
Assessment of fluoride hazard in groundwater of Palghat District, Kerala: a GIS approach

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Abstract: Fluoride contamination of groundwater is an emerging problem all over the world. Occurrence of fluoride in groundwater has drawn worldwide care due to its significant influence on human physiology. Fluoride is a vital element, which is good for the teeth enamel and helps to avoid dental and skeletal caries. In excessive doses, it leads to fluorosis. In India most of the people in rural areas are dependent on groundwater for drinking purposes and have a possible chance of developing fluorosis. In the present study, assessment of fluoride hazard of groundwater quality was carried out in Palghat District from January and December 2012. Assessed 64 groundwater sample locations were interpolated using inverse distance weighted (IDW) method in ArcGIS 9.3. The results shows that fluoride contamination in groundwater is high in month of January (>0.87 mg/l) compared to December (>0.69 mg/l). Among the 12 blocks of Palghat District, Kollengode block is highly affected by fluoride contamination in the month of January and Chittur block in December. Groundwater quality of Kollengode and Chittur blocks is highly affected and it is unhealthy for drinking with prior treatment.

Keywords: groundwater; fluoride; geographical information system; GIS; inverse distance weighted method; IDW.

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1 Introduction

Groundwater is an important source of drinking water all over the globe. It can be contaminated from numerous human activities such as residential, municipal, commercial, industrial and agricultural activities. The indiscriminate use of this vital natural resource is generating groundwater-mining problems in numerous parts of the world (Todd, 2007). The groundwater resource should be assessed thoroughly, carefully and reliably on a real time basis to meet the ever rising requirements. Groundwater is a natural resource for the economic and secure provision of drinking water without which human survival is unimaginable (Sunitha et al., 2012). However, pure drinking water is not available everywhere, due to water shortage and contamination of current water resources (Ramesh and Vennila, 2012).

Fluoride in groundwater has drawn global attention due to its considerable impact on human physiology (Ashley and Burley, 1995; Miller, 1997; Camargo, 2003). The intake of fluoride is mainly through the drinking water. The fluoride content in the groundwater is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, temperature, pH, concentration of calcium and bicarbonate ions in water, et.c (Chandha and Tamta, 1999).

The main source of fluoride in groundwater is considered to be fluoride-bearing minerals such as fluorspar (CaF_2), fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$], cryolite and hydroxyl apatite in rocks. A number of issues of fluorosis have been reported mostly from the granite and gneissic complex of different states in India (Kundu et al., 2001). Edmunds

and Smedley (2005) have been stated high fluoride ground water most often in crystalline basement aquifers, active volcanic zones with geothermal sources and arid, sedimentary basins. Basilev (1977) has studied that chemical geology of granitic materials in rocks and melts. Bailey (1980) has been reported that fluoride is important in a variety of minerals like fluorite, topaz, cryolite, villimanite, chiolite, mallarite and carobbite etc.

Fluorosis is endemic in many parts of the world (Ortiz et al., 1998), mostly in the African countries of Morocco, Tunisia, Algeria, Sudan, Egypt, Somalia, Uganda, Kenya, Tanzania, Segal, Nigeria and South Africa (Manji et al., 1986; Brouwer et al., 1988; Smet, 1992) and the USA (Leone et al., 1955; Murry, 1960). In these countries, fluoride levels in the range of 10–60 mg/l in ground waters have been reported. The World Health Organization (WHO) has set an upper guideline limit for drinking water fluoride of 1.5 mg/l (WHO, 1984, 1996, 2000).

In India about 62 million people are at risk of developing fluorosis from drinking high fluoride water (Andezhath and Gosh, 1999; UNICEF, 2002). In India, out of 29 states 17 are affected as endemic fluorosis (Sisodia, 1994; Pillai and Stanley, 2002; Susheela, 2003) and TamilNadu is one among them where 23 out of 32 districts are prone to fluorosis in drinking water (Misra et al., 2006; Ramesh and Vennila, 2012). The people living in rural areas are more exposed since there is no centrally supplied treated water in these areas. Instead, groundwater accessed through dug wells, is their only water supply (Farooqi et al., 2007).

Karro et al. (2006) have examined the content and spatial distribution of fluoride in drinking water using 2-(4-sulfophenyl)-1,8-dihydroxy-3,6-naphthalene-disulphonic acid, trisodium salt (SPADNS) method in Estonian territory. Fordyce et al. (2007) have reported that fluoride is a powerful calcium-seeking element and can interfere with the calcified structure of bones and teeth in the human body at higher concentrations causing dental or skeletal fluorosis. Rao et al. (1993) have stated in apatite and fluoride, besides the replacement of hydroxyl by fluorine ions in mica, hornblende and soil that mostly consists of clay minerals, are the major sources of fluoride in circulating water. The same was reported by Sahu and Ma (1989), Wodeyar and Sreenivasan (1996), Bardson et al. (1996), Sumalatha et al. (1999) and Saxena and Ahmed (2001) in their study.

Geographical information system (GIS) can be used as a tool for spatial surveillance of epidemiological diseases and also as a spatial decision support system for public health management (Sunitha et al., 2012). Dhiman and Keshari (2001) have used GIS to quantify the spatial geological data and statistical analysis to determine the relation between groundwater quality parameters and geological units. They studied the degree of fluoride contamination and identification of hydrogeochemical process in mobilising the fluoride contamination. Thangavelu (2013) has mapped the quality of groundwater using GIS in Coimbatore, India. GIS provides sophisticated map-generation capabilities, useful in communicating results of data analysis (Burrough and McDonnell, 1998).

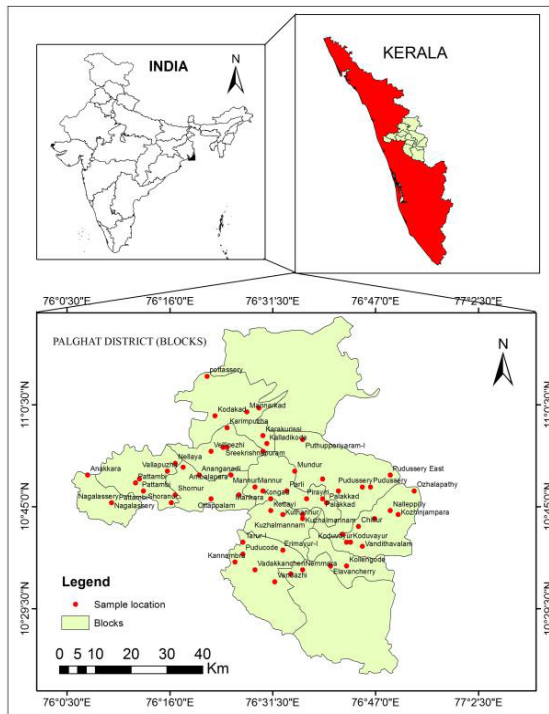
The inverse distance weighted (IDW) method was used interpolating the point hydrogeochemical data to depict the spatial distribution of fluoride abundance in groundwater into different classes (Beg et al., 2011). Cross validation and validation are two common statistical techniques for comparison of models (Philips et al., 1992; Garen et al., 1994; Carroll and Cressie, 1996; Zimmerman et al., 1999). The method controls the significance of known points upon the interpolated values based upon their distance from the output point thereby generating a surface grid as well as thematic isoclines. The main objective of the study is to identify the fluoride contamination in Palghat District using

GIS and to generate IDW maps for identifying the concentration of fluoride in groundwater.

