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Role of Weathering of Ferromagnesian Minerals and Surface Water Irrigation in Evolving and Modifying Chemistry of Groundwater in Palakkad District, Kerala, with Special Reference to its Fluoride Content

J. P. Kukillaya and T. Narayanan
Agriculture and Ecosystem Management Group, Leela vilas, Golf Links Road,
Kawadiyar, Thiruvananthapuram - 6950 03
Email: gwkuki@yahoo.co.in

Abstract: The chemical characteristics of groundwater in parts of Palakkad district, Kerala show the role of slow weathering of rocks rich in ferromagnesian minerals in increasing the residual alkalinity of water, and promoting calcium carbonate precipitation and dissolution of fluoride from minerals like biotite and hornblende. Alkaline clayey soils having high cation exchange capacity have a significant role in the process. Leaching of fluoride from soil and weathered rock in the vadose zone appears to be a major cause for high fluoride in groundwater. No relation is seen between fluoride contents in rocks and soils, and in groundwater, while the degree of weathering is a probable controlling factor. The study indicates that, while alkaline pH promotes dissolution of F^-, a further linear increase in pH is not required for more increase in dissolution of F^-. Similarly, the correlation of F^- with HCO_3^-/Ca^{2+} ratio may be a more reliable indicator than the correlation of F^- with Ca^{2+}. Surface water irrigation has influenced groundwater quality in a large tract. Dug well and bore well waters belong to the same chemical type indicating connectivity between the two aquifers. There is evidence for influent flow from streams into the fractured rock aquifer in some areas. The study was conducted between November 2009 and May 2011.

Keywords: Groundwater quality, Geology, Weathering, Alkalinity, Fluoride, Kerala.

INTRODUCTION

Occurrence of excessive fluoride in groundwater is a problem faced by many countries, including India. BIS has set desirable and permissible limits for fluoride in drinking water as 1.0 mg/l and 1.5 mg/l respectively. Higher concentrations can cause mottling of teeth, especially in tropical climates. Concentrations higher than 3mg/l can lead to skeletal fluorosis and other problems. Fluoride content in groundwater ranges from less than 1mg/l to more than 35mg/l (Meenakshi and Maheshwari, 2006). In Kerala state excess fluoride has been reported from only two areas, viz. the coastal district of Alappuzha and the eastern part of Palakkad district (Fig.1). Thirty eight out of the eighty nine groundwater samples tested in Palakkad in 1992 showed fluoride content above 1 mg/l with 15 samples exceeding 1.5 mg/l (Raja Raja Varma, 1992). The highest fluoride concentration of 2.68 mg/l was noted in Kozhinjampara, which is in the present study area. Blom and Cederlund (2006) reported fluoride contents of 0.1 to 1.8mg/l in 31 dug well samples in Muthalamada, south of the present study area. Shaji et al. (2007) reported concentrations up to 5.75 mg/l in 15 dug well and bore well samples in Palakkad.

This paper is based on a study funded by the Kerala State Council for Science, Technology and Environment, and conducted from November 2009 to May 2011 in about 90 sq.km area at the eastern boundary of Palakkad district (Fig.2). The study covered 64 dug wells, 74 bore wells, 9 tanks and 5 streams, and included analysis of 21 rock and 10 soil samples. The study area is bounded by latitudes 10°41'20" N and 10°46' N ; and longitudes 76°45'51" E and 76°51'56" E . It is part of the plains of the Palakkad Gap, which is a wide pass in the NNW-SSE trending Western Ghats mountain range. Topography is gently undulating with a westerly slope of one percent (Fig.2). The topographic elevation ranges from 210m above mean sea level in the southeast to 120m in the west. It is an agricultural area with paddy fields in the central and western parts. Drainage density is low. The seasonal west-flowing Korayar, Varattar

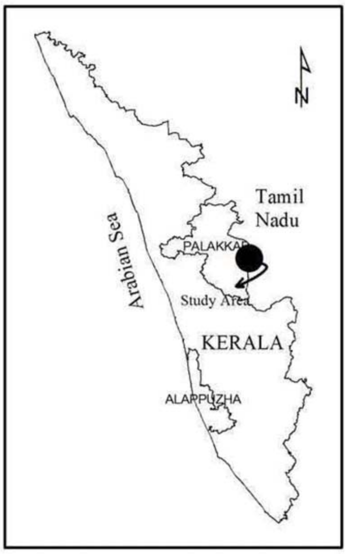

Fig.1. Location map.

and Chitturpuzha, originating from the plains of Tamil Nadu, are the major streams. Climate is tropical with two rainfall seasons, the southwest monsoon from June to September and the northeast monsoon from October to December. It is a transitional zone between the high rainfall coastal area in the west and much drier plains of Tamil Nadu in the east. The average annual rainfall during 1980-2003 was 1195mm in contrast to the state average of nearly 3000mm.

SURFACE WATER IRRIGATION

About 75% of the study area, except the area north of Korayar river, is covered fully or partly by surface water irrigation from the canals of the Moolathara project, which has weirs in Chitturpuzha river just south of the area and, to a lesser extent, by the Walayar irrigation project located further north of the study area (Fig.3). Moolathara water irrigates paddy fields in the central, western and eastern parts of the study area up to Korayar river. It delivers water to Korayar river occasionally. Most of the flow in Chitturpuzha is derived from dams in Tamil Nadu as part of an interstate transfer of water. Water from Parambikulam dam located in the Western Ghats inside Kerala, about 45 km south of the study area, is first diverted to irrigation dams in the plains of Tamil Nadu in the east. Part of this water is returned to Kerala through Chitturpuzha. The natural

