hydrology, physico-chemical conditions and neo-tectonism seem to have significantly contributed to the fluoride accumulation in groundwater. Modern agricultural practices, which involve the application of fertilizer coupled with pesticides, further facilitate fluoride transport into groundwater. Phosphatic fertilizers often contain fluoride as an impurity which is released and leached down to saturated zone by irrigation return flows but this is a minor source.

Hydrochemistry of Fluorine

Fluorine is thirteenth in the order of abundance of elements in the earth's crust. Fluoride is physiologically important and its extremely high electronegativity makes it highly reactive and therefore it occurs in a number of naturally combined forms. Its abundance in the continental crust is about 626 µg/g (Periakali et al. 2001). Chemically OH^- and fluoride are negatively charged and also possess almost similar ionic radii. Hence during the chemical reaction, fluoride can easily replace OH^- ions in many rock

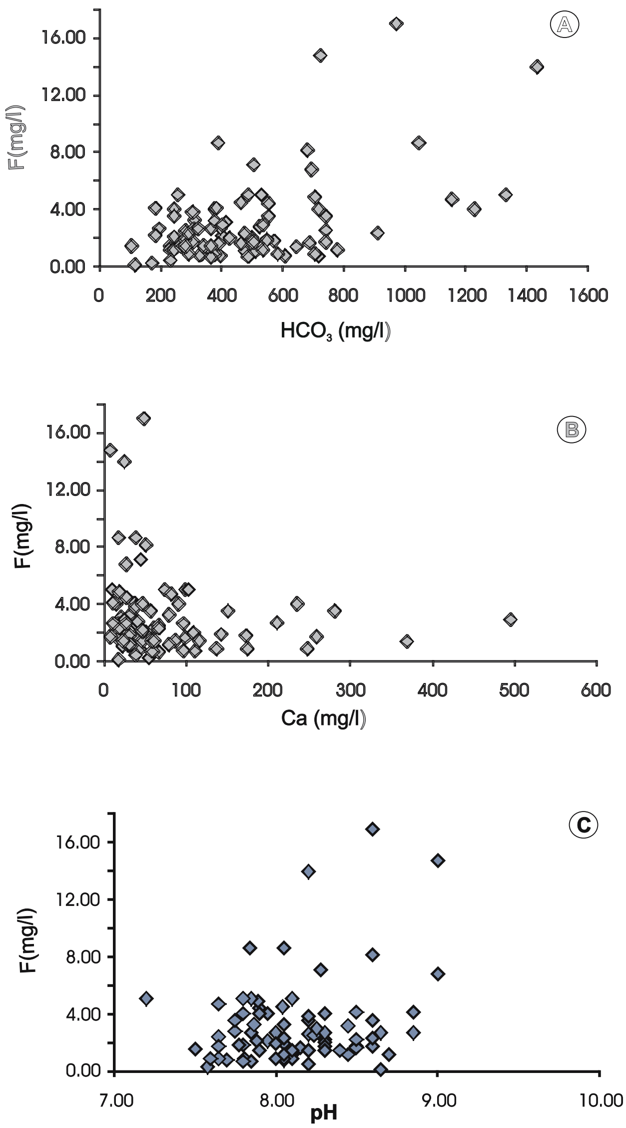

Fig.4. Mutual relationship of some hydrochemical parameters of groundwater in Ajmer district. (**A**) Fluoride vs bicarbonate cross plot showing a linear correlation; (**B**) Fluoride vs calcium cross plot showing absence of any significant correlation and (**C**) Fluoride vs pH diagram showing a positive correlation.

forming minerals. A better understanding of fluorine geochemistry in the aquatic environment under specific geographic and geologic conditions is necessary for evaluating the contamination process.