2 Study area

Palghat District is situated in the south west coast of India. The district is bounded on the north by Malappuram District, east by Coimbatore District of TamilNadu, south by Trichur District and west by Trichur and Malappuram Districts. The geographic area of the district is approximately 4,480 sq. km. The district lies between 10°21'02" and 11°14'16" North latitude and 76°02'34" and 76°54'12" East longitude. Most parts of this district fall in the midland region elevation 75–250 m. Palghat District consists of two revenue divisions, five taluks, four municipalities, 163 villages there are 13 block panchayats and 91 grama panchayats in the district. The district receives maximum rainfall during the south west monsoon followed by the north east monsoon. The other months receive considerably less rainfall. The temperature is pleasant from December to February months. Palghat the maximum temperature ranges from 28.1 to 37.4°C whereas the minimum temperature ranges from 22.2 to 25.3°C. Geological formation is from Archaean crystalline hard rock to recent alluvium soft rock. Groundwater occurs in phreatic condition in the laterite, alluvium and weathered crystalline. It is in semi confined to confined condition in the deep fractured rocks (CGWB, 2007). The study area map is shown in Figure 1.

Figure 1 Study area map of Palghat District (see online version for colours)



3 Data used and methodology

3.1 Data used

For the study, the data were collected from the following government sources.

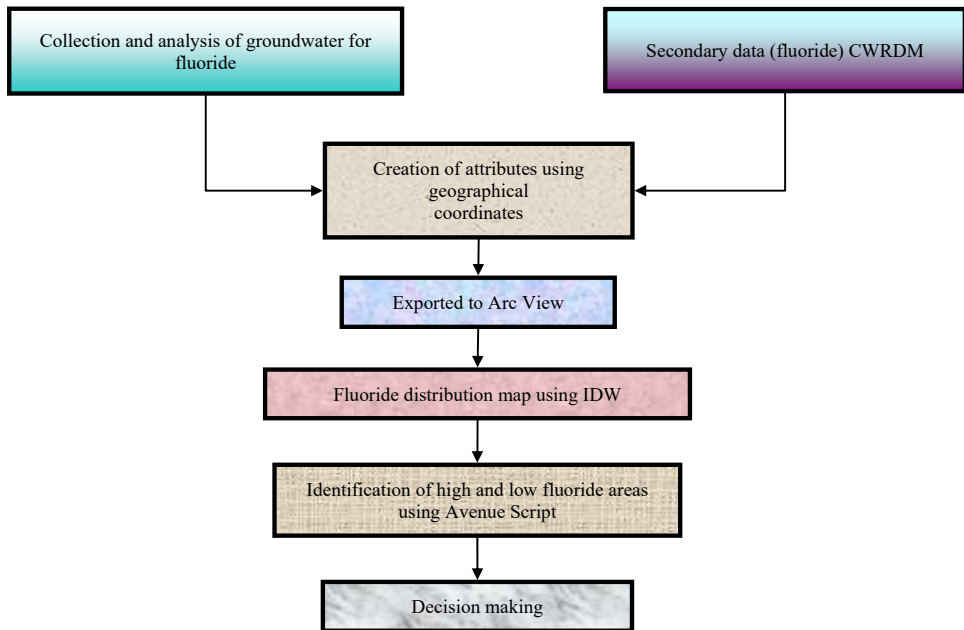
- a Groundwater data: the groundwater quality data were collected from 64 locations from Centre Water Resources Department and Management (CWRDM) (Trivandrum) two seasons in January 2012 and December 2012 respectively. The fluoride values of the 64 locations are not statistically significant between two seasons.
- b Geology map: Geological Survey of India (GSI) (Trivandrum).
- d Toposheets: Survey of India (SOI) Regional office at Bangalore.

3.2 Methodology

3.2.1 Analysis

Randomly collected groundwater samples for fluoride are estimated using calorimetric (SPADNS) method. The sampling technique and the fluoride estimation procedure are given below in detail.

Figure 2 Methodological steps for the distribution and identification of fluoride high and low risk areas in Palghat District (see online version for colours)



3.2.2 *Sampling technique*

In the present study, the groundwater samples from different bore wells were collected in twelve out of thirteen blocks Ottappalam, Thrithala, Sreekrishnapuram, Pattambi, Malampuzha, Palghat, Mannarkkad, Alathur, Nemmara, Chittur, Kollengode, Kuzhalmannam, except Attapadi. In sampling analysis, acid washed polythene cans were used for collection of groundwater samples. Bore wells fitted with motors for water lifting were allowed to run the water for five minutes in order to flush out stationary water. The sample cans were also flushed with several volumes of water before the collection of samples. The sample bottles were closed tightly and labelled. The samples were preserved, cooled and protected from breakage while transporting the bottles to the laboratory. The groundwater samples were refrigerated at 4°C.

3.2.3 *Fluoride estimation using calorimetric method (UV-visible spectrophotometer)*

The suggested methods for the fluoride ion determination are:

- the colorimetric method (SPADNS)
- the ion selective electrode method.

The colorimetric methods are subjected to errors due to the presence of interfering ions. It is necessary to distil the sample before estimating the fluoride. The addition of the prescribed buffer frees the electrode from the interference caused by the common ions such as aluminium, hexametaphosphate and orthophosphate that adversely affect the calorimetric methods simultaneously. The distillation procedure is carried out in the following manner. 400 ml of distilled water was taken in the distillation flask and 200 ml of concentrated sulphuric acid was added to it carefully. The mixture was swirled and homogenised, then 25–30 glass bits were added and then the apparatus was connected. The apparatus was heated slowly at first and rapidly until the temperature of the flask reached exactly 180°C. The distillates were discarded. This process removes the fluoride contamination and adjusts the acid water ratio for subsequent distillations.

After cooling the acid mixture to 120°C or below, 300 ml of collected groundwater sample was added, thoroughly mixed and distilled before the temperature reached 180°C. After the distillation of high fluoride samples flushed with 300 ml of distilled water and then the two fluoride distillates were combined. After the periods of inactivity, the still was flushed and the distillate was discarded. The prepared samples are ready for reading the fluoride concentration. 10 ml of acid zirconyl SPADNS reagent was added to all the samples. The sample was mixed well and then read the optical density of bleached colour at 570 nm using reference solution. 1 ml of sample was added with 10 ml of acid zirconyl-SPADNS reagent, mixed well the solution and percentage transmission or absorbance was recorded. Using the spectrophotometer, the fluoride mg/l was calculated.

3.2.4 GIS analysis

Geographical information system (GIS) is to process spatial information. GIS processing functions of these systems can be broadly grouped into three functional areas, which are computer mapping, spatial database management and cartographic modelling (Chang, 2002). The mapping and data base capability have proved to be the backbone of current GIS application and as a considerable potential for influencing environmental modelling (Tomlin, 1990; Goodchild, 1993). The GIS has subsystems to handle the data, of which three can be considered mandatory viz. data input/data manipulation and analysis, data output and display (Chrisman, 1997).