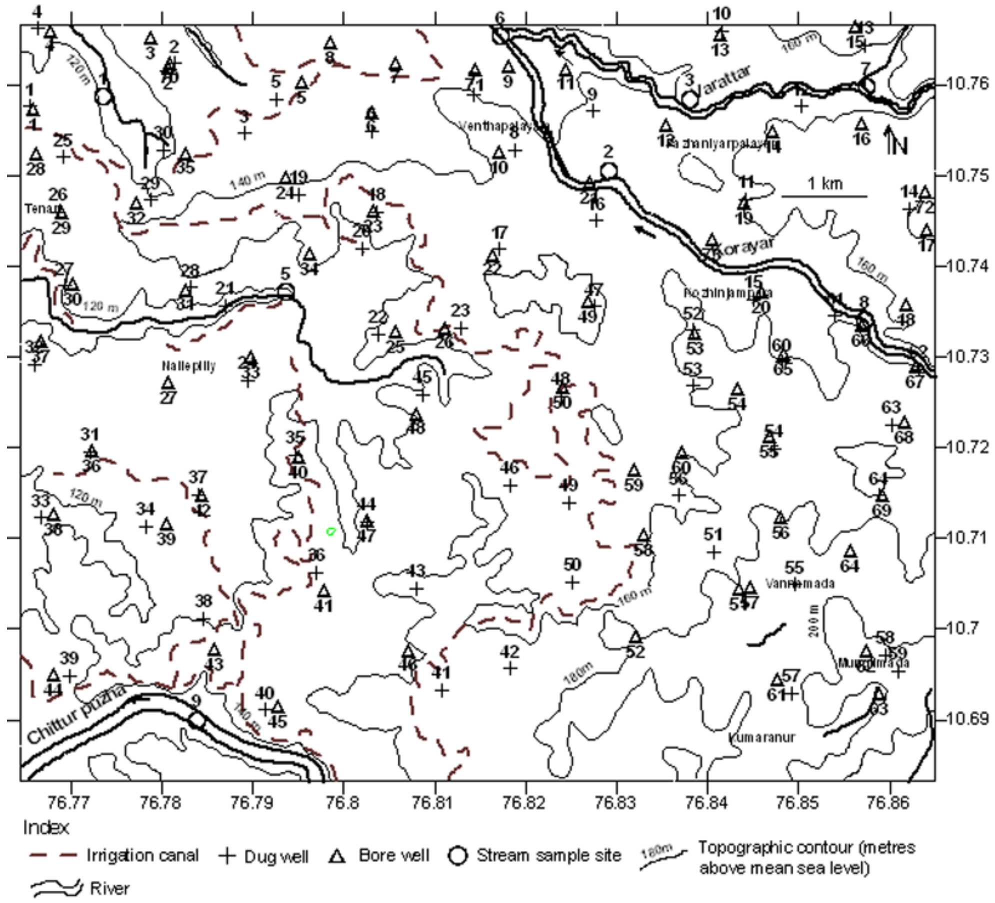

Fig.2. Map showing topography, drainage, irrigation canals and locations of wells and stream sites.

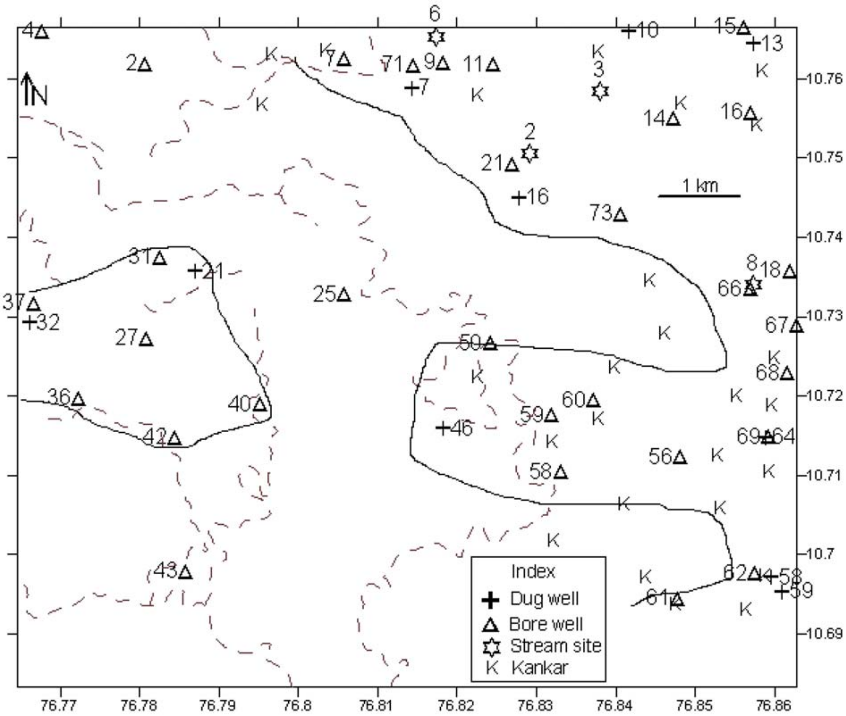

Fig.3. Well and stream locations with high fluoride and occurrences of kankar (irrigation canals as broken line, continuous line shows approximate boundary of areas with high fluoride wells).

discharge of Chitturpuzha from its catchment in Tamil Nadu is low and probably has chemical characteristics similar to that of the seasonal Korayar and Varattar rivers, which also originate from the plains of Tamil Nadu. However, most of the actual flow of Chitturpuzha consists of low-TDS water from the mountains. Electrical conductivity of stream water samples collected four times during different seasons ranged from 900 to 1950 micro siemens/cm in Korayar and Varattar, while it was around 400 micro siemens/cm in Chitturpuzha. Similarly, fluoride concentration ranged from 1.5 to 2.7 mg/l and 0.9 to 1.1 mg/l respectively in the two cases. Lower variation in chemical quality in Chitturpuzha water is in keeping with its origin in the recharge areas in the hills. Thus, the chemistry of Moolathara irrigation water is not natural to this area and it significantly influences groundwater chemistry.

HYDROGEOLOGY

Palakkad Gap proper is mainly composed of migmatites consisting of hornblende biotite gneisses traversed by granitic materials (Nageswara Rao and Srinivasan, year unknown). The study area is part of Archaean metamorphic terrain and is underlain by banded migmatitic gneisses, hornblende biotite gneisses and granitic gneisses with widespread conformable bands and lenses of older pyroxenites and amphibolites. The geological mapping (Fig.4) done earlier (Kukillaya et al., 1992) has been refined during the present study. The pyroxenite is a dense coarse grained rock, metamorphosed to varying degrees with the formation of amphiboles and biotite. Two highly fractured WNW-ESE trending zones with large number of irrigation bore wells are present in the study area, one within the mafic pyroxenite formation in Thenari and another in the gneissic rock in Eruthempathy (Fig.4). Gneisses richer in ferromagnesian minerals are more in the valleys compared to hilltops where granitic rocks predominate.

Comparatively low rainfall has resulted in slow weathering over a long period, leading to the formation of alkaline clayey soils in the area. A brown sandy clay loam is the most common soil type (Bench Mark Soils of Kerala, 2007, p. 375-377). A dark brown to black plastic clay with carbonate nodules occurs in the valleys and adjacent slopes, mostly in the eastern part. This has probably developed on gneisses rich in hornblende and biotite. Sandy loam is seen on higher ground. In less humid climate, where not all dissolved calcium is leached away, calcium carbonate may precipitate in the soil zone (Drever,, 1988). Such precipitates called 'kankar' occur in many places in the eastern part (Fig.3) at a depth of 1 to 2.5 metres, mostly at the contact of soil and weathered rock. It forms hard nodules and veins often extending along joints below the water table. The weathered zone has a thickness of 4m to more than 9m in the central and western parts, and 6m to more than 12m in the east. The highly weathered top zone is 1.5m to 8m thick in the former area, compared to 1.5m to 5m in the latter. Thicker vadose zone in the east, especially the zone of partially weathered rock, may cause percolating water to be more influenced by weathering reactions. Groundwater composition depends partly on interaction with weathered soil and organic activity in the soil through which water percolates before reaching the water table (Walther, 2010).