During the process of chemical weathering, dissolution of fluoride species in the natural water is controlled by calcium and governed by thermodynamic principles. The calcium ion activity in the natural environment is determined mainly by carbonate ion, which forms insoluble calcite. The equilibrium constant with respect to calcite can be evaluated from the following reactions.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad \text{(i)}$$

$$K_{CaCO_3} = \frac{a\,(Ca^{2+}).\,a\,(HCO_3^-)}{a\,(H^+)} = 97 \text{ at } 25°C \qquad \text{(ii)}$$

The fluoride concentration in groundwater is controlled by mineral fluorite as per the formula given below:

$$CaF_2 \rightarrow Ca^{2+} + 2F^- \qquad \text{(iii)}$$

$$K_{CaF_2} = a\,(Ca^{2+})\,.\,a\,(F^-)^2 = 10^{-10.58} \text{ at } 25°C \qquad \text{(iv)}$$

(Brown and Roberson, 1977)

Where *K* represents the solubility product constant and *a* denotes the activities of the corresponding ions. Thus the activities of calcium and fluoride are negatively correlated. Minerals rich in calcite ($CaCO_3$) also favour the dissolution of fluoride from fluoride rich minerals. Decreasing Ca concentrations are found under alkaline conditions with a corresponding rise in Na. Therefore, fluoride can accumulate in water if soils and groundwater are low in calcium. In the present case, a broad negative correlation is seen between calcium and fluoride (Fig.4B).

Arid climatic conditions and low rainfall facilitate evapotranspiration, which leads to increased alkalinity of soil and groundwater. Groundwater in contact with calcite and fluorite develops equilibrium reactions with both the solid phases. The following equation explains the saturation of groundwater with respect to calcite and fluorite (*see also* Handa, 1975).

$$CaCO_3 + 2F^- + H^+ = CaF_2 + HCO_3^- \qquad \text{(v)}$$

Handa used a combined law of mass action as given by

$$K_{CaF_2 \leftrightarrow CaCO_3} = \frac{(HCO_3^-)}{(H^+).(F^-)^2} \qquad \text{(vi)}$$

Since $K_{CaF_2 \leftrightarrow CaCO_3}$ is a constant, any change in concentration will be accompanied by a corresponding change in F^- concentration indicating a positive correlation between these variables. It has been observed that groundwaters having high concentration of fluoride are mostly alkaline (Ramasesha et al. 2002) and have residual alkalinity i.e. alkalinity in excess of calcium and magnesium. It is clear that if pH is constant, the activity of fluoride is directly proportional to HCO_3 abundance. This relationship is independent of Ca because of the low solubility product of CaF_2. A positive correlation between HCO_3

and fluoride in groundwater samples of Ajmer district is seen in Fig.4A.

In groundwater, the solubility of fluoride varies from one rock formation to other. Under normal temperature and pressure conditions, most of the fluorine-bearing minerals are sparingly soluble in water. However, under certain physico-chemical conditions, dissolution activity may become faster. In acidic medium (low pH) fluoride is adsorbed in clays; however, in alkaline medium, it is desorbed and thus alkaline pH is more favourable for fluoride dissolution activity (Saxena and Ahmed, 2003). Ion activity product and saturation index (SI) of fluoride and calcite in the analyzed groundwater samples of the study area have been calculated using the geochemical program PHREEQC. Results of saturation index (SI) have shown that the groundwater in the high fluoride bearing wells are oversaturated with calcite and undersaturated with fluoride in general. The positive value of SI with respect to calcite in groundwaters of the Ajmer district suggests a precipitation of calcite caused by higher rate of evapotranspiration. A positive correlation between high evapotranspiration and F^- content in groundwater of Rajasthan has been provided by Datta et al. (1999). Evidence of increase in soil pH and alkalinity in Rajasthan has been given by Jaglan (1996). In the study area, a positive correlation is observed between fluoride and pH in the groundwater samples (Fig.4C). Here, most of the water samples are alkaline in nature with about 84% of samples having pH range of 7.0 to 8.5 (Table 1). The aqueous ionic concentrations of groundwater also appear to have influenced the solubility behaviour of fluoride. It has been observed that the bicarbonate type of groundwater dominates the study area. The following reactions may occur during the water – mineral interaction:

$$CaF_2 + Na_2CO_3 \leftrightarrow CaCO_3 + 2F^- + 2Na^+ \quad \text{(vi)}$$

$$CaF_2 + 2NaHCO_3 \leftrightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \quad \text{(vii)}$$

The above reactions (vi and vii) suggest that the $NaHCO_3$ type water in a weathered rock formation allows precipitation of calcite from Ca^{2+} and CO_3^{2-} ions and accelerates the dissolution of CaF_2 and thereby releases fluoride into groundwater. Such observations are supported by the findings of Lahermo et al. (1991) and Saxena and Ahmed (2003). Similarly, the increasing concentration of TDS (Mean - 1889 mg/l) in groundwater samples of the study area is an another factor, which might have accounted for acceleration in the dissolution of CaF_2 to release F^- into the waters, as higher TDS would enhances the ionic strength effect (Freeze and Cherry, 1979), leading to an increased solubility of CaF_2 in the groundwater (Perel'man, 1977). The dissolution activity is further enhanced by the combined effect of evapotranspiration and long residence time of waters in the aquifer due to the low hydraulic conductivity of the weathered zone of the formation.

