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Research paper

Fluoride contamination in groundwater resources of Alleppey, southern India



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ARTICLE INFO

Article history:

Available online 27 January 2016

Keywords:

Fluoride contamination
Groundwater
Coastal aquifers
Health hazard
Alleppey

ABSTRACT

Alleppey is one of the thickly populated coastal towns of the Kerala state in southern India. Groundwater is the main source of drinking water for the 240,991 people living in this region. The groundwater is being extracted from a multi-layer aquifer system of unconsolidated to semi-consolidated sedimentary formations, which range in age from Recent to Tertiary. The public water distribution system uses dug and tube wells. Though there were reports on fluoride contamination, this study reports for the first time excess fluoride and excess salinity in the drinking water of the region. The quality parameters, like Electrical Conductivity (EC) ranges from 266 to 3900 $\mu\text{S}/\text{cm}$, the fluoride content ranges from 0.68 to 2.88 mg/L, and the chloride ranges between the 5.7 to 1253 mg/L. The main water types are Na-HCO₃, Na-CO₃ and Na-Cl. The aqueous concentrations of F⁻ and CO₃²⁻ show positive correlation whereas F⁻ and Ca²⁺ show negative correlation. The source of fluoride in the groundwater could be from dissolution of fluorapatite, which is a common mineral in the Tertiary sediments of the area. Long residence time, sediment-groundwater interaction and facies changes (Ca-HCO₃ to Na-HCO₃) during groundwater flow regime are the major factors responsible for the high fluoride content in the groundwater of the area. High strontium content and high EC in some of the wells indicate saline water intrusion that could be due to the excess pumping from the deeper aquifers of the area. The water quality index computation has revealed that 62% of groundwater belongs to poor quality and is not suitable for domestic purposes as per BIS and WHO standards. Since the groundwater is the only source of drinking water in the area, proper treatment strategies and regulating the groundwater extraction are required as the quality deterioration poses serious threat to human health.

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1. Introduction

Groundwater is a renewable resource, yet the world's supply of groundwater is steadily decreasing especially in Asia and North America (Gleeson et al., 2012). Groundwater quality deterioration and supply of safe drinking water is a major concern throughout the world. Groundwater with high fluoride concentration (>1.5 mg/L), according to WHO (2011), is affecting more than 260 million people around the world (Amini et al., 2008). Globally, fluoride contamination in groundwater is widespread especially in China, India, Nigeria, South America (Andes and western Brazil) and Africa (Rift valley zone), northwest Iran, Pakistan, Kenya, and Sri Lanka (Gaciri and Davies, 1993; Brunt et al., 2004; Moghaddam and

Fijani, 2008; Rafique et al., 2009; Chandrajith et al., 2012; Craig et al., 2015). Several studies have demonstrated that areas with fluoride contamination in groundwater are mostly characterized by the presence of crystalline basement rocks/volcanic bedrocks with the dissolution of F⁻ promoted by arid/semi-arid climatic conditions, Ca deficient Na-HCO₃ type groundwater, long groundwater residence time and distance from the recharge area (Handa, 1975; Apambire et al., 1997; Rao, 1997a; Genxu and Guodong, 2001; Saxena and Ahmed, 2001; Edmunds and Smedley, 2005; Jacks et al., 2005; Sreedevi et al., 2006; Guo et al., 2007; Shaji et al., 2007; Amini et al., 2008).

High fluoride in groundwater has been reported from 19 states in India (CGWB, 2010) with fluoride contamination in groundwater resources being widespread, intense, and alarming. Endemic fluorosis is prevalent in India since 1937 (Shortt et al., 1937). Jacks et al. (2005) observed that high fluoride in groundwater in many parts of India was due to evapotranspiration of groundwater with residual

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Peer-review under responsibility of China University of Geosciences (Beijing).

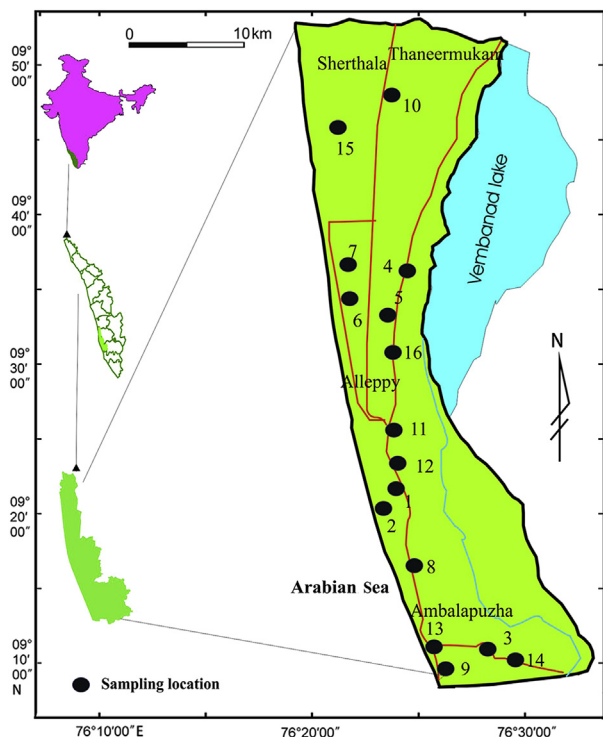


Figure 1. Location map of study area.

alkalinity. High fluoride content in the deeper aquifers of Maharashtra is due to long residence time than the shallow aquifers (Madhnure et al., 2007). The granitic rocks in Nalgonda district contain fluoride from 325 to 3200 mg/kg and are the main source of fluoride in groundwater (Brindha et al., 2011 and references therein). High fluoride groundwater has been reported from Palghat, Kerala by Shaji et al. (2007).