Groundwater occurs under unconfined condition in the shallow weathered zone, and under semi-confined and confined conditions in the weathered and fractured crystalline rocks. Dug wells tap the unconfined aquifer, and

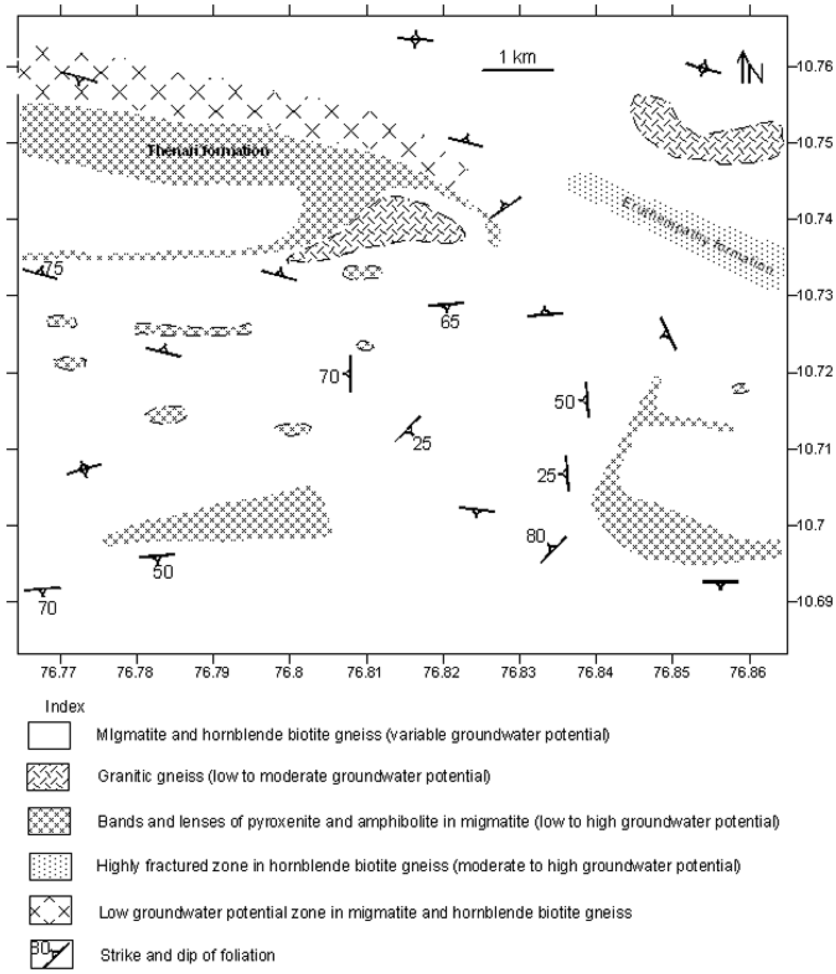

Fig.4. Geological map of the study area.

are 2.60m to 13m deep. Depths to water table in dug wells ranged from near ground level to 9.80m below ground level (average 3.75m) in the post monsoon season, and 1m to12m below ground level (average 5.44m) in the summer. In majority of the wells, water table is below the top highly weathered zone in the post monsoon season, and the unconfined aquifer consists primarily of partially weathered rock. Water table maps, drawn using GPS elevation readings, show a flow pattern from east to west. Water table gradient is 0.80 percent compared to the ground slope of one percent. Bore wells tap the semi-confined and confined aquifers in the fractured crystalline rocks. They have a depth range of 33m to 210m (average 87m), with water yielding zones at depths of 7m to 119m. Large seasonal water level fluctuations of 21m to 56m were noted in a bore well at Eruthempathy during the period 1991-94 (Kukillaya, 1995). The eastern part faces problems of seasonal dewatering of shallow fracture zones, possibly leading to increased weathering and changes in groundwater quality.

RESULTS AND DISCUSSION

Field Parameters

Dug well water had a mean temperature of 27.1^{0}C in December and 28.7^{0}C in March, while bore well water had higher values of 29.3^{0}C and 30.2^{0}C respectively. pH ranged from 5.47 to 8.20 in dug wells and 6.40 to 8.14 in bore wells. Mean values are higher in bore wells due to higher residence time of water and longer association with weathering processes. pH increased slightly towards the eastern part, where soil is more alkaline. Fluoride is desorbed from clay in alkaline medium and hence alkaline pH is more favourable for its dissolution (Saxena and Ahmed, 2003). No relation of pH to topography is seen, but average pH in dug well waters increased from 6.58 in sandy soils to 7 in black clay soils. Stream, tank and canal waters had pH in the range 7 to 8.60. Eh varied from 120mv to 200mv in dug well waters and -30mv to 200mv in bore well waters. Several bore well waters gave negative Eh values, suggesting localized reducing conditions in the fractured rock aquifer. EC was in the range 400 to 1800 μSiemens/cm in the majority of the dug wells and bore wells. A few isolated values up to 2500 μSiemens/cm in the dug wells and 4160 μSiemens/cm in the bore wells were noted. Low groundwater velocities in the deeper fractures in metamorphic rocks can increase salinity due to higher residence times (Langmuir, 1997, p.270). The mean values were only slightly higher in the bore wells. The low TDS Moolathara irrigation water has diluted groundwater in a large part of the area (Fig.5). EC increased towards east and was higher in clay-rich soils. EC of stream water was comparable to that of nearby dug wells.

Fluoride

Fluoride content was determined in the State Groundwater Department Laboratory using ion selective electrode. Fluoride concentrations ranged from 0.43 to 1.98 mg/l in dug well waters, and from 0.32 to 2.78 mg/l in bore well waters. 42% of dug wells and 70% of bore wells had F^- higher than the desirable limit of 1mg/l. In 8% of dug wells and 20% of bore wells F^- was higher than the permissible limit of 1.5mg/l. Spatial variation is broadly

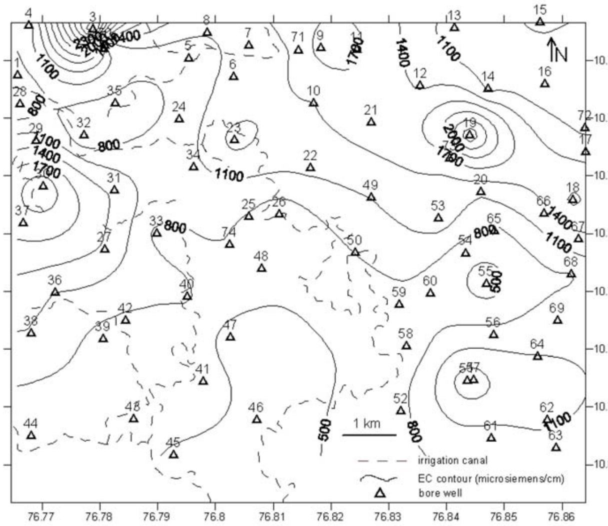

Fig.5. Electrical conductivity contour map of bore wells, March 2010.

similar in dug wells and bore wells, as reported elsewhere (Ramesam, V. and Rajagopalan, K., 1985).