In the study area 68% of groundwater samples have EC values within the permissible limits for drinking water standards (BIS, 1991) and the rest have EC values more than 3000 mmhos/cm at 25^0C (Table 1, Fig. 5). Fluoride has a unique chemical behaviour towards most of the anions and can be easily replaced even under normal pressure and temperature conditions (Wenzel and Blum, 1992). The less soluble products of fluoride in the presence of Ca make the dissolution activity more effective. Fluoride shows negative correlation with Ca and positive correlation with HCO_3 as well as Na in the groundwater samples analyzed in the study area (Figs. 4A and B). In addition to these, it is also observed that in almost 81% of samples, the HCO_3/Ca (epm) ratio lies between 0.9 and 3.5. Thus, the ranges of such ionic species may suggest favourable chemical conditions for fluoride dissolution process in the Ajmer district.

Impact on Human Health

Fluoride in water can be a blessing or a hazard depending on the concentration levels. Bureau of Indian Standards (BIS) and Indian Council of Medical Research (ICMR) prescribe a fluoride concentration of 1.0 mg/l as the desirable limit, and 1.5 mg/l as the maximum permissible limit in drinking water, if there is no alternate source. These guidelines vary depending on the climate and the total fluoride intake from other sources, since the absorption of fluoride by body fluids depends on temperature. The study area falls in the climatic zone where average summer temperature is greater than 27.5°C and the average drinking water consumption is higher than 4 litres per day. For these population groups, drinking water containing less than 0.6 mg F/l is fit for consumption (Deshkar et al. 1999). Assimilation of fluorine by the human body from potable water at the level of 1 mg/l enhances bone development and prevents dental carries. It is found to cause fluorosis when it exceeds a limit of 1.2 mg/l (Kundu et al. 2001). It is a deadly disease with no cure so far. In the study area, villagers who consume non-potable high fluoride water suffer from yellow, cracked teeth, joint pains and crippled limbs and also age rapidly. Skeletal fluorosis may occur when fluoride concentrations in drinking water exceeds 4-8 mg/l, which leads to an increase in bone density, calcification of ligaments, rheumatic or arthritic pain in