Groundwater is one of the primary sources of water for domestic and agriculture uses in Kerala. During the last two decades, the groundwater scenario of Kerala has been witnessing several changes (Shaji et al., 2008) with over dependence on this resource due to the bad quality of surface water.

Alleppey is one of the small coastal towns and famous tourist destinations of Kerala with a population of over 240,991. The whole water distribution system of the area is fully depended on groundwater. Although groundwater characteristics of Alleppey has been investigated in some previous studies (Born et al., 1990; Shaji et al., 2009) no detailed investigations have been done on the nature of aquifers, and quality parameters with regard to suitability of groundwater for drinking as per WHO and BIS (1991) standards. In this study, we report the results of a systematic investigation of the hydrogeochemical scenario of the aquifer units of the region with a view to evaluate the water quality and drinking water standards.

2. Study area

The study area (260 km²) located within the Alleppey district lies between latitude 9°35'00"N and longitude 76°10'00"E (Fig. 1). The major townships are Alleppey municipality, Mararikulam, Neerkunnam, Sherthala, Thaneermukkam etc. The Pampa River drains through the major part of the study area with its tributaries Achankovil and Manimala rivers. The Vembanad Lake flanking the eastern part of the area plays an important role in the hydrology and drainage network of the area (Fig. 1). The general elevation of

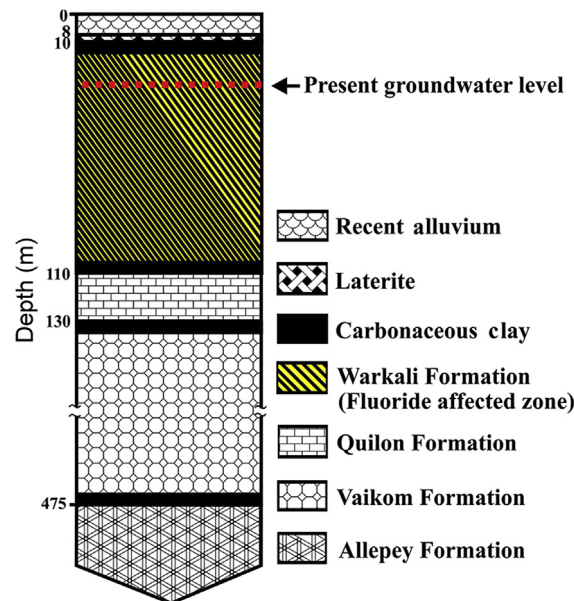


Figure 2. Lithology shows fluoride affected zone and groundwater level.

the area is less than 6 m above mean sea level and certain areas lie below mean sea level also. The area lying below mean sea level is prone to continued flood submergence during monsoon. The Thaneermukkam barrier, constructed in the north of Vembanad Lake, is aimed to prevent salinity intrusion in dry season to the lakes as well as to maintain the fresh water availability from rivers. Geomorphologically, the area lies in the coastal plain and major units are beaches, shore platforms, spit and bars, beach ridges etc.

3. Materials and methods

Detailed hydrogeological investigations were carried out in the area. Key wells were established for water level monitoring and sampling (Fig. 1). Sixteen water samples were collected from open wells and tube wells (water supply wells) spaced ~4.0 km apart, covering the entire study area. Samples were analysed in the chemical laboratory of Geology Department for the physico-chemical attributes like pH, electrical conductivity (EC), total hardness (TH), dissolved oxygen (DO), total dissolved solids (TDS), dissolved silica and major ions (Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, HCO₃⁻ and SO₄²⁻). The methods used for the analysis were standardized as per procedures laid down by APHA (1995). ESICO Digital Clinical Flame Photometer 391 was used for analyses. The hydrogen ion concentration (pH), electrical conductivity (EC), total dissolved solids (TDS) are computed with the help of the portable pH meter. Fluoride content of the groundwater is determined using ion chromatography (IC, Basic Plus, Metrohm) at the Laboratory of Environmental Engineering Division, School of Mechanical and Building Sciences, VIT University, Chennai, India. The trace element chemistry is determined using ICP-MS (iCAP-QC, Thermo scientific) at central facility of University of Kerala. Sample introduction of ICP-MS consists of the standard PFA-ST Nebulizers with cyclonic and spray chamber. All quantitative measurements were performed using the instrument software (Qtegra). Working voltage of the instrument is 1550 W. Reagents: mixed element standard solutions (Tune B iCAP Q, Setup solution iCAP Q) which were used to calibrate ICP-MS were obtained from Thermo Scientific Germany. Multi element standards for the analysis were purchased from Thermo scientific. All the spatial variation maps are prepared by

Table 1
Geochemical data of groundwater samples from Alleppey.