3.2.5 IDW interpolation method

Interpolation is used to predict unknown values for geographic parameters such as elevation, chemical concentrations and noise levels with a limited number of sampled data points where it is difficult, impossible or expensive to visit every location in the study area (McCoy and Johnson, 2001). Interpolation has primarily been used in mapping of soils, bedrocks, surface and groundwater and air quality studies (Monmoiner, 1982; Schelder et al., 2001). IDW also provides flexibility in performing good and choice interpolation based on the number of samples and their spatial distribution (Salih et al., 2005), where the degree of influence or the weight is expressed by the inverse of the distance between points raised by power, the general equation of the IDW is

$$Z_0 = \frac{\sum_{i=1}^S Z_i \frac{1}{d_i^k}}{\sum_{i=1}^S \frac{1}{d_i^k}}$$

where

Z_0 is the estimated value at point 0

Z_i is the Z value at control point i

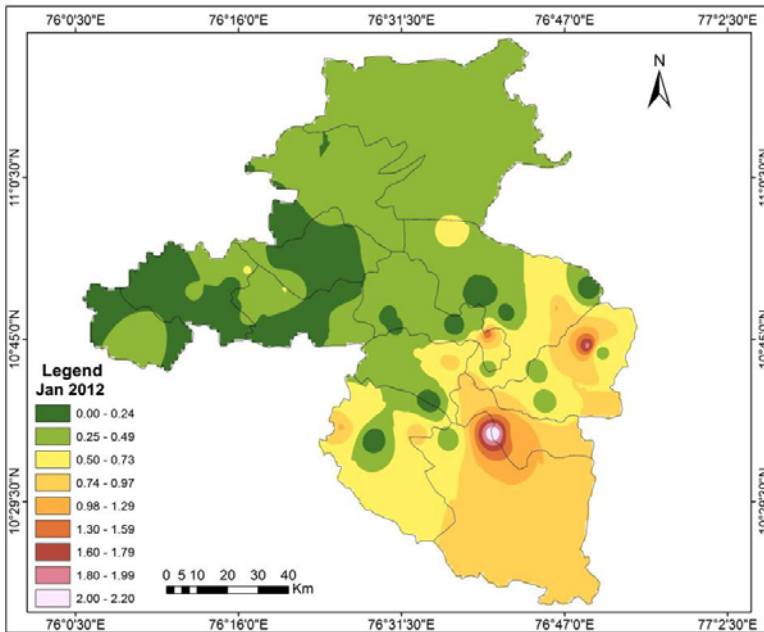
d_i is the distance between control point i and control point 0

S is the number of control point used in estimation

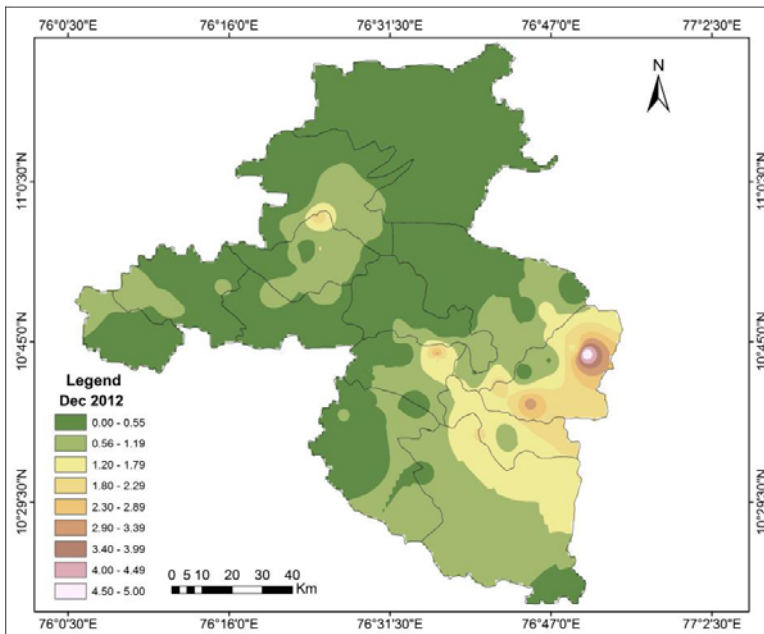
k the specified power.

Using the 64 locations, a groundwater fluoride distribution map was prepared and presented as Map 1 and Map 2.

Map 1 Fluoride contamination of groundwater in IDW method of Palghat District, January 2012 (see online version for colours)



Map 2 Fluoride contamination of groundwater in IDW method of Palghat District, December 2012 (see online version for colours)



4 Results

4.1 Statistical assumptions

a Basic statistical assumptions

The purpose of this study is to assess the relationships among a set of data. The analysis of data provides valid statistical inferences that lead to conclusions about a population of measurements in the case of experimental results based on the information obtained from the population. The result deals with the organisation and summarisation of data by means of 'descriptive statistics'. The remaining part of the results shows GIS analysis and spatial interpolation techniques. The methods will increasingly influence not only the analytical aspects of research but also decision making and problem solving.

Be it starting from scratch with a new database or building on established database, the first steps in determining whether a statistically significant difference has occurred, should be the same. Before choosing the statistical method, an evaluation must be made as to whether the available data meet a few basic assumptions necessary for a particular test to perform with the greatest accuracy and power. Assumptions basic to all methods include independence of samples, determination of the background dataset, sampling frequency and corrections for seasonality. Statistical analysis is based on the assumption that all data points are generated independently of each other. For wells recovering reasonably quickly, it may be possible to collect multiple independent samples in one scheduled event by purging a well and collecting the third independent sample from the well and collecting the second independent sample, etc., until all necessary samples have been collected. Uncertainty a regulated entity proposes this option, it must supply data indicating the rate of the well.

To develop a representative ground water quality database, temporal and seasonal water level variations must be accounted for. In other words, just because there is adequate recharge it does not mean that the complete background dataset may be collected at one sampling event. Generally, the replicate samples are unacceptable for statistical analysis because the information they provide indicate only the accuracy of the laboratory and not the groundwater quality. When more than one sample is collected for the same parameter from the same bailer or same aliquot of groundwater, the samples are considered replicate samples. For all statistical methods, employing the use of pooled background data, the background dataset should be such that it reflects naturally occurring changes in hydro geology.

b Sampling frequency

Minimum sampling frequency shall be consistent with the appropriate statistical method chosen.

c Statistical assumptions that vary with methods

Once the basic assumptions have been met or the dataset has been transformed to meet the basic assumptions, a statistical method may be chosen. The next step in making the choice is to determine the best fit between the site-specific data available

and the specific assumptions that allow each method to perform with the greatest accuracy and power. Assumptions that vary between methods include minimum sample size, determination of distribution, homogeneity of variance, treatment of non-detect parameter levels, and experiment wise and comparison wise errors. Another factor to take into account for each of the following assumptions is, as the site-specific database changes over time, it may be necessary to change to a different statistical method.

d *Determination and distribution*

Based on the above assumptions and the basic statistical methods, the groundwater quality data of Palghat District was analysed. The permissible limits of fluoride in drinking water by various organisations are given in Table 1.

Table 1 Permissible limit of fluoride in WHO and BIS value

<i>Name of the organisations</i>	<i>Permissible limit of fluoride (mg/l)</i>
World Health Organization (WHO) international standards for drinking water	1.5
Bureau of Indian Standards (BIS)	1.0
The committee on Public Health Engineering (PHE), Govt. of India	1.0
Indian Council of Medical Research (ICMR), Govt. of India	1.0

4.1.1 Summary statistics of fluoride in Palghat District

An important aspect of statistical inference is estimating population values i.e. parameters from a sample data. The statistical inference is usually discussed as two separate but related sets of procedures and hypothesis testing estimation. The former allows making simple decisions about a population based on data of the sample. Estimation of population value addresses the question of magnitude or the extent of the effect. Both of these approaches are important parts of statistical inference and both are applied in the study to describe the status of fluoride content in the groundwater of Palghat District. The summary statistics of the fluoride concentration are compiled in Table 2.