Wells having fluoride ≥1.40mg/l in at least one season are categorized as high F^- wells for the purpose of this study. They consist mostly of bore wells located in the east and in a small pocket in the west (Fig.3). High F^- bore wells in the central and western parts had low Eh of -32 to +61mv, suggesting lack of dilution by irrigation return flow, probably due to poor connectivity of the fracture aquifer with the unconfined aquifer. Tank and canal waters had F^- content of 0.65 to 1.13 mg/l.

Wells in low F^- areas showed very little spatial variation in F^- (Figs.6 and 7) due to dilution by irrigation water. Bore wells showed increase in F^- from hilltop (average 1mg/l) to valley (average 1.5mg/l) probably due to presence of more easily weathered mafic gneisses in the valleys. Increase in F^- with increase in soil clay content is seen in both types of wells. Jacks et al. (1993) reported higher F^- in valleys. Fifty percent of bore wells and most of the dug wells in the north and east as well as the streams showed increase of 0.13 to 0.79 mg/l in F^- in December due to leaching of salts by monsoon recharge. Ahmed et al. (2002) reported similar cyclic variation.

Dug well No.13 had isolated high F^- values of 5.11 to 8.36 mg/l and pH of 7.34 to 8.39 possibly due to the presence of the collapsed parapet wall in the well. Portlandite, Ca $(OH)_2$, which is a component of concrete, might cause high pH in newly completed wells (Langmuir, 1997, p163). F^- content was observed to be 1.45 to 1.76 mg/l in five nearby wells.

Detailed Chemical Analysis

Analysis of major cations and anions was done in 20 bore well, 12 dug well and 5 stream water samples in summer (Table 1). 16 of the wells were high F^- wells. TDS increased from dug well waters to bore well and stream waters in the north east in that order. Higher Na^+ and Cl^- in Korayar and Varattar could be due to evaporation. Na^+ and Cl^- contents were lower by an order of magnitude in Chitturpuzha, which receives water from the Western Ghats. In fresh waters, Ca^{2+}/Mg^{2+} ratio is usually well above one (Drever, J.I., 1988). Here Ca^{2+}/Mg^{2+} ratio was below one in 5 dug and 12 bore wells and in all streams (Table 2). Weathering of hornblende biotite gneiss, precipitation of $CaCO_3$ in alkaline water and adsorption of Ca^{2+} in soils might be the probable reasons. Similarly, in fracture zones, calcite may precipitate on water-yielding rock faces (Hem, 1989, p.91) as noticed in some drill cuttings. Since magnesium is more soluble

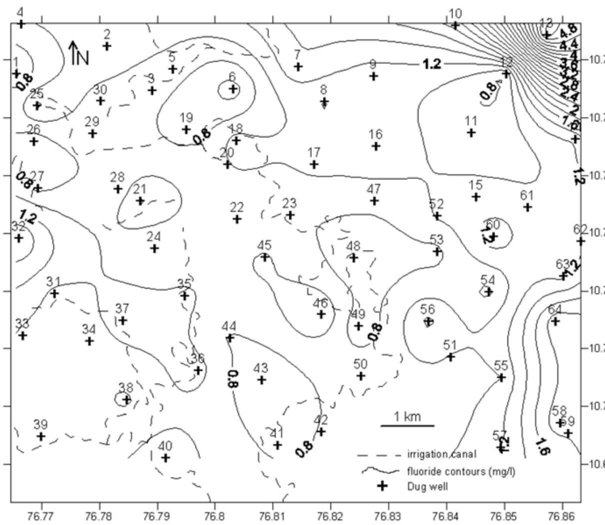

Fig.6. Fluoride contour map of dug wells, December 2009.

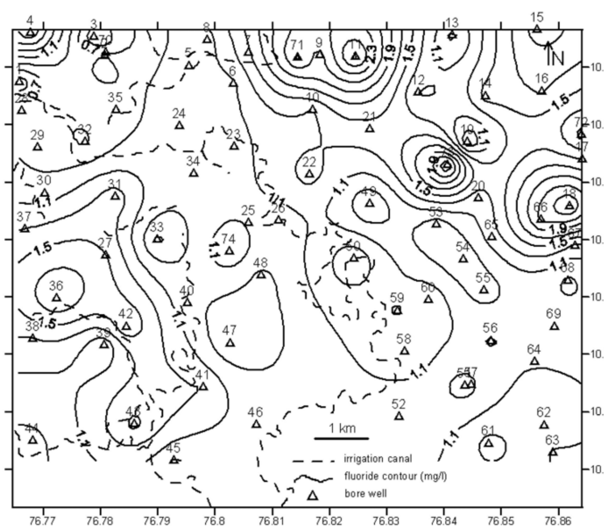

Fig.7. Fluoride contour map of bore wells, March 2010.

Table 1. Results of detailed chemical analysis (dug wells, bore wells, streams) - March, 2010