No.	pH	EC ($\mu\text{S}/\text{cm}$)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^{-} (mg/L)	SO_4^{2-} (mg/L)	Cl^{-} (mg/L)	F^{-} (mg/L)
1	9.04	882	14.028	36.432	93	8	205	19.63	53.25	1.86
2	10.15	812	42.084	31.538	60	17	170	35.27	39.05	0.81
3	10.26	639	26.052	35.2	57	8	215	15.08	10.65	0.68
4	10.22	733	20.04	27.92	77	7	225	15.21	24.85	1.63
5	10.43	883	20.04	36.425	77	7	300	14.56	35.5	1.34
6	9.97	2870	56.112	58.25	198	12	265	18.72	337.25	2.36
7	8.3	705	14.028	21.852	63	6	200	12.35	24.85	2.88
8	9	476	14	9.7	75	8.9	234	0.81	21	1.72
9	8.61	266	22	1.5	26	2.4	71	8.4	35	1.52
10	7.25	1415	15.86	15.3	98	9	300	0.39	349.5	2.62
11	7.08	449	17.6	9.1	29	6	230	19.63	364.8	1.58
12	7.4	690	24.5	15.7	28	7	230	27.56	108.8	1.64
13	7.33	431	17.6	12.6	22	6	220	25.22	36.4	1.32
14	6.65	3900	71.8	34	98	12	190	15.08	1253	1.41
15	8.74	371	41	13	12	4.1	212	0.81	5.7	1.06
16	6.93	885	20.5	11.5	29	6	252	1.56	155.5	2.04

using ArcGIS 9.3. The graphical representation of the parameters was plotted with the help of the Gnu plot 4.6 software.

4. Hydrogeological settings

The sedimentary formations of the area represented by Tertiary beds are overlain by laterites and Recent alluvium (CGWB, 1993) and underlain by Precambrian crystalline basement. The Tertiary formations of Kerala are composed of four distinct units known as Warkali bed (late Miocene to early Pliocene), Quilon bed (early Miocene), Vaikom bed and Alleppey bed (CGWB, 1993). The Alleppey bed is composed of highly carbonaceous clay with intercalations of sandstone, with thickness ranging from 4 to 140 m, and the thickest portion occurring around Alleppey town. The Vaikom bed overlying the Alleppey bed with thickness varying from 25 to 238 m is a potential aquifer. It is composed of gravel, coarse sand, clay and lignite. The Quilon bed (6 to 10 m thick) comprises of limestone and occurs above the Vaikom bed. The groundwater in the zone is not very promising and is mostly brackish. The Warkali bed overlying the Quilon bed is another potential aquifer, and is the most extensively developed aquifer in the study area. Lithology prepared based on CGWB data (SIDA report, CGWB, 1993) is given in Fig. 2. The Tertiary formations are separated from the recent alluvium by a confining clay layer, which prevents *in situ* recharge from rainfall (Fig. 2). The alluvial formations are represented by the deposits along the coast, the backwater and lagoons. The deposits were brought down by the west flowing rivers and the other types of deposits in the swamps and estuaries and subsequently reworked by wave action. These deposits comprise pure quartz sand including the glass sand deposits around Sherthalai and the placer deposits of heavy minerals all along the coast, silty sand, silts and various types/colours of clays. The thickness of these beds varies from a few metres to more than 50 m at Kattoor north of Alleppey.

Groundwater occurs in unconfined condition in the top alluvial zones and confined condition in the Tertiary sequences. Groundwater is extracted from the Warkali beds and top alluvium. The groundwater from other aquifer units remains untapped. Hence this study focuses on the groundwater from the alluvial and Warkali aquifers. The depth to water level in the alluvial zone ranges from 2 to 5 mbgl. The piezometric surface in the Warkali formation (monitored from the tube wells) ranges from 10 to 35 mbgl (Fig. 2). Initially (around 15 years back) the wells were artesian wells with piezometric head above the ground level. Due to excessive pumping from the aquifer the piezometric head has gone down considerably.

4.1. Hydrochemistry

The chemical analysis data of 16 groundwater samples are presented in Table 1. The data shows deterioration in the groundwater quality as per the BIS standards. The electrical conductivity (EC) ranges between 266 and 3900 $\mu\text{S}/\text{cm}$ and indicates the level of mineralisation. The fluoride concentration ranges between 0.68 and 2.88 mg/L, far exceeding the permissible limit of F^{-} as 1.5 mg/L. Chloride is in the range between 5.7 and 1253 mg/L, bicarbonate ranges from 71 to 300 mg/L and calcium is in the range between 14