The overall mean fluoride value has been observed in groundwater of the Palghat District in January (0.50 mg/l), which is less than the means of Chittur (0.69 mg/l), Kollengode (1.65 mg/l), Kuzhalmannam (0.61mg/l), and Nemmara (0.58 mg/l) and greater than in Alathur, Malampuzha, Mannarkkad, Ottapalam, Palghat, Pattambi, Sreekrishnapuram and Thrithala blocks. The overall mean fluoride value has been observed in December (0.68 mg/l), which is less than the mean value of Alathur, Malampuzha, Mannarkkad, Nernmara, Ottapalam, Palghat, Pattambi, Thrithala blocks and greater than Chittur, Kollengode, Kuzhalmannam and Sreekrishnapuram blocks. The skewness and kurtosis values support the normality and hence it is decided that there is no need for any data transformation.

Table 2 Block wise mean fluoride concentration in Palghat district with descriptive statistics for the month of January and December (n = 64)

Block name	N	Range		Minimum		Maximum		Sum		Mean		Std. dev		Variance		Skewness		Kurtosis	
		Jan	Dec	Jan	Dec	Jan	Dec	Jan	Dec	Jan	Dec	Jan	Dec	Jan	Dec	Jan	Dec	Jan	Dec
Alathur	6	1.00	0.75	0.00	0.00	1.00	0.75	3.00	2.50	0.43	0.42	0.42	0.27	0.17	0.07	0.24	-0.53	-1.95	-0.02
Chittur	9	1.54	4.80	0.26	0.20	1.80	5.00	6.21	15.00	0.69	1.67	0.69	1.52	0.25	2.31	1.45	1.51	2.34	2.24
Kollengode	2	1.10	0.95	1.10	0.80	2.20	1.75	3.30	2.55	1.65	1.28	0.78	0.67	0.61	0.45	0	0	0	0
Kuzhalmannam	4	0.57	2.75	0.43	0.25	1.00	3.00	2.43	5.25	0.61	1.31	0.26	1.18	0.07	1.39	1.90	1.44	3.72	2.71
Malampuzha	5	1.00	1.50	0.00	0.00	1.00	1.50	2.25	2.75	0.38	0.55	0.40	0.67	0.16	0.45	0.74	0.86	-0.75	-1.53
Manmarkad	6	0.75	1.00	0.25	0.00	1.00	1.00	2.46	1.60	0.41	0.27	0.30	0.43	0.09	0.19	2.08	1.32	4.31	0.21
Nemmara	2	0.60	0.55	0.30	0.20	0.90	0.75	1.20	0.95	0.58	0.48	0.40	0.39	0.16	0.15	0	0	0	0
Ottappalam	6	0.00	0.90	0.00	0.00	0.00	0.90	1.00	2.23	0.20	0.37	0.22	0.37	0.05	0.14	0.56	0.44	-1.80	-1.61
Palghat	9	1.50	1.00	0.00	0.00	1.50	1.00	3.16	2.20	0.35	0.24	0.44	0.33	0.19	0.11	2.73	1.72	7.92	3.10
Pattambi	8	1.00	1.10	0.00	0.00	1.00	1.10	2.00	2.55	0.22	0.32	0.17	0.40	0.03	0.16	0.69	1.28	0.34	0.92
Sreekrishnapuram	5	0.41	2.00	0.00	0.00	0.41	2.00	0.86	4.35	0.17	0.87	0.21	0.77	0.05	0.60	0.57	0.70	-3.28	-0.12
Thirithala	2	0.31	0.80	0.10	0.00	0.41	0.80	0.51	0.80	0.26	0.40	0.22	0.57	0.05	0.32	0	0	0	0
Overall	5.3	0.82	1.51	0.20	0.12	1.02	1.63	2.37	3.56	0.50	0.68	0.36	0.63	0.16	0.53	1.10	0.87	1.09	0.59

The fluoride range of the district is 0.82 for January and 1.51 for December, which implies that the distribution of fluoride in groundwater is spatially not uniform. The block wise range values also varied in January 0–1.54 and in December 0.55–4.80, which again supports above observations that fluoride content in groundwater is not even. From these results, it is inferred that a uniform strategy cannot be applied to remove the groundwater for drinking/agricultural purposes, for which a better analysis tool is necessary for decision makers.

The Central Ground Water Board (CGWB) has reported the ground water fluctuation level in Palghat District. Ground water level has been measured in April and November. In Palghat District, the maximum of the blocks showing the groundwater level in the range of depth is 5–10 m (hilly areas were present in Nemmara, Attappady and Mannarkkad blocks) and limited areas were present the range of 2–6 m in Kuzhalmannam and Palghat blocks. For this study, most of the blocks in Palghat District show increased ground water level in November and December by ground water fluctuation of 2–5 m depth level. In November, the groundwater level was within 2 m in Kollengode, Palghat, Pattambi, and Mannarkkad blocks by increasing water table. For this study, fluoride levels change by this month and less fluoride was present in January in study area.

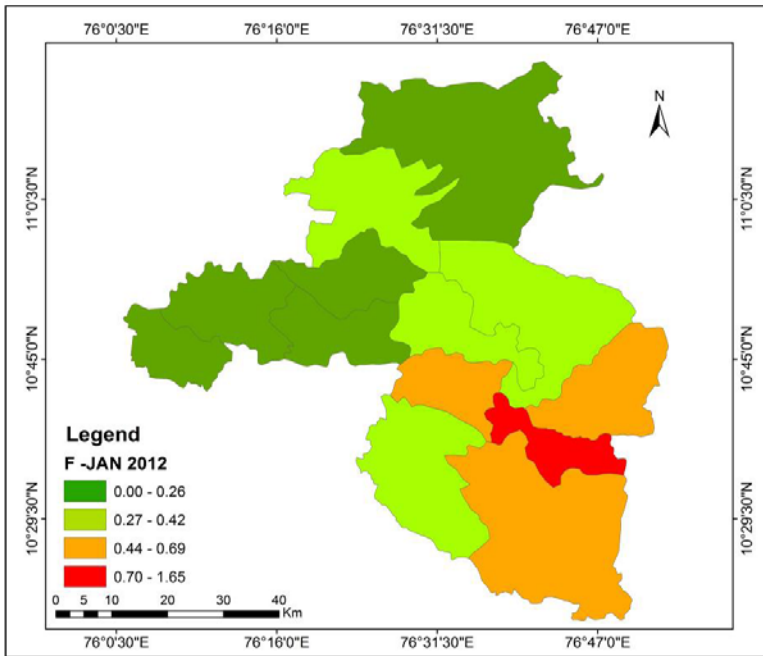
In December, fluoride level of ground water increased more than in January. The ground water table is related to fluoride contamination. Fluoride level changes by changing ground water table in an area and rain water is major influencing factor of ground water. In 2012, rainfall was greater than 2011 according to the report of the Indian meteorological department (IMD). Accordingly, year 2012 ground water table was increased by the monsoon.