Well no.	pH (field)	EC µmS/cm	TDS mg/l	TH, mg $CaCO_3$/l	TA, mg $CaCO_3$/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	CO_3, mg/l	HCO_3, mg/l	Cl mg/l	SO_4, mg/l	NO_3- N, mg/l	F mg/l
DW1	6.42	250	131	55.0	76	14	4.88	23.3	2.6	0	92.72	35.7	4.7	0.12	0.43
DW10	7.10	1030	575	446.6	550	32	89.1	68.7	4.3	0	671	41.5	10.19	0	1.78
DW13	8.39	1540	1006	190.4	728	26	30.5	372.5	2.6	64.8	756.4	87.7	48.36	2.9	8.36
DW14	6.62	1030	574	440.3	334	102	45.1	58.3	2.2	0	407.5	130.1	35.82	1.2	1.01
DW17	6.71	970	513	327.9	282	50.9	48.8	77.1	2.3	0	344.04	146.5	18.62	0.04	1.20
DW30	7.09	490	269	190.1	228	44	19.5	28.7	1.63	0	278.2	24.1	15	0	0.88
DW32	6.25	570	311	95.9	186	14.6	14.44	84.3	1.24	0	226.9	67.5	17.05	0.22	1.98
DW37	6.62	610	350	232.2	280	54.6	23.3	46.3	0.95	0	341.6	39.5	17.64	0.12	1.15
DW41	6.66	400	213	136.4	136	29.1	15.5	25.8	1.2	0	165.9	36.6	23.61	0.35	0.86
DW56	6.96	820	447	341.9	386	50.9	52.2	49.6	2.5	0	470.9	33.7	23.13	4.5	1.33
DW59	7.85	870	490	354.9	348	96.5	27.7	54.4	7.5	0	424.6	76.16	13.72	5.9	1.35
DW64	7.15	1100	582	386.8	314	94.6	36.6	95.4	3.8	0	383.08	100.3	45.22	18.6	1.43
BW1	7.08	630	364	239.7	248	94	1.22	37.5	5.2	0	302.6	55.9	22.29	0.03	0.34
BW11	7.05	1790	1043	416.1	604	46	73.2	293	8.7	0	736.9	172.6	87.76	0.72	2.78
BW14	6.74	1010	559	445.9	352	82	58.6	54.1	7.9	0	429.4	40.5	105.4	0.03	1.58
BW18	7.34	1760	1036	416.1	578	46	73.2	293	6.9	0	705.2	160.9	109.5	0.47	2.53
BW21	7.02	1560	888	420.9	466	70	59.8	204	6.8	0	568.5	198.6	70.18	0.55	1.42
BW22	6.94	1020	549	350.5	282	74.6	39.9	85.2	9	0	344.04	129.2	42.09	0.079	1.39
BW28	6.90	500	277	190.2	230	48	17.1	26.7	5.7	0	280.6	26.99	15.4	0.007	0.89
BW31	7.62	1360	646	475.4	350	106	51.2	90.3	4.6	0	427	62.66	121.6	0.05	1.42
BW32	6.54	500	278	200.2	224	52	17.1	26.9	3.7	0	273.3	31.8	12.35	0.32	0.67
BW33	6.67	830	469	319.2	310	60.1	41.1	68.7	6	0	378.2	75.19	32.46	0.59	0.65
BW35	6.87	700	393	275.2	290	70	24.4	42.6	6.4	0	353.8	50.1	26.02	0.3	0.84
BW36	6.66	1060	577	400.8	322	67.4	56.5	73.8	5.9	0	392.8	155.2	26.02	0.02	1.92
BW40	6.88	820	433	296.0	280	52.8	39.9	45.6	5.2	0	341.6	96.4	25.42	0.583	0.96
BW41	7.40	580	329	245.8	278	63.7	21.08	31.1	4.5	0	339.2	26.03	15.09	1.68	1.30
BW43	7.15	760	433	342.3	400	34.6	62.2	40.5	12.2	0	488	21.2	23.01	0.003	1.56
BW51	7.84	1510	727	510.9	242	82	74.4	93.6	9	0	295.2	271.8	24.94	26.9	0.80
BW60	7.70	710	389	323.6	334	58.24	43.31	27	9.4	0	407.5	28.92	17.94	4.2	1.28
BW61	6.93	940	538	378.3	428	56.4	57.7	68	11.4	0	522.2	43.4	45.11	0.06	1.37
BW69	7.89	920	493	291.2	230	76.4	24.4	84.3	4.2	0	280.6	110.9	41.42	14.1	1.03
BW74	7.48	780	429	277.9	332	50.9	36.65	57.7	5.9	0	405.04	51.09	28.67	0.041	1.28
S 5	7.86	563	302.21	240.389	254	32	39	37	2	0	310	28.5	11.7	0.11	1.14
S 6	7.27	1923	1026.4	386.06	610	32	74.4	225	12.3	0	744	245	73.1	0	1.84
S 7	7.42	1277	722.97	330.863	494	30	62.2	172	4.4	0	603	116	42.9	0	2.24
S 8	7.4	1886	1076.8	521.987	508	22	113.5	251	15.5	0	620	274	97	0.02	2.03
S 9	8.12	434	236.74	185.192	192	30	26.8	29.4	1.85	4.8	224	22.8	11.3	0.03	0.91

DW: dug well, BW: bore well, S: stream (Source: Analytical Laboratory of State Groundwater Department, Ernakulam)

than calcium in water (Hem, 1989, p.97), high Mg^{2+} / Ca^{2+} ratios could occur in waters with residual alkalinity as seen here.

The lowest values of Ca^{2+}/Na^{+} ratio and the highest Na^{+}content were noted in the bore well waters in the north east. Similarly, higher chloride values of 96 to 270 mg/l were found in some wells. Since high nitrate content was present in only a few of these wells, contamination from agricultural effluents may not be the reason for the higher chloride values. However, the streams in this area have comparable Ca^{2+}/ Na^{+} and Cl^{-} values. Since the streams flow over fractured bedrock in many places, recharge to the fractured rock aquifer by surface water concentrated by evaporation in the slow moving streams is possible. High HCO_3^{-}/ Ca^{2+} ratios of 1 to 9.6, positive residual carbonate values and positive $CaCO_3$ saturation index in the majority of the samples, especially from the east, indicate residual alkalinity and precipitation of Ca^{2+}. This is a favourable factor for dissolution of fluoride (Jacks, G. and others, 1993 and Saxena, V.K. and Ahmed, S., 2003). HCO_3^{-} / Ca^{2+} and residual carbonate were higher and Ca^{2+}/ Mg^{2+}lower in high F^{-} wells. Average ionic concentrations were higher in high F^{-} wells indicating role of weathering in mobilization of fluoride. Comparatively higher sulphate was noted in waters of bore wells located in and around the Eruthempathy fracture zone, where seasonal dewatering and aeration of shallow fracture zones occur. Sulphur is oxidized to sulphate ions when sulfide minerals weather in contact with aerated water (Hem, J.D., 1989, p.112).