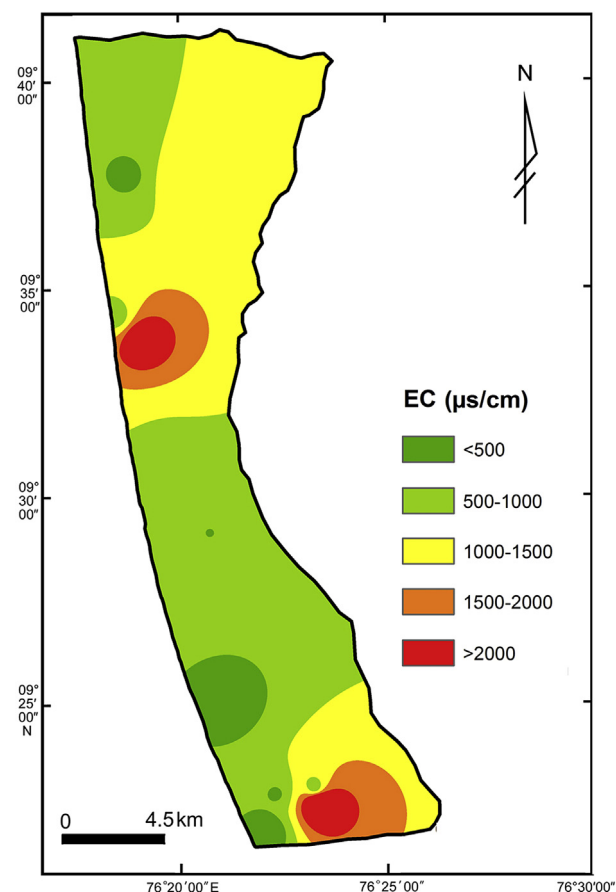


Figure 3. Spatial variation of electrical conductivity (EC).

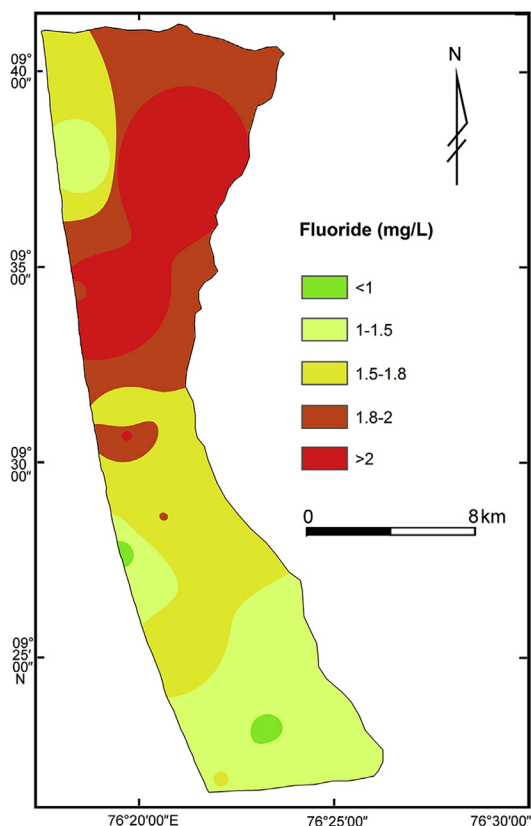


Figure 4. Spatial variation of fluoride.

and 71.8 mg/L. Spatial variation maps of these parameters were prepared with the help of the ArcGIS 9.3. Figs. 3 and 4 represent the spatial variation of electrical conductivity and fluoride respectively.

4.1.1. Piper diagram

Water-quality interpretation is attempted by plotting the data in the Piper diagram. The anions and cations of 16 samples were plotted in the piper diagram using the software Geochemist's workbench student10.0. This diagram consists of three distinct fields including two triangular fields and a diamond-shaped field. The cations expressed as percentage of total cations in meq/L as a single point on the left triangle while anions plot in the right triangle (Piper, 1944). Each point is then projected into the upper field along a line parallel to the upper margin of the field and the point where the extension intersects indicates the character of the water as represented by the relationship among Na^+ , K^+ , Ca^{2+} , Mg^{2+} , CO_3^{2-} , HCO_3^- and Cl^- , SO_4^{2-} ions. Similarities and differences among groundwater samples can be revealed from the trilinear diagram because water of similar qualities will tend to plot together as groups. The data plots in the Piper diagram (Fig. 5) show that 50% of the samples fall in the central part of the diamond field, which indicates the non-domination of any of the cation or anion pairs. The plot reveals that the main water types is $\text{Na-HCO}_3 < \text{Na-CO}_3 < \text{Na-Cl} < \text{Ca-HCO}_3$. The water types are listed in Table 2.