4.1.2 Inverse distance weighted interpolation

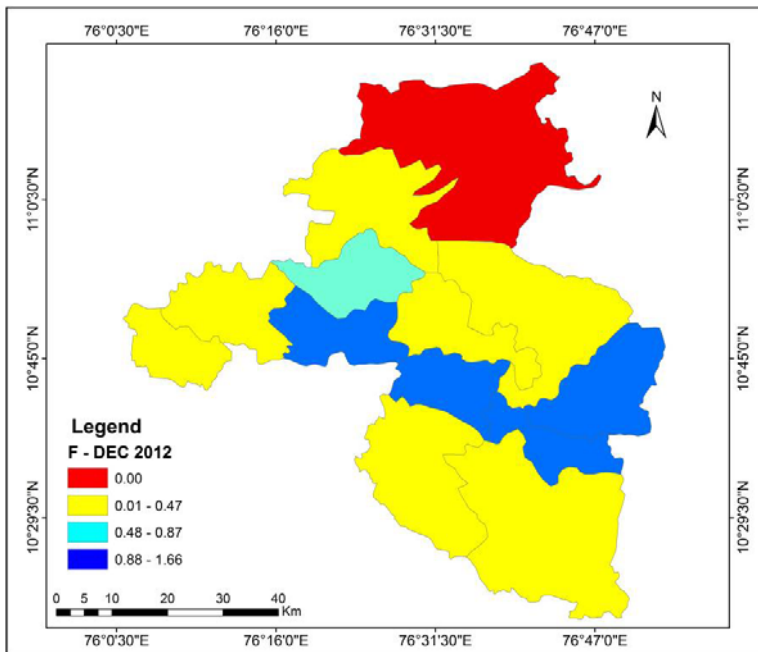
For this study, two blocks studied were the highly affected areas Kozhinjampara and Chittur. The blocks have similar geographical area and similar rock type. The water in the western part of the area is not suitable for drinking purposes. The fluoride level in the water sample has less than permissible limit. Better quality of water was present in Mannarkkad, Sreekrishnapuram, Pattambi, Nemmara, and Alathur blocks. In January, the groundwater samples were observed within the permissible limit. High fluoride contamination was found in Elevanchery area of Kollengode block. The geological area contained fluoride bearing rocks such as granitic, hornblende, biotite, and gneiss. Fluoride level affected very few areas as shown in Maps 1 and 2.

Fluoride distribution map concise the better to understand the spatial interpolation techniques. The resultant map was reclassified in January as four classes, i.e., very low (0–0.25 mg/l), low (0.25–0.42 mg/l), moderate (0.42–0.69 mg/l) and high (0.69–1.65 mg/l) which is presented as Map 3; in December three classes viz., low (0–0.47 mg/l), moderate (0.47–0.87 mg/l) and high (0.87–1.86 mg/l) are presented as Map 4. The map depicts the high fluoride risk areas where the water is not recommended for human consumption.

Map 3 Classification of fluoride level in groundwater of Palghat District, January 2012 (see online version for colours)



Map 4 Classification of fluoride level in groundwater of Palghat District, December 2012 (see online version for colours)



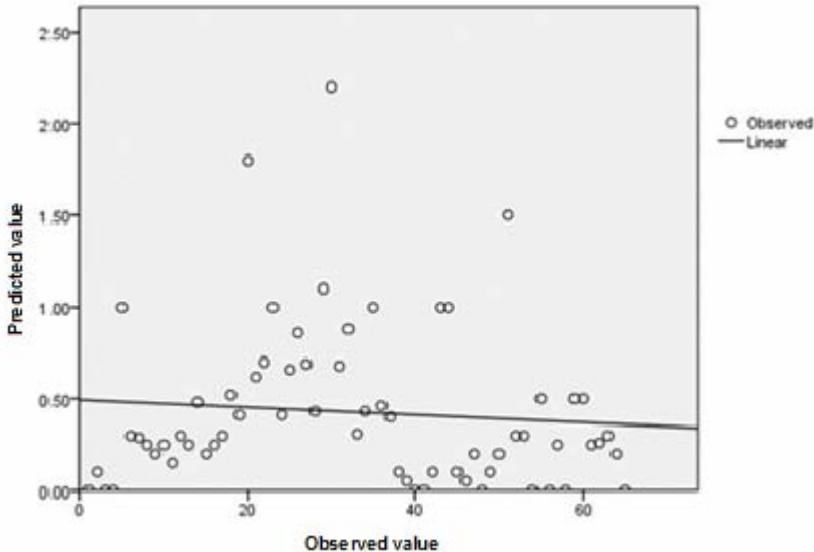
Map 3 shows that in January fluoride contamination in higher concentration (>0.69 mg/l) is observed in Kollengode block. Moderate concentration of fluoride was observed in Chittur, Kuzhalmanam and Nemmara blocks. The low concentration of fluoride was present in Alathur, Mannarkad, Malampuzha and Palghat blocks. The very low areas were Ottapalam, Pattambi, Sreekrishnapuram and Thritala blocks.

Map 4 shows that in December fluoride contamination is present in higher concentration (>0.87 mg/l) and observed in Chittur, Ottapalam, Kollengode and Kuzhalmanam blocks. Moderate concentration of fluoride was observed in Sreekrishnapuram block. The low concentration of fluoride was observed in Alathur, Mannarkad, Malampuzha, Nemmara Palakkad, Pattambi and Thritala blocks. The result shows that the fluoride is not evenly distributed in Palghat District.

4.1.3 Validation test

Cross validation was made, after the IDW interpolation of fluoride concentration in the district. In order to check the precision of the interpolation done, the fluoride values of nearly 20 locations were taken randomly in the district. In the validation technique values were selected randomly and the IDW predicted values (20) of fluoride are compared with the observed values of fluoride in the ground water of the Palghat District. Cross validation compares the interpolation methods by fluoride value of the known point is removed from the dataset and unknown fluoride value of the point is estimated using the remaining points. Using the Statistical Package for the Social Science (SPSS), the predicted error values are calculated by comparison with the observed values. The resultant figure shows that (regression) $R = 0.088$, $R^2 = 0.008$ and the standard error is 0.046 as shown in Figure 3.