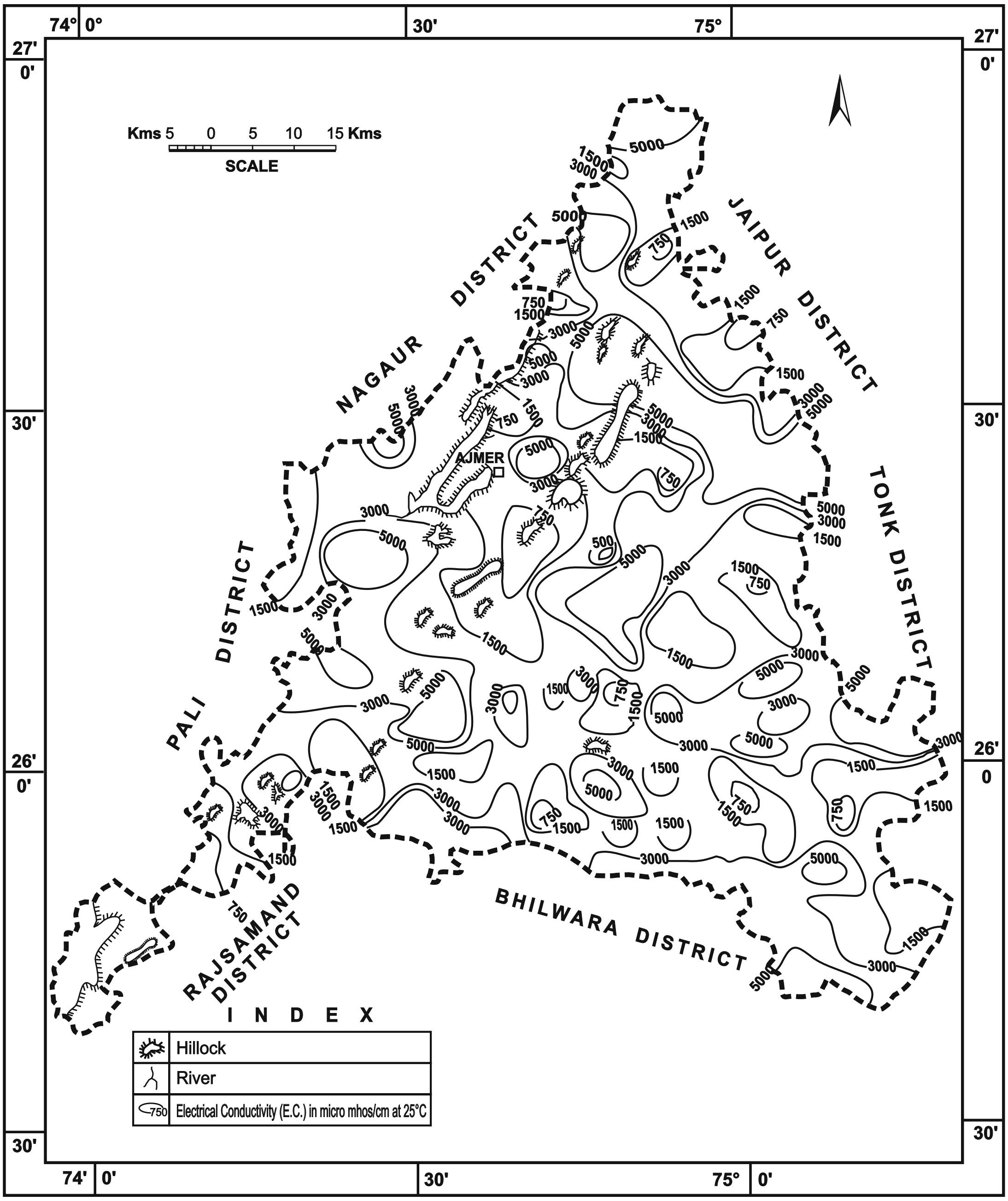

Fig.5. Isoconductivity map of groundwater (pre-monsoon 2004) in Ajmer district.

joints and muscles along with stiffness and rigidity of the joints, bending of the vertebral column, etc. The disease may be present in an individual at subclinical, chronic or acute levels of manifestation (Teotia and Teotia, 1988). Higher doses of fluoride induce osteoporosis and collapsed vertebrae (Sharma, 2003). It has been found that the IQ of the children living in the high fluoride areas (drinking water fluoride > 3.15 mg/ml) was significantly lower. Statistical analysis revealed a positive correlation between fluoride levels and fluorosis (dental and skeletal) in children and adults (Choubisa, 2001). It is prevalent in areas where groundwater is highly alkaline, low in calcium, thus favouring high concentration of fluoride in groundwater. People suffering from dental and skeletal fluorosis are reported from the study area which can be related to the usage of high fluoride groundwater.

Remedial Measures

It is high time that an affordable solution is found to minimize the fluoride contamination for maintaining good health of the large population of the State. Two kinds of defluoradation techniques, namely Nalgonda (based on addition of lime and alum) and Prasanthi (based on adsorption using activated alumina) are practiced (Bulusu and Nawlakhe, 1990). Based on these techniques, the following types of defluoradation plants are being adopted:

(i) Community defluoradation plants (Fill and draw type).
(ii) Hand pump attached defluoradation plants.
(iii) Domestic defluoradation system.

Soils having high alkalinity can be remedied through the application of gypsum, pyrite, or sulphuric acid. On long term basis, planting of trees like *Acacia nilotica, Prosopis juliflora, Albizia lebbek and Populus deltoids* may alleviate sodicity in soils (Garg, 2000). As indicated by the relationship between soil pH and F^- in groundwater (Fig. 4C), lowering alkalinity may also reduce the mobility of F^-. Since gypsum is fairly abundant in Rajasthan, the gypsum treatment method of reducing soil alkalinity may be feasible and cost effective. This may also have an added advantage as the higher intake of Ca mitigates the effect of F^-. While excess F^- may induce hypocalcaemia, Ca can prevent F^- uptake in the intestine (Teotia and Teotia, 1988). The fluoride levels in groundwater can be brought down by the artificial recharge of groundwater. Borewell waters with low concentration (<0.5 mg/L) of fluoride can be blended with high fluoride waters before being supplied for domestic purpose. In areas of high fluoride concentration, easily available local raw materials such as clay, serpentine, and marble can be used to reduce fluoride content. A general socio-economic uplift and diet supplements might reduce the vulnerability of low-income population to fluorosis.