4.1.2. Saturation index

Since high F is observed in the area, groundwater geochemistry is examined based on saturation with respect to fluorite and its nature as revealed by the Piper diagram. Saturation indices are used to evaluate the degree of equilibrium between water and minerals. Changes in saturation state are useful to distinguish different stages

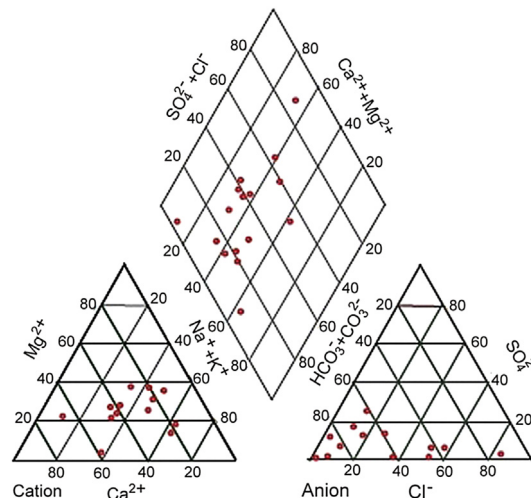


Figure 5. Chemical data plots in Piper diagram to classify water types.

of hydrochemical evolution and help to identify which geochemical reactions are important in controlling water chemistry (Güler and Thyne, 2004). The saturation index of a mineral is obtained from the following equation (Appelo and Postma, 1996):

$$SI = \log(IAP/K_{sp}) \quad (1)$$

where IAP is the ion activity product of the dissociated chemical species in solution, K_{sp} is the equilibrium solubility product for the chemical involved at the sample temperature. Saturation indices of minerals are useful for evaluating the extent to which water chemistry is controlled by equilibrium with solid phases (Appelo and Postma, 1996; Drever, 1997). When the SI is below zero, the water is under-saturated with respect to the mineral fluorite. An SI of zero means water is in equilibrium with the mineral, whereas an SI greater than zero means a supersaturated solution with respect to the mineral in question (Yidana et al., 2010).

The saturation indices with respect to CaF_2 were calculated for the 16 samples and given in Table 2. The solubility product of the fluorite at 25 °C and 1 atm was taken as $10^{-10.96}$. The ionic strength ranged from -0.21 to -2.74 . Here the extended Debye-Huckel equation was used to calculate the activity coefficients of ionic strength and the saturation index was calculated with the activities of Ca and F instead of their concentration (Shaji et al., 2007). The intensity of soluble minerals is expressed as saturation index.

Table 2
Saturation index, ionic strength and water types.

No.	Location	Ionic strength	Saturation index	Water type
1	Chandanakavu	0.25	−2.34	Na-HCO ₃
2	Vadakkal Punnapra	0.29	−2.28	Na-CO ₃
3	Karumadi	0.32	−2.24	Na-CO ₃
4	Chudukadu	0.36	−2.1	Na-CO ₃
5	Karumadi Kattukulam	0.5	−0.21	Na-CO ₃
6	Kulamakkikolani	0.57	−2.03	Na-Cl
7	Kattor	0.19	−2.45	Na-HCO ₃
8	Vandanam	0.2	−2.13	Na-HCO ₃
9	Purakkad	0.1	−2.74	Na-HCO ₃
10	Mararikulam	0.39	−2.17	Na-Cl
11	Chandanakavu	0.36	−2.19	Na-Cl
12	Pazhaveedu	0.258	−2.33	Na-HCO ₃
13	Ambalapuzha	0.2	−2.43	Na-HCO ₃
14	Karumadi	0.9	−1.89	Na-Cl
15	Kanichukulangara	0.15	−2.55	Ca-HCO ₃
16	Kommadi	0.23	−2.37	Na-HCO ₃

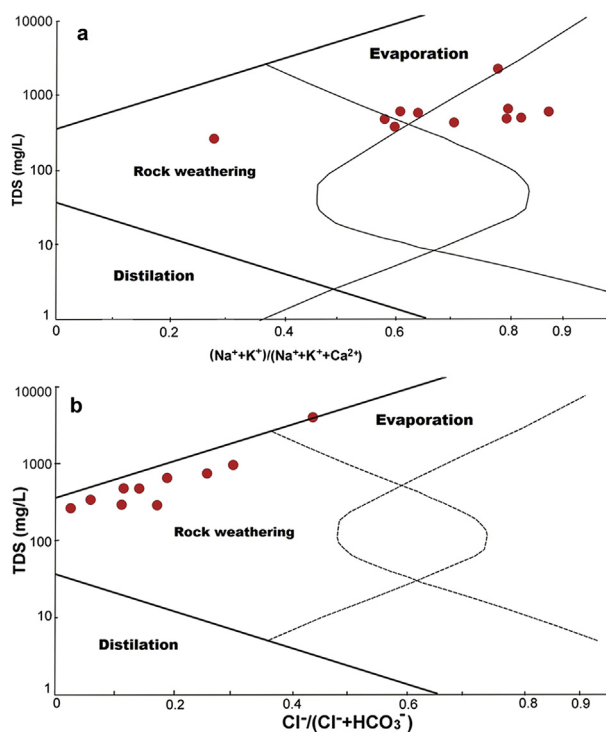


Figure 6. Gibbs's diagram of cation (a) and anion (b).

A range of values for saturation index near zero are generally considered to be within the equilibrium zone for a mineral. Saturation index $\pm 5\%$ is considered here. It is found that all the samples are in under-saturated condition with respect to CaF_2 . The computed saturation index and ionic strengths are given in Table 2. In the under saturation condition could be due the long residence time of groundwater, high rock water interaction and cation exchange especially between Na and Ca.