Groundwater Types

The Hill-Piper trilinear plots show that no single cation

Table 2. Chemical characteristics of water in wells and streams

Well no.	Area	Topo-graphy	Soil (as identified in field)	Ca/Mg	Ca/Na	Na/Cl	HCO_3/Ca	Cl/CO_3+HCO_3	Na%	RC	SI
DW1	CW	Sl	SS	1.74	0.69	1.01	2.18	0.66	49.5	0.42	-1.91
DW10	E	SNV	SC	0.22	0.53	2.55	6.89	0.11	25.8	2.07	-0.04
DW13	E	SNV	SC	0.52	0.08	6.55	9.56	0.17	81	10.8	1.22
DW14	E	Sl	CS	1.37	2.01	0.69	1.31	0.55	22.7	-2.12	-0.27
DW17	CW	Sl	CS	0.63	0.76	0.81	2.22	0.73	34.2	-0.91	-0.57
DW30	CW	SNV	CS	1.37	1.76	1.84	2.08	0.15	25.3	0.76	-0.29
DW32	WP	TOH	CS	0.61	0.2	1.93	5.1	0.51	65.9	1.8	-1.72
DW37	WP	Sl	SC	1.42	1.35	1.81	2.06	0.2	30.5	0.96	-0.61
DW41	CW	Sl	CS	1.14	1.29	1.09	1.87	0.38	29.7	-0.01	-1.15
DW56	E	SNV	SC	0.59	1.18	2.27	3.04	0.12	24.5	0.89	-0.18
DW59	E	Sl	CS	2.11	2.04	1.1	1.45	0.31	26.5	-0.13	0.95
DW64	E	Sl	CS	1.57	1.14	1.47	1.33	0.45	35.5	-1.45	0.23
BW1	CW	Sl	CS	46.75	2.88	1.03	1.06	0.32	24.9	0.17	0.07
BW11	E	SNV	BC	0.38	0.18	2.62	5.26	0.4	59.9	3.76	0.04
BW14	E	TOH	CS	0.85	1.74	2.06	1.72	0.16	20.5	-1.87	-0.2
BW18	E	V	BC	0.38	0.18	2.81	5.04	0.39	60	3.24	0.35
BW21	E	V	BC	0.71	0.39	1.58	2.67	0.6	50.8	0.91	0.11
BW22	CW	TOH	CS	1.13	1	1.02	1.51	0.65	33.9	-1.36	-0.13
BW28	CW	V	SC	1.7	2.06	1.53	1.92	0.17	22.7	0.8	-0.43
BW31	WP	SNV	SS	1.26	1.35	2.22	1.32	0.25	29	-2.5	0.79
BW32	CW	TOH	CS	1.85	2.22	1.3	1.73	0.2	22.2	0.48	-0.77
BW33	WP	Sl	CS	0.89	1	1.41	2.07	0.34	31.4	-0.18	-0.46
BW35	CW	V	BC	1.74	1.89	1.31	1.66	0.24	24.6	0.3	-0.21
BW36	WP	SNV	SC	0.72	1.05	0.73	1.91	0.68	28.2	-1.57	-0.41
BW40	WP	Sl	CS	0.8	1.33	0.73	2.13	0.49	24.7	-0.32	-0.35
BW41	CW	Sl	CS	1.83	2.35	1.84	1.75	0.13	21.2	0.65	0.23
BW43	CW	Sl	SC	0.34	0.98	2.95	4.63	0.07	19.8	1.16	-0.08
BW51	E	Sl	CS	0.67	1.01	0.53	1.18	1.58	28	-5.37	0.73
BW60	E	SNV	SC	0.82	2.48	1.44	2.3	0.12	14.9	0.21	0.61
BW61	E	Sl	CS	0.59	0.95	2.42	3.04	0.14	27.4	1	-0.07
BW69	E	Sl	CS	1.9	1.04	1.17	1.21	0.68	38.2	-1.22	0.79
BW74	CW	V	SC	0.84	1.01	1.74	2.61	0.22	30.5	1.09	0.32
S5	Vandithodu			0.5	0.99	2	3.18	0.16	24.9	0.28	0.27
S6	Jn.of Korayar and Varattar			0.26	0.16	1.42	7.64	0.57	54.9	4.48	0.02
S7	Varattar			0.29	0.2	2.29	6.6	0.33	52.6	3.27	0.08
S8	Korayar			0.12	0.1	1.41	9.26	0.76	50.2	-0.27	-0.06
S9	Chittur puzha			0.68	1.17	1.99	2.45	0.17	25.4	0.13	0.46

E=eastern part, CW=central and western parts, WP=western pocket, V=valley, SNV=slope near valley, Sl=slope, TOH=top of hillock, BC=black clay, SC=sandy clay, CS=clayey sand, SS=silty sand, DW=dug well, BW=bore well, S=stream

dominates in most dug well and bore well samples (Figs.8 and 9). Bicarbonate is the dominant anion in groundwater and stream water in the area. Weathering of ferromagnesian minerals and plagioclase feldspar in the hornblende biotite gneiss appears to be the most important control on groundwater chemistry in the area. Calcium carbonate precipitation and cation exchange, mostly in the soil, and dilution by Moolathara irrigation water influence the chemistry. Groundwater in unconfined and fractured rock aquifers mostly belonged to the same type, indicating connectivity. Wells that had Na^+- HCO_3^- type water (DW 13 and 32 and BW 11, 18 and 21) had the highest F^- concentration in both seasons. Four of these are in the northeastern part and have higher TDS as well. Dissociation of F^- will be high in the presence of excessive Na HCO_3 in groundwater (Saxena, V.K. and Ahmed, S., 2003). Chae, G.T. and others (2007) found higher F^- concentration in Na^+- HCO_3^- water compared to Ca^{2+}- HCO_3^- water. Here, four bore wells with Ca^{2+}- HCO_3^- water, located in the zone of pyroxenite bands in the canal command area, had low F^-. They were the only bore wells with calcium percentage above fifty. However, out of the twenty wells (8 DW and 12 BW) having Ca^{2+}- Mg^{2+} - HCO_3^- type water, six (DW 10 and 64 and BW 14, 31, 36 and 43) had high fluoride content of 1.40 mg/l or more. Hence, while $NaHCO_3$ promotes dissociation of F^-, it seems likely that other factors may lead

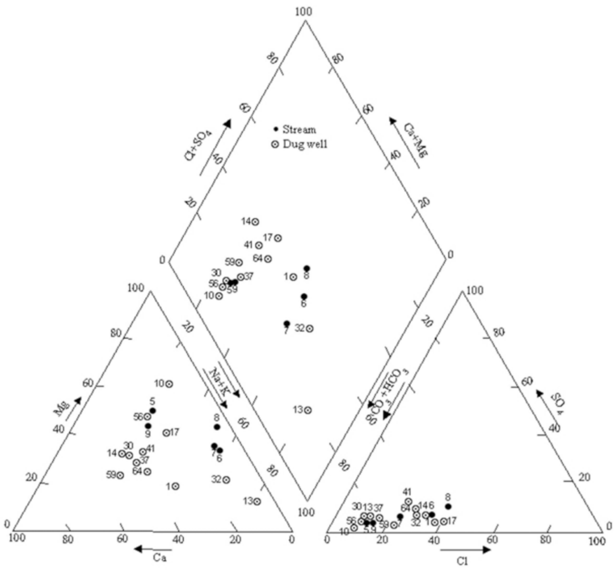

Fig.8. Piper diagram (dug wells and streams)

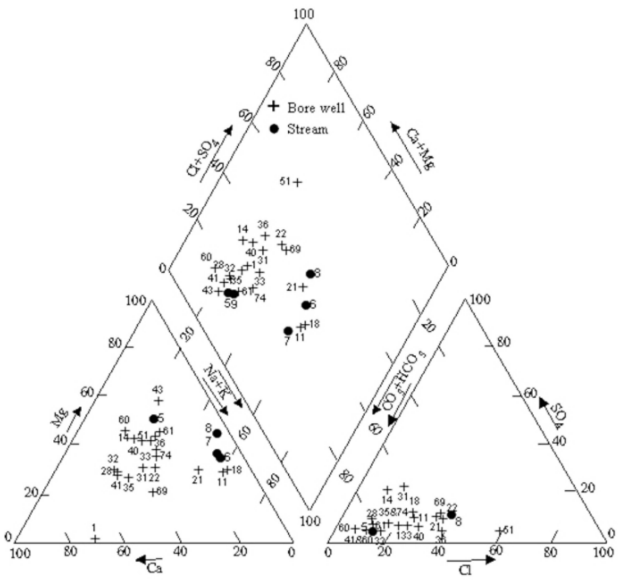

Fig.9. Piper diagram (bore wells and streams)

to concentration of the ion in other types of waters also. It is also possible that there is a lag in fluoride precipitation in response to enrichment of calcium resulting from cation exchange.