CONCLUSIONS

Most parts of the study area show F^- concentrations above the maximum permissible limit (i.e. 1.5 mg/l) with high fluoride groundwater noticed in the discharge areas as compared to recharge areas. Presence of fluoride bearing minerals in the host rocks and their interaction with water is considered to be the main cause for fluoride enrichment in groundwater. Decomposition, dissociation and dissolution are the main chemical processes responsible for mobility and transport of fluoride into groundwater. Chemical weathering under arid to semiarid conditions with relatively high alkalinity and long residence time of interaction seem to have favoured high concentration of fluoride in groundwater. Geochemical behaviour of groundwater from the study area suggests that high fluoride groundwater contain low levels of Ca and high alkalinity. High pH and HCO_3/Ca ratio between 0.9 and 3.5 suggest favourable chemical conditions for fluoride dissolution process. Regular intake of fluoride rich waters seems to be the main cause for high incidence of fluorosis in the region. Dilution by blending, artificial recharge, efficient irrigation practices and well construction are some common cost effective fluoride control measures which can be adopted to improve the health status of the community.

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References

APHA (1995) Standard methods for the examination of water and wastewater, 19th edn, American Public Health Association, Washington, D.C.

BIS (1991) Drinking water specifications: (First revision), IS: 10500: 1991.

Brown, D.W. and Roberson, C.E. (1977) Solubility of natural fluorite at at 25°C, USGS Jour. Res., v.5(4), pp.506-517.

Bulusu, K.R. and Nawlakhe, W.G. (1990) Defluoridation of water with activated alumina, batch operations. Indian Jour. Environ. Health, v.32, pp.197-218.

Choubisa, S.L. (2001) Endemic fluorosis in southern Rajasthan, Fluoride, v.34, pp.61-70.

Datta, P.S., Tyagi, S.K., Mookerjee, P. Bhattacharya, S.K., Gupta, N. and Bhatnagar, P.D. (1999) Groundwater NO_3 and F contamination process in Pushkar valley, Rajasthan as reflected from ^{18}O isotopic signature and ^{3}H recharge studies. Environ. Monitor. Assess, v.56, pp.209-219.

Deshkar, S.M., Deshmukh, A.N. and Vali, S.A. (1999) Safe limit of fluoride content in drinking water in different climatic zones of India. Indian Jour. Envir. Health, v.2, pp.17-20.

Freeze, R.A. and Cherry, J.A. (1979) Groundwater. Prentice-Hall Inc, New Jersey, 603p.

Gaciri, S.J. and Davies, (1993) The occurrence and geochemistry of fluoride in some natural water of Kenya. Jour. Hydrol., v.143, pp.395-412.

Garg, V.K. (2000) Bioreclamation of sodic waste land - a case study, Land Degrad. Develop, v.11, pp.487-498.

Gupta, R.K. Singh, N.T. and Sethi, M. (1994) Ground water quality for irrigation in India. Tech. Bull, No.19, Central Soil Salinity Research Institute, Karnal, India, 13p.

Gupta, S.C., Rathore, G.S. and Doshi, C.S. (1993) Fluoride distribution in groundwaters of southeastern Rajasthan, Indian Jour. Environ. Health, v.35, pp.97-109.

Handa, B.K. (1975) Geochemistry and genesis of fluoride containing groundwater in India, Groundwater, v.13, pp.275-281.

Jacks, G., Bhattacharya, P., Chaudhary, V. and Singh, K.P. (2005) Controls on the genesis of some high-fluoride groundwaters in India. App. Geochem, v.20, pp.221-228.

Jacks G., Sharma, V.P. and Sharma, G.K. (1980) Hydrochemical Studies, SIDA-assisted groundwater project in Kerala – A Report, pp.1–5.