4.1.3. Gibbs diagram

In order to prove the rock water interaction the data is plotted in the Gibbs diagram, which is widely used to establish the relationship of water composition and aquifer lithological characteristics. Three distinct fields such as precipitation dominance, evaporation dominance and rock–water interaction dominance areas are shown in the Gibbs diagram (Gibbs, 1970). The samples fall in the rock–water interaction dominance and evaporation dominance field of the Gibbs diagram (Fig. 6a and b). The rock–water interaction dominance field indicates the interaction between rock chemistry and the chemistry of the percolated waters under the subsurface. The figure shows that the samples fall in the rock–water interaction dominance field. Hence the chemistry of the water is mainly controlled by the facies changes during the groundwater interaction with the aquifer material.

4.1.4. Water quality index calculation

The water quality index (WQI) is calculated for evaluating the quality of water and the influence of natural and anthropogenic activities based on several key parameters of groundwater chemistry. To calculate the WQI, the weight has been assigned for the physico-chemical parameters according to the parameters of relative importance in the overall quality of water for drinking water purposes. Water quality index (WQI) is an important parameter for identifying the water quality and its sustainability for drinking purposes (Rao, 1997b & 2006; Mitra et al., 2006;

Table 3
Relative weight of physico-chemical parameters.

Chemical parameters	WHO standards	Weight (w_i)	Relative weights $W_i = w_i / \sum_{i=1}^n w_i$
EC ($\mu\text{S}/\text{cm}$)	500	4	0.28
F^- (mg/L)	1.5	5	0.35
TH (mg/L)	300	3	0.21
Cl^- (mg/L)	250	2	0.14
		$\sum w_i = 14$	$\sum W_i = 1$

Magesh et al., 2013). WHO (2011) standards for drinking water quality have been used to calculate the WQI. The assigned weight ranges from 1 to 5. The maximum weight of 5 has been assigned for fluoride, EC for 4, the total hardness for 3 and chloride for 2 (Vasanthavignar et al., 2010). The relative weight is computed from the following equation:

$$W_i = w_i / \sum_{i=1}^n w_i \quad (2)$$

where W_i is the relative weight, w_i is the weight of each parameter, n is the number of parameters.

The quality rating scale for each parameter is calculated by dividing its concentration in each water sample by its respective standards (WHO, 2011) and multiplied by 100. The relative weight and water quality parameters used for calculation are listed in Table 3.

The quality rating is determined using the formula:

$$q_i = (C_i/S_i) \times 100 \quad (3)$$

where, q_i is the quality rating, C_i is the concentration of each chemical parameter in each sample in mg/L, S_i is the World Health Organization standard for each chemical parameter in mg/L according to the guidelines of WHO (2011) and BIS (1991).

For computing the final stage of WQI, the SI is first determined for each parameter. The sum of SI values gives the water quality index for each sample.

$$\text{SI}_i = W_i \times q_i \quad (4)$$

where SI_i is the sub-index of i th parameter, q_i is the rating based on concentration of i th parameter.

The water quality classification is based on the WQI values. If the values are within the range between 50 and 100, the water is considered to be good quality; and if the values are between 100 and 300, the water is considered to be not suitable for drinking purposes.

The water quality index is determined using the formula:

$$\text{WQI} = \sum \text{SI}_i \quad (5)$$

The water quality index (Table 4) shows that 50% of the samples belong to poor quality (WQI values: 68 to 361), 13% come under very poor to unsuitable water category, and 37% under good water quality.

4.1.5. Groundwater quality zonation

Based on the analytical data, a groundwater quality zonation map has been prepared, by assessing suitable rank and weightages to relevant water quality parameters, which do have explicit control on the quality of the water in the region as shown in Table 5. The groundwater zonation map prepared using GIS (Fig. 7) for various parameters like EC, Cl^- and TH reveals that 47% of study area falls in the unsuitable category and 27% falls under moderate quality condition.

Table 4
Water quality index (WQI) classification.

No	Location	Source	WQI	Type
1	Chandanakavu	Water supply well	130.42	Poor
2	Vadakkal Punnappa	Dug well (domestic)	92.46	Good
3	Karumadi	Water supply well	74.88	Good
4	Chudukadu	Water supply well	111.04	Poor
5	Karumadi Kattukulam	Water supply well	112.34	Poor
6	Kulamakkikolani	Water supply well	288.81	Very poor
7	Kattor	Water supply well	150.42	Poor
8	Vandanam	Water supply well	93.35	Good
9	Purakkad	Dug well (domestic)	74.26	Good
10	Mararikulam	Water supply well	200.59	Poor
11	Chandanakavu	Water supply well	106.58	Poor
12	Pazhaveedu	Water supply well	110.95	Poor
13	Ambalapuzha	Water supply well	79.09	Good
14	Karumadi	Water supply well	361.27	Unsuitable
15	Kanichukulangara	Water supply well	68.98	Good
16	Kommedi	Water supply well	136.56	Poor

4.2. Trace element hydrochemistry

The trace element hydrochemistry was determined using ICP-MS. All the parameters are in the permissible limit of BIS except for strontium and the data is given in Table 6. The increase in Sr content in groundwater indicates sea water intrusion into the aquifer. This is the first report of high Sr in the deeper aquifers of Alleppey and the results indicate that saline water is slowly intruding into the Warkali formation due to excess pumping from the aquifer units.