Figure 3 Observed vs. predicted value of fluoride in Palghat District

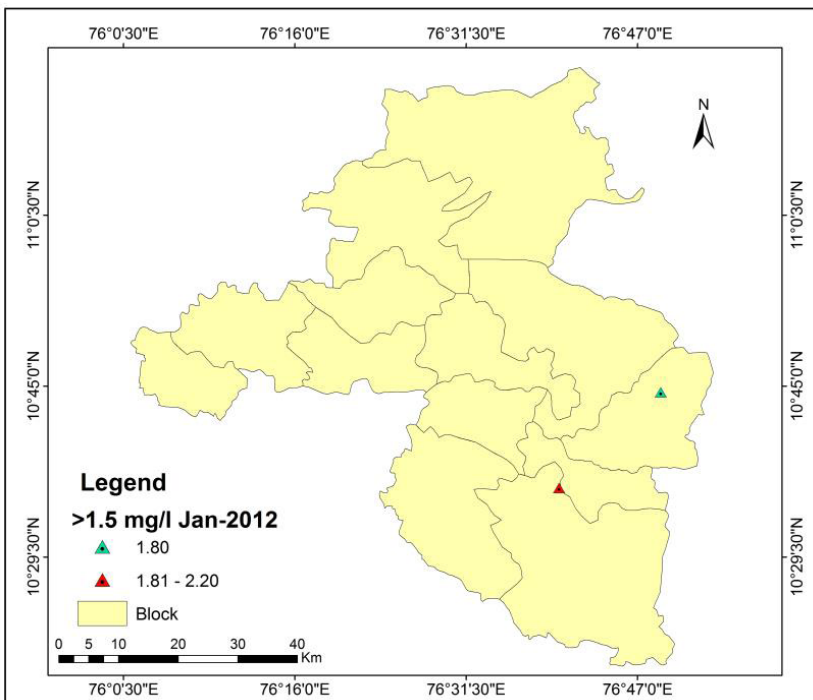


The existing Avenue Script extension tool developed is capable of facilitating the spatial and non-spatial information in multi-constraint query. The attribute table can be used to raise a query by the decision makers or administrators. This tool can be extended to new attributes and new areas. In Avenue a new menu was developed as ‘groundwater’ with query and interpolation functions (Map 1, Map 2 and Figure 1). Using the query function the areas that exceeded the WHO limits were identified. Along with this a new icon was created in Arc view window for easy display of the fluoride values and named as ‘WHO greater and WHO lesser’ in Arc View using the Avenue Script for decision making. The icon created for fluoride will reduce the process timing, and speeds up the decision making for the planners.

4.1.4 Mapping of areas exceeding WHO limits

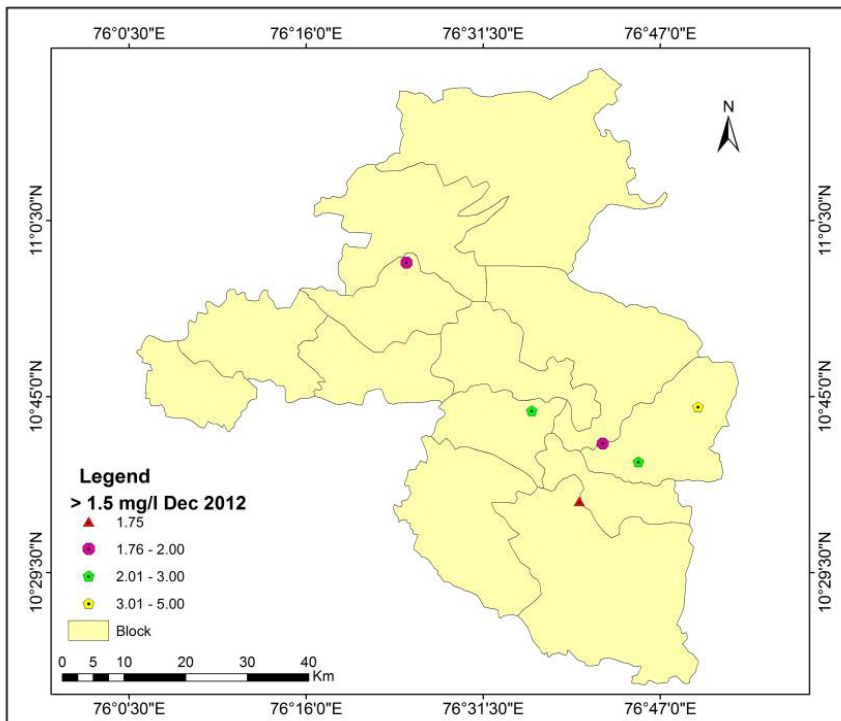
The high risk of fluoride contamination is present in the eastern part of the district and is considered as the rain shadow region. These areas have a small amount of rainfall compared to the other districts in Kerala. Chittur and Attappady blocks have black cotton soil and formed due to the low rainfall. These regions contain foliated granite rock. Compared to January 2012, fluoride is less abundant in December. In December fluoride is high in Chittur block. Kollengode, Sreekrishnapuram and Kuzhalmannam blocks had high fluoride concentrations (up to 5 mg/l) as shown in Map 5 and Map 6.

Map 5 The location of greater than (1.5 mg/l) WHO limit Palghat District, January 2012 (see online version for colours)



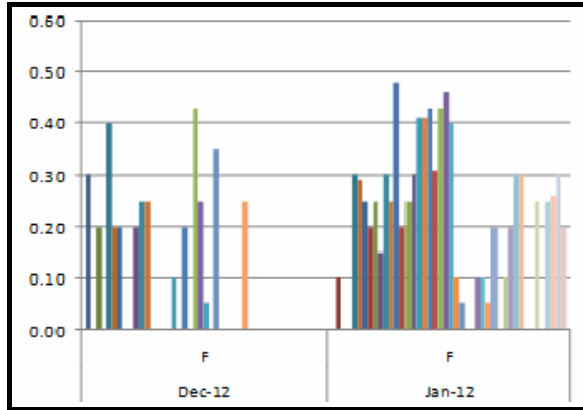
In January and December, 33.5% of groundwater was observed within the range and is fit for drinking purposes. The remaining of 59.3% of groundwater samples had fluoride below the range of 0.6 mg/l and is unfit for drinking purposes. Two samples from January 2012 and six samples from December 2012 were observed to have very high concentration of fluoride, i.e., above 1.5 mg/l in WHO limit. Thus, on the whole, 11% of samples of groundwater had more than 1.5 mg/l of fluoride. It was found that the concentration of fluoride in 76.5% of 64 groundwater samples did not fall within the desirable range of 0.6 to 1.5 mg/l. In general, it is found that the fluoride concentration in groundwater increases with geomorphology and groundwater fluctuation.

Map 6 The location of greater than (1.5 mg/l) WHO limit Palghat District, December 2012 (see online version for colours)



In the present study, the rainfall level was increased by south western and north eastern monsoon in 2012 and the fluctuation of ground water affected by fluoride contamination. Geological survey studies show occurrence of fluoride is affected by climate conditions, rock type, hydrogeological strata and contact time between rocks and circulating water. In December, high fluoride levels increased the amount of bicarbonate, pH, EC and TDS as shown in Figure 4.

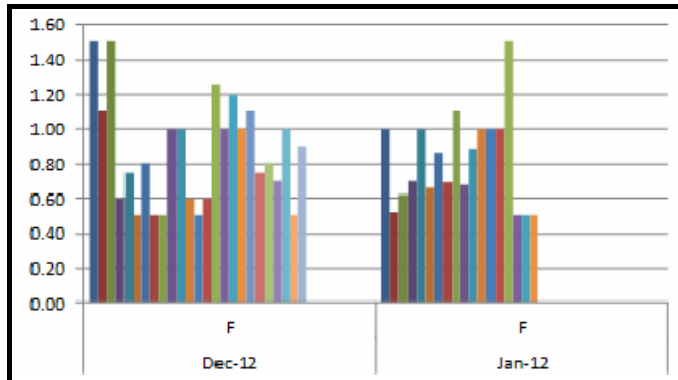
Figure 4 Fluoride level greater than WHO permissible limit (<0.5) (see online version for colours)