Jaglan, M.S. (1996) Irrigation development and its environmental consequences in arid regions in India. Environ. Management, v.20, pp. 323-336.

Kullenberg, B. and Sen, G.R. (1973) Flouride in Baltic. Geochim. Cosmochim. Acta, v.37, pp.1327-1337.

Kundu, N., Panigrahi, M.K., Tripathy, S., Munshi, S., Powell, M.A. and Hart, B.R. (2001) Geochemical appraisal of fluoride contamination of groundwater in the Nayagarh district of Orissa. Indian Jour. Environ. Geol., v.41, pp.451-460.

Lahermo, P., Sandstrom, H. and Malisa, E. (1991) The occurrence and geochemistry of fluorides in natural waters in Finland and East Africa with reference to their geomedical implications. Jour. Geochem. Expl., v.41, pp.65-79.

Madhavan, N. and Subramanian, V. (2002) Fluoride in fractionated soil samples of Ajmer district, Rajasthan. Jour. Environ. Monitoring, v.4, pp.821-822.

Madhavan, N. and Subramanian, V. (2003) The fluoride problem in Ajmer district, Rajasthan. *In:* A.L. Ramanathan and R. Ramesh (Eds.), Recent Trends in Hydrogeochemistry (Case Studies from Surface and Subsurface Waters of Selected Countries), Capital Publishing Co., New Delhi, 296p.

Maithani P.B., Gurjar, R., Banerjee, R., Balaji, B.K., Ramachandran, S. and Singh, R. (1998). Anomalous fluoride in groundwater from western part of Sirohi district, Rajasthan and its crippling effects on human health. Curr. Sci., v.74, pp. 773-777.

Mathur, G.M., Tamboli, B.I., Mathur, R.N. Roy, A.K., Mathur, G.C. and Goyal, O.P. (1976) Preliminary epidemiological investigation of fluorosis in Surajpura and Pratappura villages in Ajmer district. Indian Jour. Prev. Soc. Med., pp.90-94.

Muralidharan, D., Nair, A.P. and Sathyanarayana, U. (2002) Fluoride in shallow aquifers in Rajgarh Tehsil of Churu District, Rajasthan – an arid environment, Curr. Sci., v.83, pp. 699-702.

Perel'man, A.I. (1977) Geochemistry of Elements in Suprgene Zone, Keter Publ. House, Jerusalem Ltd., 266p.

Perez, E.S. and Sanz, J. (1999). Fluoride concentration in drinking water in the province of Soria, Central Spain. Environ. Geochem. Health, v.21, pp.133-140.

Periakali, P., Subramaniam, S., Eswaramoorthi, S., Arul, B., Rajeshwara Rao, N. and Sridhar, S.G.D. (2001). Distribution of fluoride in the groundwater of Salem and Namakkal districts, Tamilnadu. Jour. Appl. Geochem., v.3(2), pp.120-132.

Ramasesha, C.S., Kumar, E.S., Suresh, S. and Kumar, A.R. (2002) Occurrence of nitrate and fluoride in groundwater and their impacts in and around Dindigul, Tamilnadu, India. *In:* M. Thangarajan, V.S. Singh and S.N. Rai (Eds.), International Conference on Sustainable Development and Management of Groundwater Resources in Semiarid region with special reference to Hard rocks (IGC - 2002), pp.31-39.

Ramesham, V. and Rajagopalan, K.J. (1985) Fluoride ingestion into the natural water of hard rock areas, Peninsular India. Jour. Geol. Soc. India, v.26, pp.125-132.

Saxena, V.K. and Ahmed, S. (2003) Inferring the chemical parameters for the dissolution of fluoride in groundwater. Environ. Geol, v.43, pp. 731-736.

Sharma, S.K. (2003) High fluoride in groundwater cripples life in parts of India, Diffuse Pollution Conference, Dublin, pp.7-51-52.

Teotia, S.P.S. and Teotia, M. (1988). Endemic skeletal fluorosis: clinical and radiological variants. Fluoride, v.21, pp.39-44.

Wenzel, W.W. and Blum, W.E.H. (1992) Fluoride speciation and mobility in fluoride contaminated soils and minerals. Soil Sci., v.153, pp.357-364.

WHO (1984) Guidelines for drinking water quality, Values 3; Drinking water quality control in small community supplies. WHO, Geneva, 212p.

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