5. Discussion

Detailed hydrogeological investigations have revealed that the groundwater is Ca-HCO₃ type south of the study area (Kayamkulam) and it changes to Na-HCO₃ type in the study area. The geochemical profile shows a decline in calcium content accompanied by an increase in sodium. Magnesium also decreases but the decrease is not as pronounced as that of calcium. The anion continues to be dominated by bicarbonate. In some areas, the water is dominated by mixed cation and bicarbonate. The electrical conductivity (EC) shows an increase in trend in groundwater marked by mixed cation-Cl type or Na-Cl type. The change in degree and type of mineralisation of the water in the Warkali aquifer can be explained as reflection of the different stages of interaction of the recharging fresh water with sediments deposited under marine environment. Initially, Ca-HCO₃ type water was formed by the

Table 5
Ranking of parameters to delineate groundwater quality zones.

Sl No.	Parameter	Class	Rank	Weightage	Index
1	EC (μs/cm)	<750	1	45	45
		750–1000	2		90
		1000–1200	3		135
		>1200	4		180
2	F ⁻ (mg/L)	<0.5	1	40	40
		1–1.5	2		80
		1.5–2	3		120
		>2	4		160
3	TH (mg/L)	<100	1	10	10
		100–150	2		20
		150–200	3		30
		>200	4		40
4	Cl ⁻ (mg/L)	<50	1	5	5
		50–100	2		10
		100–150	3		15
		>150	4		20

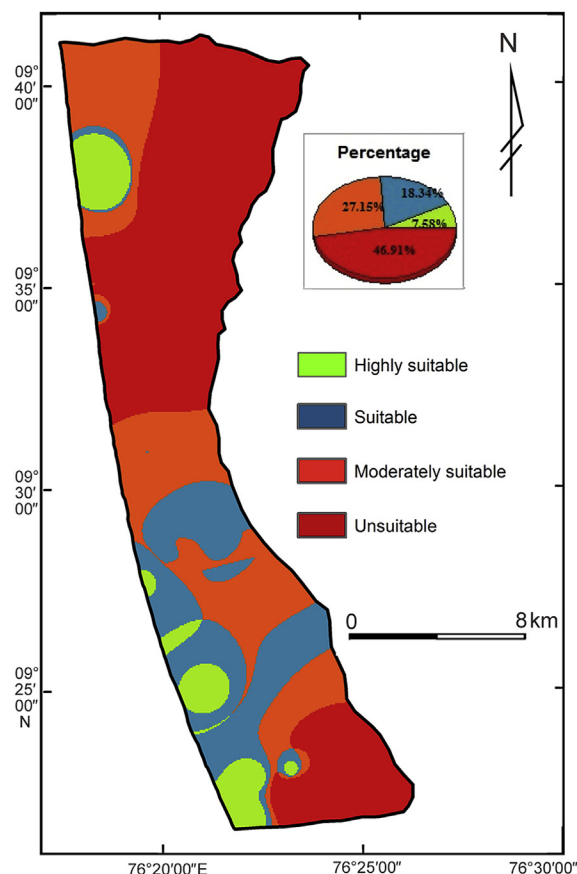


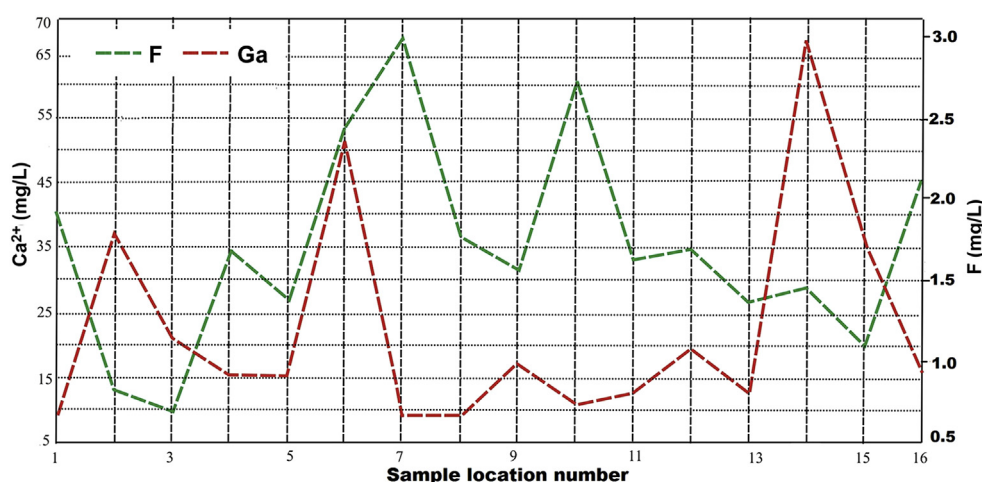
Figure 7. Water quality zonation map.