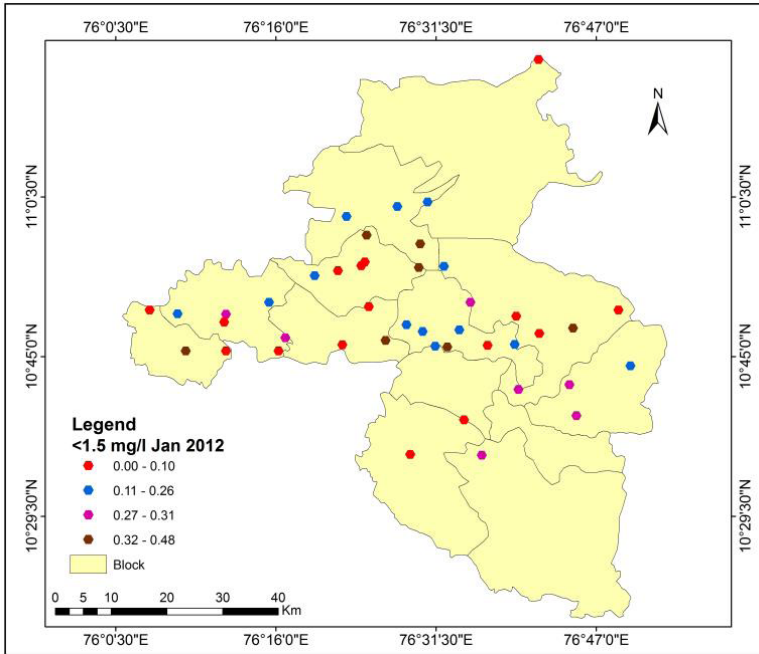
4.1.5 Mapping of areas less than WHO limits

The lower amount of fluoride was found in January 2012 and 44 out of 64 samples were less than the WHO less permissible limit. For this study, 30 locations showed very low quantity of fluoride observed (0.00–0.25) in western part of the district. In groundwater, pH values varied from 7.1–8.5. In December, 32 out of 64 samples had less than the WHO permissible limit and the pH ranged from 7.5–9. The comparison of Maps 7 and 8 shows pH, EC, alkalinity and TDS slightly increased in December. Hence pH is directly proportional to the fluoride level in the sample area. The January (68%) and December (50%) samples were found to be below the permissible limit of WHO as shown in Figure 5.

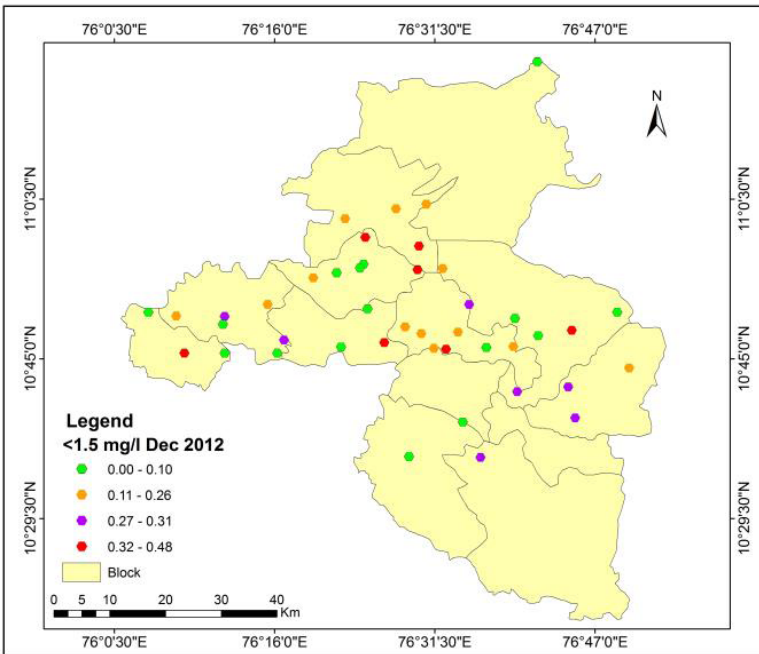
Figure 5 Fluoride level less than WHO permissible limit (>1.5) (see online version for colours)



Map 7 The locations of less than (1.5 mg/l) WHO limit, January 2012 (see online version for colours)



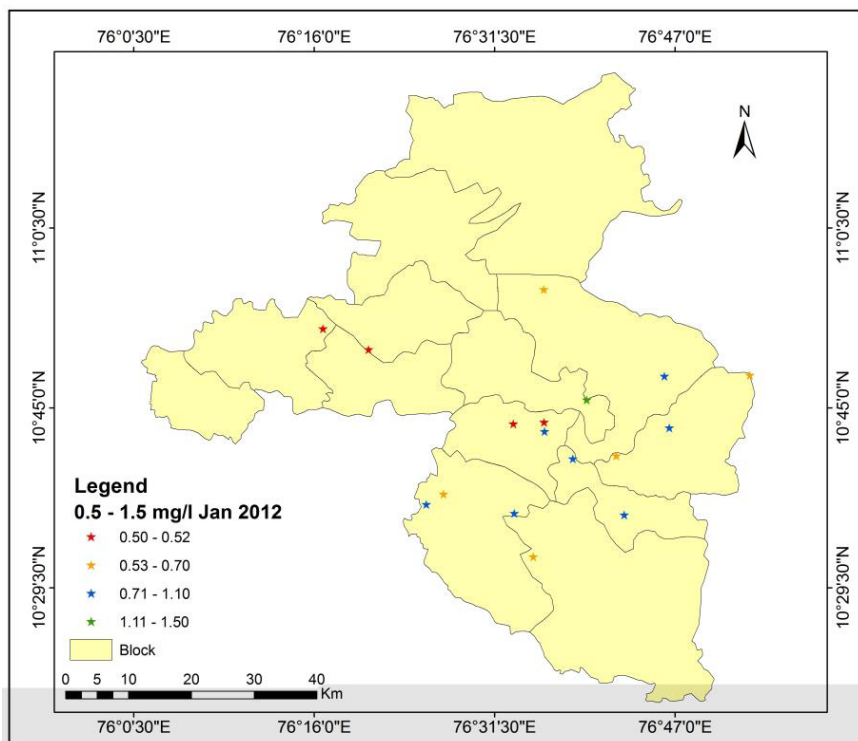
Map 8 The location of less than (1.5 mg/l) WHO limit, December 2012 (see online version for colours)



4.1.6 Mapping of areas within WHO limits

According to WHO, permissible limit of fluoride level is essential for the teeth and it prevents dental decay. In January, 17 samples were present in the district within the permissible limit, i.e., 26% of samples have the fluoride value between 0.5–1.5 in north central part of the district. The pH range is 7.5–8.5 and moderate levels of Ca and Mg were found in the groundwater sample. The amount of EC was within the WHO limit and the high amount of bicarbonate was present in the range of high fluoride. In December 26 out of 64 samples were within the permissible limits in the Chittur and Alathur blocks (Maps 9 and 10). The pH, EC and TDS were observed closed to the WHO limit and there was no significant variation of Ca and Mg in Chittur and Alathur blocks as shown in Figure 6.