Stream plots (Fig.8) form two clusters, S5 and S9 representing low TDS Chitturpuzha water and S6 to S8, from Korayar and Varattar, representing stream flow natural to the area. Assuming influence of irrigation return flow on the unconfined aquifer, a mixing line between the two clusters is considered in the cation triangle for dug wells. Plots of dug well nos. 30, 37, 41 and 64, which are in the irrigated area, fall near the fresh water end of this line, suggesting influence of irrigation water. Three of these wells are low TDS wells. The points are displaced laterally from the line due to higher percentage of Ca^{2+} in groundwater. Plots of dug well nos. 10, 13, 32 and 59, which are outside the command area, fall in vastly different areas showing influence of diverse rock-water and soil-water interactions. However, DW 14, 17 and 56 do not conform to this pattern. In the anion triangle, samples from the slow-flowing Korayar and Varattar streams indicate concentration of chloride, probably by evaporation.

In the bore well plot (Fig.9), plots of bore well nos. 11, 18 and 21 fall near the S6-S8 end in both triangles. These wells are located on low ground between the streams in the northeastern part, and have higher TDS, Cl^- and F^-, comparable with the streams. Influent flow to the fractured rock aquifer is possible, since the streams flow over highly fractured bedrock in many places. The bore wells with plots near the S5-S9 end in the cation triangle are scattered over the study area and do not indicate influence of stream water.

Correlation of Chemical Data

Blom and Cederlund (2006) found a positive correlation between F^- and pH in dug well water samples in Palakkad district. However, correlation is absent in the present case (Table 3). The present study indicates that while alkaline pH promotes dissolution of F^-, continued increase in F^- is not dependent on a linear increase in pH. Among the 41 high F^- wells, only nine had pH less than 7. Similarly, there was a clear increase in average F^- in bore well waters from the hilltops to the valleys, without a corresponding change in pH. Spatial variation in F^- is probably dependent on the degree of weathering which mobilizes the fluoride. Positive correlation between F^- and EC was weak to moderate. There was no correlation of F^- and EC with water table depth, well depth and elevation.

High F^- is more likely in water with low Ca^{2+} (Hem, J.D., 1989, p. 121). However, Blom and Cederlund (2006) did not find good correlation between F^- and Ca^{2+} in dug well water samples from a nearby area. According to Ramesam and Rajagopalan (1985), Ca may not have a decisive role in the control of F^- content due to super saturation of the sample with calcium fluoride. However, other studies have shown negative correlation of F^- with Ca^{2+} and positive correlation of F^- with Na^+ and HCO_3^- (Jacks et al. 1993; Guo et al. 2006; Chae et al. 2007). The present study shows good positive correlation of F^- with Na^+, but there is no correlation of F^- with Ca^{2+}. Bicarbonate is the major anion produced by weathering (Langmuir, 1997, p.235) and is an indicator of intensity of weathering of silicate rocks. In this study, good positive correlation of

Table 3. Correlation of chemical data (concentrations of ions in mg/l, ion ratios in meq/l)

	Dug wells except DW13 (N=11)	Bore wells (N=20)
Na v/s F	0.78	0.76
Ca v/s F	0.04	-0.33
Mg v/s F	0.49	0.71
HCO_3 v/s F	0.58	0.85
Cl v/s F	0.15	0.32
Ca/Na v/s F	-0.4	-0.65
Ca/Mg v/s F	-0.54	-0.4
Total ions v/s F (meq/l)	0.55	0.77
pH v/s F	0.15	0.04
pH v/s Na	0.07	0.1
pH v/s Mg	0.31	0.13
pH v/s Ca	0.58	0.25
pH v/s CO_3+HCO_3	0.54	-0.02
Ca v/s Mg	0.21	-0.17
Ca v/s Na	0.33	-0.16
Mg v/s Na	0.43	0.63
Na v/s HCO_3	0.45	0.85
Mg v/s HCO_3	0.92	0.72
Ca v/s HCO_3	0.4	-0.35
Total ions v/s Na (meq/l)	0.69	0.94
Total ions v/s Mg (meq/l)	0.83	0.82
Total ions v/s Ca (meq/l)	0.66	-0.02
Total ions v/s HCO_3 (meq/l)	0.88	0.84
SI v/s F	0.26	0.15
Ca v/s SI	0.79	0.4
TA v/s SI	0.72	0.12
TDS v/s SI	0.74	0.33
HCO_3/Ca v/s F	0.66	0.77
RC v/s F	0.37	0.46
SO_4 v/s F	0.13	0.62

Na^+ and Mg^{2+} with HCO_3^- and TDS, and positive correlation of F^- with Mg^{2+} indicate the role of weathering of ferromagnesian minerals in the release of fluoride in this area. Magnesium shows better distribution of data points compared to sodium. Positive correlations of F^- with HCO_3^- / Ca^{2+} ratio and residual carbonate, as seen here, indicate the role of residual alkalinity in fluoride dissolution.

Soil Analysis

Analysis of ten samples shows that the soils in the east are relatively more clayey and alkaline with pH of 7.2 to 8.2 (Table 4). Ion exchange reactions exert an important control on water chemistry since cation exchange capacity of soils is much higher than the concentration of dissolved cations in dilute groundwater (Drever, 1988, p.84). CEC ranged from 6 to 21 cmol/kg in the analysed samples. High level of Ca^{2+} (38 to 81% of exchangeable bases) and low level of Na^+ (0.5 to 4.4%) in these samples suggest cation exchange with water containing calcium. This is a favourable factor for dissolution of fluoride. Further, fluoride is not easily adsorbed in alkaline soils.

Source of Fluoride

Average content of fluoride in igneous rocks is 715 ppm (Hem, 1989, p.5). Fluorite is a common fluoride mineral, but its solubility in fresh water is low. Amphiboles such as hornblende and some of the micas may contain fluoride, which has replaced part of the hydroxide in the mineral structures (Hem, 1989, p.121). In an analysis of samples of gneiss, Jacks et al. (1993) found 65% of total F^- to be in the dark fraction of the rock and the highest concentration of F^- in kankar. Ramesam and Rajagopalan (1985) found F^- contents of 510 ppm and 410 ppm in biotite gneiss and granite gneiss respectively, but did not find correlation between F^- content in the bulk rock or soil with the content in groundwater. In the present study, analysis of 17 rock