chemical reaction of rainwater containing CO₂ on CaCO₃ bearing minerals in the recharge zone. During its movement, the water exchanges Ca for Na by ion exchange process. This resulted in Na-HCO₃ type water, which also explains the higher fluoride content in Alleppey area, since the alkaline water depleted in Ca is effective in releasing fluoride from the minerals like fluorapatite. The zone with high fluoride groundwater is marked in Fig. 2 and the present groundwater level of the Warkali confined aquifer is also shown. In the aquifer system, the process of flushing/freshening is incomplete or the groundwater movement was sluggish, with hard brackish water of Ca-Mg-Cl or Na-Cl type (Agerstrand et al., 1981). The relationship between Ca²⁺ values and F in the groundwater is studied and comparative plots prepared using Gnu plot 4.6 (Fig. 8). This plot shows an inverse relationship as the Ca²⁺ decreases the fluoride content increases in the water. The facies classification indicates that the water type is Na-HCO₃ < Na-CO₃ < Na-Cl < Ca-HCO₃, supporting our observation. The groundwater is calcium depleted; hence fluorine can independently exist in the water. The groundwater zonation map reveals that 47% of study area falls in the unsuitable category and 27% falls under moderate quality condition. The water quality index (Table 4) shows that 50% of the samples belong to poor quality (WQI values: 68 to 361), 13% of the samples come under very poor to unsuitable water category, and 37% of the samples fall under good water quality. The analyses show that the groundwater extracted from the aquifers of the region is contaminated with geogenic materials. Since groundwater is the only dependable source for drinking water in this region, our study alerts that the water needs to be treated properly before supplying to the people. Continuous consumption of this high fluoride water would lead to serious health hazards.

Table 6

Trace element hydrochemistry of samples from Alleppey (in ppm).

Sample no.	Sr	Ba	As	Fe	Cr	Mn	Pb
1	0.4334	0.05158	0.00017	0.006952	0.00014	0.000054	0.000147
2	0.1824	0.0219	0.01111	0.01416	0.000602	0.00045	0.000169
3	0.3742	0.01052	0.01858	0.0292	0.000433	0.000268	0.000276
4	0.4969	0.04783	0.000266	0.008796	0.000185	0.000125	0.000123
5	0.4389	0.08683	0.000232	0.08598	0.000236	0.000085	0.000125
6	0.465	0.1203	0.000184	0.09704	0.00062	0.000252	0.000258
7	0.3572	0.03482	0.000055	0.04852	0.000544	0.000048	0.000115
8	0.03208	0.00592	0.000048	0.06356	0.000328	0.000225	0.000315
9	0.2541	0.09577	0.00013	0.05646	0.000425	0.000145	0.00016
10	2.405	0.05749	0.005509	0.01438	0.00016	0.000109	0.000034
11	0.2987	0.06866	0.0003	0.006327	0.000404	0.000254	0.000211
12	0.3412	0.02244	0.000184	0.01691	0.000819	0.000989	0.000362

**Figure 8.** Relationship between fluoride and calcium.

6. Conclusion

The major conclusions arising from our study are as follows:

- (1) Groundwater is the prime source of drinking water for the populace of Alleppey coastal town and the heavy groundwater extraction has resulted in the decline of groundwater level (piezometric head) up to 35 mbgl. This poses a threat to the efficiency of the pumping wells and productivity of Warkali aquifers of the region.
- (2) Groundwater (drinking water) shows high fluoride content (up to 2.88 mg/L) and high salinity and is only confined to the Warkali formation.
- (3) Water type is identified as $\text{Na-HCO}_3 < \text{Na-CO}_3 < \text{Na-Cl} < \text{Ca-HCO}_3$.
- (4) Gibbs diagram reveals that the water samples fall in the rock water interaction dominance field and the hydrochemistry of water is evolved by the continuous interaction of water with sediments.
- (5) Na-HCO_3 type groundwater favours the higher fluoride content and the Ca depleted alkaline water under high pH conditions is effective in releasing fluoride from the minerals like fluorapatite.
- (6) In the confined aquifer system, the process of flushing/freshening is incomplete or the groundwater movement was sluggish, as evidenced by the occurrence of hard brackish water of Ca-Mg-Cl or Na-Cl type, because of the lack of direct recharge from the rainfall.
- (7) The water quality index shows that 50% of the samples belong to poor quality (WQI values: 68 to 361), 13% of the samples come under very poor to unsuitable water category, and 37% of the samples fall under good water quality.
- (8) Zonation map reveals that 47% of water is not suitable for drinking purpose.
- (9) Groundwater samples with high Sr content indicate saline water intrusion.
- (10) Proper treatment strategies are recommended in all the pumping stations of the region including individual households.

Acknowledgements

Sincere thanks are due to Dr. Shihabudheen Maliyekkal, VIT University, Chennai, for Fluoride analysis. Smt. Bindhu J. Viju Scientist, CGWB Kerala region, Dr. Satheesh Kumar K, Department of Futures Studies, University of Kerala, Dr. Jobin Thomas research associate, Dr. A.P. Pradeepkumar, Head and SAP coordinator, Department of Geology, Julekh A., technical officer in ICP-MS lab in University of Kerala are thanked for their respective inputs. Field work component is supported by UGC SAP DRS II.

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