Map 9 The WHO permissible limit of fluoride level in groundwater (0.5–1.5 mg/l) January 2012 (see online version for colours)



Map 10 The WHO permissible limit of fluoride in level groundwater (0.5–1.5 mg/l), December 2012 (see online version for colours)

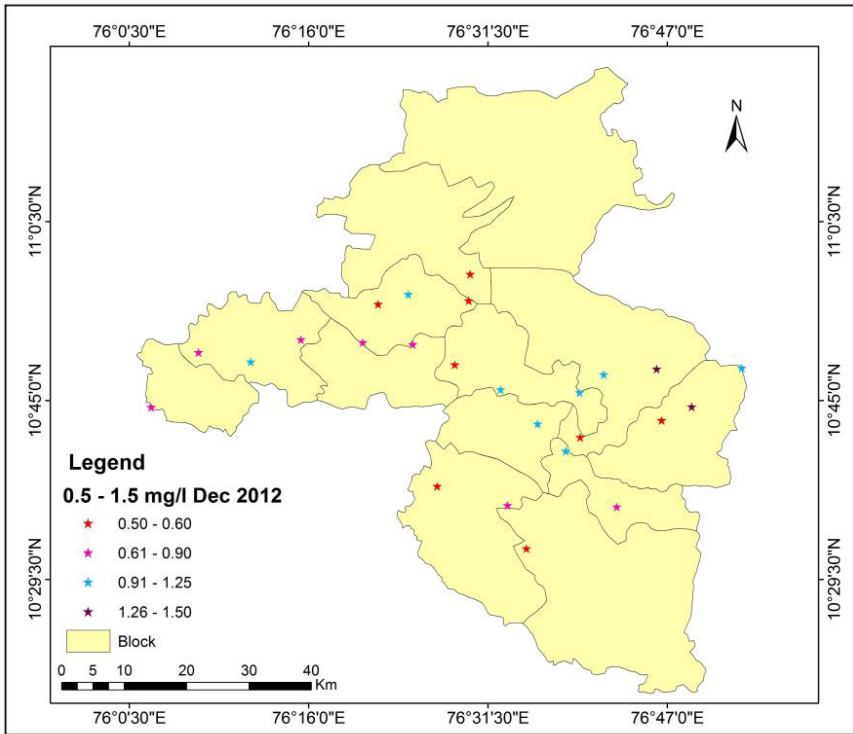
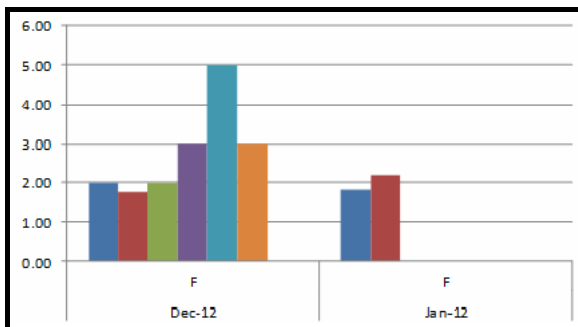


Figure 6 Fluoride level within the WHO permissible limit (0.5–1.5) (see online version for colours)



5 Conclusions

The present study has been undertaken to assess the spatial distribution of fluoride in groundwater of Palghat District and to suggest suitable methods to manage the fluoride content in groundwater using GIS. Fluoride occurs in sellaite, fluorite, cryolite, fluorapatite, apatite, fluormica, biotite, amphibole and several other rocks. Weathering of

these rocks and prolonged residence time leads to high fluoride content in groundwater. Low calcium, high sodium and high bicarbonate are typical of high fluoride groundwater.

It is well known that trace elements are essential and beneficial to human health in minute concentrations, as they play an important role in many metabolic processes and act as co-factors. However, exceeding their permissible intake is known to be toxic and has adverse effects on general body metabolism. One such trace element, which is ubiquitously distributed in soil, earth and water, is fluoride. Low amount of fluoride (0.3–1.0 mg/l) in drinking water is helpful in prevention of dental caries and in treatment of osteoporosis. However, high intake of fluoride (>1.5 mg/l) in drinking water can cause damage (teeth enamel and eventually leads to skeletal) complications in fluorosis. For this study, 11% samples were found exceeding permissible limit. Out of 11% of the groundwater samples 85% were in the north-eastern part of the district in Chittur block.

Fluoride drinking water might help to prevent tooth decay if the level of fluoride intake is within the permissible range of 0.5 to 1.5 mg/l. Consumption in excess of 1.5 mg/l over long periods of time can produce severe effects on human health such as dental and skeletal fluorosis, osteoporosis, hip fracture, arthritis, mental retardation and premature death. Intake of lower concentration of fluoride (<0.5 mg/l) may cause dental caries and neurological effects.

It is interesting to note that increase of alkalinity is due to the increase of carbonate and bicarbonate ions, although these ions have no direct influence on pH level. Hence, the increase of alkalinity does not increase the pH observed when high fluoride groundwater is associated with high sodium-bicarbonate-iron affinity with elevated pH values (i.e., >7.0) and relatively low magnesium. High concentration of fluoride is due to temperature, pH, and solubility of fluoride bearing minerals, ion exchange capacity of aquifer materials (OH- and halogens), and the geological formations drained by water and accordingly the contact time of water with a particular formation.

The fluoride concentration in groundwater of this area varied between 0.00 and 5 mg/l. The desirable range of fluoride concentration in drinking water is from 0.6 to 1.2 mg/l according to the Indian standard specifications (BIS). Thus, if the concentration of fluoride is below 0.6 or above 1.2 mg/l, the water is not suitable for drinking purposes. However, it is suggested that the maximum limit can be extended up to 1.5 mg/l (BIS). Based on the concentration of fluoride, the groundwater samples obtained from the study area have been classified into four groups as low (0.1 to 0.6 mg/l), medium (0.6 to 1.5 mg/l), high (1.5 to 3 mg/l), and very high (3 mg/l) as shown in Table 1.

In all the two months of sampling, 33.5.5% of the samples were within the range and thus fit for drinking purpose. Of the rest of the groundwater samples, 59.3% had fluoride below 0.6 mg/l; hence, it is unfit for drinking purpose. Two samples from January 2012 and six samples from December 2012 had very high concentration of fluoride, i.e., above the 1.5 mg/l WHO limit. Thus, on the whole, 11% of samples of groundwater had more than 1.5 mg/l of fluoride. It was found that the concentration of fluoride in 76.5% of the total 64 groundwater samples did not fall within the desirable range of 0.6 to 1.5 mg/l of fluoride. In general, it is found that the fluoride concentration in groundwater increases with geomorphology and groundwater fluctuation.

Fluoride in groundwater of Palghat District is mainly due to dissolution from fluoride bearing minerals like fluorspar, fluorite, etc. In this 11% samples were found exceeding permissible limit. A total of 11% samples had 85% fluoride contamination in Chittur

block. That is north-eastern part of the district. In this study area, local people ingesting the groundwater have not received medical attention although they are dependent on the groundwater for domestic use. So, remedial measures such as defluoridation techniques and rainwater harvesting are needed. A nutritional diet such as calcium and phosphorus rich food should be recommended to those affected with fluorosis as it decreases the rate of accumulation of fluoride in the human body. A government attention is very necessary.

Palghat District is in a bad position owing to depletion of groundwater sources and increased risk of fluoride contamination. There are modern and efficient technological tools to identify contamination sources and innovative, cost effective removal suggestions. Therefore, this study was initiated to identify the fluoride high and low risk areas, and the source of groundwater contamination by fluoride. Owing to such health hazards, several methods for the removal of fluoride from groundwater have been described, generally termed as defluoridation. However, the adaptations of such methods are expensive, time consuming and have to be extended to large areas. This result is practical information which may be used by decision makers and water conversationalists. This view is suitable for other areas and related problems and hence can be adopted by planners and managers for decision making.

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