Table 4. Soil characteristic

Nearby well no.	Sand %	Clay %	Silt %	Soil type	pH (soil)	EC (soil), µS/cm	CEC, cmol/kg	Exchangeable bases, cmol/kg (meq/100g)				Total exchangeable bases, cmol/kg
								Na	K	Ca	Mg	
DW 3	72.84	20.81	6.35	sandy clay loam	7.2	60	10	0.08	0.06	5.03	1.72	6.89
DW 13	65.76	20.81	13.42	sandy clay loam	7.8	190	13.1	0.06	0.32	10.4	2.13	12.91
DW 14 and BW72	79.38	10.42	10.21	sandy loam	7.3	70	6	0.06	0.07	2.13	1.39	3.65
DW 32	72.34	25.33	2.33	sandy clay loam	6.3	70	10.6	0.11	0.19	3.55	1.64	5.49
DW 64 and BW69	56.91	41.24	1.86	sandy clay	7.4	170	17.4	0.12	0.15	9.23	2.79	12.29
BW 18	46.76	41.19	12.05	sandy clay	8.2	330	21	0.97	0.71	11.93	8.2	21.81
BW 31	62.25	36.5	1.25	sandy clay	6.5	50	9.9	0.07	0.25	3.25	1.72	5.29
BW 43	62.73	27.09	10.18	sandy clay loam	6.9	210	17.6	0.08	0.92	9.13	2.7	12.83
BW 46	71.76	21.98	6.26	sandy clay loam	7.4	220	11.1	0.13	0.45	7.1	2.62	10.3
BW 61	77.93	20.53	1.54	sandy clay loam	7.4	100	8	0.13	0.27	3.15	2.21	5.76

DW: dug well, BW: bore well (Source: Central Soil Analytical Laboratory of Soil Survey, Govt. of Kerala)

Table 6. Fluoride concentration in soil samples

Nearby well	Texture	Fluoride (soil), mg/kg	Fluoride (gw), mg/l, in well
DW 3	Sandy clay loam	36.80	0.98
DW 13	Sandy clay loam	36.00	6.97
DW 14	Sandy loam	31.20	1.12
DW 32	Sandy clay loam	36.80	1.84
DW 64	Sandy clay	45.60	1.62
BW 18	Sandy clay	38.40	2.48
BW 31	Sandy clay	40.00	1.74
BW 43	Sandy clay loam	46.40	1.6
BW 46	Sandy clay loam	31.20	0.87
BW 61	Sandy clay loam	38.40	1.41
BW 69 (same sample as DW 64)	Sandy clay	45.60	1.25
BW 72 (same sample as DW 14)	Sandy loam	31.20	1.02

DW: dug well, BW: bore well, gw: groundwater (Source: Central Water Analysis Laboratory of the Centre for Water Resources Development and Management, Kozhikode)

Table 5. Fluoride concentration in rock samples

Source of sample	Rock type	Fluoride (rock), mg/kg	Fluoride , (gw) mg/l, in well
Quarry between BW 29 and 30	Hornblende biotite gneiss	52.50	
Korayar riverbed in north eastern part	Migmatite	74.40	
Soil near Korayar river in north-eastern part	Kankar	99.00	
DW 1	Hornblende biotite gneiss	67.50	0.49
DW1	Basic band in gneiss	175.50	0.49
DW 13	Hornblende biotite gneiss	78.40	6.97
DW13	Basic rock	76.10	6.97
DW14	Hornblende biotite gneiss	445.00	1.12
DW 32	Weathered	413.50	1.84
BW1 (same sample as DW1)	Hornblende biotite gneiss	67.50	0.49
BW1 (same sample as DW1)	Basic band in gneiss	175.50	0.49
BW 4	Drill cuttings, not identified	417.50	1.41
BW 18	Hornblende biotite gneiss and basic rock	432.00	2.48
BW 28	Ultrabasic	68.90	1.04
BW 31	Granitic band in banded gneiss	274.00	1.74
BW 43	Drill cuttings, not identified	416.95	1.60
BW 46	Outcrop, not identified	416.00	0.87
BW 72 (same sample as DW14)	Hornblende biotite gneiss	445.00	1.02
Drill cuttings from dry well between BW 68 and 69	Drill cuttings, not identified	365.00	
Drill cuttings from second dry well between BW 68 and 69	Drill cuttings, not identified	470.50	

DW: dug well, BW: bore well, gw: groundwater (Source: Central Water Analysis Laboratory of the Centre for Water Resources Development and Management, Kozhikode)

and10 soil samples, carried out at the Centre for Water Resources Development and Management, Kozhikode, shows that fluoride content in groundwater is not related to its concentration in rocks and soils (Tables 5 and 6). Fluoride content in the formation is not a deciding factor, since its availability in all rock types and soils in the area is much higher than in groundwater. The rock samples have F^- content ranging from 52 to 470 mg/kg, while kankar has 99 mg/kg. Soil samples have F^- content of 31 to 46 mg/kg. Lower values in soil suggest that most of the F^- mobilized by weathering is leached away. This may be a reason for the high F^- noted in stream waters in the north east in all seasons. Weathering of biotite and hornblende in the gneisses and amphibolites may be the most important source of F^- in the study area. Kankar may be another source. Leaching of fluoride from the alkaline soils and the weathered formation into the recharge water appears to be important mechanisms here. Degree of weathering of rocks and the leachable F^- are important factors controlling F^- concentration in groundwater (Ramesam, V. and Rajagopalan, K., 1985). Weathering consumes H^+ ions and raises pH of the solution. Greater weathering in the eastern part of the study area has probably contributed to slightly higher pH and higher F^- content in groundwater.

SUMMARY

Slow weathering of rocks rich in ferromagnesian minerals in the gently undulating terrain in a relatively hot climate has formed alkaline soils with high cation exchange capacity and poor fluoride adsorption, and a vadose zone of partially weathered rock. The soil and the weathering reactions in the vadose zone have given rise to alkaline groundwater in which calcium is precipitated, while HCO_3^-, Na^+ and Mg^{2+} concentrations increase. High residual alkalinity has caused dissolution of fluoride, probably from biotite, hornblende and kankar. As it percolates down, this water is further enriched in fluoride, possibly by replacement of fluoride in mineral structures, resulting in higher fluoride content in the water of the fractured rock aquifer as compared to that of the unconfined aquifer. Leaching of fluoride from

soil and weathered rock in the vadose zone appears to be a major cause for high fluoride in the area. The degree of weathering is probably a controlling factor. There is no relation between F^- contents in rocks and soils, and in groundwater. The study indicates that, while alkaline pH promotes dissolution of F^-, continued increase in F^- is not dependent on further linear increase in pH. Similarly, the correlation of F^- with HCO_3^- / Ca^{2+} ratio may be a more reliable indicator than the correlation of F^- with Ca^{2+} in a study of this kind. Factors such as alternating granitic and mafic zones in gneisses, differences in cation exchange capacity, highly heterogeneous conduits in weathered crystalline rocks and different residence times of groundwater may be responsible for spatial variation in fluoride content. Influent flow of stream water, high in TDS, Cl^- and F^-, into the fractured rock aquifer through fractured bedrock outcrops is indicated in one area. Surface water irrigation with low TDS water dilutes groundwater in a large part of the area. Dug well and bore well waters generally belong to the same chemical type indicating connectivity of unconfined and fracture aquifers. A small isolated pocket in the area, having high fluoride groundwater, has acidic soils and the groundwater here does not have the chemical characteristics favourable for fluoride dissolution. The reason for this anomaly is not clear. However, the wells here have comparatively higher EC, and the bore wells have low Eh suggesting less connectivity between unconfined and fracture aquifers.

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