ORIGINAL ARTICLE

Appraisal of groundwater quality in upper Manimuktha sub basin, Vellar river, Tamil Nadu, India by using Water Quality Index (WQI) and multivariate statistical techniques

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Abstract

Groundwater is a major natural resource for drinking and irrigation purpose. The overexploited of groundwater is increase year by year and quality of groundwater simultaneously decreases. Groundwater quality is the main issue because water is linked with our metabolism. In order to know the groundwater pollution and controlling factors of groundwater quality in the upper Manimuktha sub basin, Vellar river, Tamil Nadu, India. Forty eight groundwater samples were collected from entire study area on January 2014 and analysed for physicochemical properties. Major ions were as abundance of $Na > Ca > Mg > K$, and $HCO₃ > Cl > SO₄ > NO₃$ respectively. Multivariate statistical analyses display the good correlation between all the physicochemical parameters except pH and F. The dendrogram reveals cluster 3 (EC and TDS), cluster 2 (alkalinity, TH, HCO₃) and cluster 1 (F, K, NO₃, Ca, Mg, Na, SO₄, Cl). The hydrochemical processes reveal rock-weathering interactions and ion-exchange processes play an important role in groundwater quality of the study area. The WQI indicates 50.03% of the samples fall in excellent to good for drinking in the center of the study area. Remaining samples fall poor to very poor categories, signifying northern and southern side mainly polluted. Maximum of lakes located in the northern side also indicate poor quality, because of the contamination of wastewater at or near the lakes, migrate in the groundwater. This study has shown the great combination of GIS, statistical analysis and WQI in assessing groundwater quality give a clear view for decision makers can plan better for the operation and maintenance of groundwater resources.

Keywords Dendrogram · Groundwater pollution · Ion exchange process · Statistical analyses · WQI

Introduction

Groundwater is the first source of water for human consumption, as well as for agriculture, drinking and industrial uses (Jalali [2009;](#page-13-0) Mokarram [2016\)](#page-14-0). Groundwater is limited and also overexploited for various purposes. However, river water is insufficient to meet the ever increasing demand of the cities. This scarcity of water has increased the overexploitation of groundwater. Groundwater serves as major and natural source of water for domestic and agricultural purposes in many cities (Mondal et al. [2010](#page-14-1); Kumar [2016\)](#page-14-2). In the arid and semi arid regions groundwater is main resources for drinking, irrigation and domestic purposes.

 \boxtimes S. Deepa deepaearthscience@gmail.com The overexploitation leads to decrease of quantity and quality in groundwater. The quality of groundwater is mainly depending on the physicochemical characteristics of the groundwater. In India tremendous variation of the utilization of lands, from place to place and without strict environmental norms, causing a lot of variation in quality of groundwater within a short distance, which constrains the developmental activities drastically everywhere (Kumar et al. [2015](#page-14-3)). The contamination of the surface also related with increase in population, urbanization and industrialization has those tapping water from shallow unconfined aquifers (Amadi [2011;](#page-13-1) Oluseyi et al. [2011;](#page-14-4) Sadat-Noori et al. [2014\)](#page-14-5). The most common source of groundwater pollutions are the discharge of sewage, industrial and agricultural waste, both organic and inorganic, mining, fertilizers and pesticides washed off the land by rain (Nwajei et al. [2012](#page-14-6); Boateng et al. [2016](#page-13-2)). Several researchers have proposed different methods of analyzing water quality data depending on the purpose, samples types and the size of the sampling area (Alobaidy

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et al. [2010](#page-13-3); Venkateswaran and Kannan [2015](#page-15-0); Arulbalaji and Gurugnanam [2016;](#page-13-4) Pradeep et al. [2016](#page-14-7); Saravanan et al. [2016;](#page-14-8) Ehteshami et al. [2016;](#page-13-5) Yazdanpanah [2016\)](#page-15-1). The direct dumping of human wastes into water bodies (Singh et al. [2008](#page-14-9)) is a major direct effect to contaminate the water with a direct way. Water pollution not only affects water quality but also threats human health, economic development, and social prosperity (Milovanovic [2007](#page-14-10)). This the main reason to detailed study about groundwater quality of every place and as well as in the study area.

Numerous publications have reported that urban development and agricultural activities directly or indirectly affect the groundwater quality (Fantong et al. [2009;](#page-13-6) Ramkumar et al. [2011;](#page-14-11) Kim et al. [2012](#page-14-12); Gnanachandrasamy et al. [2012,](#page-13-7) [2015;](#page-13-8) Venkateswaran and Deepa [2015;](#page-15-2) Gopinath et al. [2016](#page-13-9); Saravanan et al. [2016](#page-14-8)). One important study that give appropriate knowledge about quality of groundwater that is water quality index (WQI) for assessing groundwater quality and its suitability for drinking purposes (Vasanthavigar et al. [2010](#page-15-3); Gibrilla et al. [2011;](#page-13-10) Jasmin and Mallikarjuna [2014](#page-14-13); Sadat-Noori et al. [2014;](#page-14-5) Boateng et al. [2016](#page-13-2)). Another one type studies that various geostatistical concepts are used for the interpretation of complex data sets which give a better perceptive of the water quality (Srinivasamoorthy et al. [2011](#page-15-4)). The maps gives better view of maximum details of a studies in a work this is possible with GIS environment (Gnanachandrasamy et al. [2012](#page-13-7)). The Manimuktha sub basin one of the main sub basin at Villupuram district. Surface water sources are normally uneven to get their supply during nonmonsoon seasons in the study area. Therefore in the study area peoples mainly depends on groundwater for their drinking as well as irrigation activities (Prakash and Venkateswaran [2014](#page-14-14)). So a proper test to need assess the groundwater quality and WQI of a local body is vital to establish a continuing record for possible water remediation.

The aim of this paper was to utilize the WQI model and geostatistical techniques for assessment of water quality. As well as in regulate to purpose of connection among every groundwater aspects used the correlation analysis in study area.

Description of the upper Manimuktha sub basin

Manimuktha sub basin one of the main tributaries of Vellar river originates from Kalrayan hills in Villupuram district, traverses about 111 km (69 mi) and joins Vellar near Srimushnam in Chidambaram taluk of Cuddalore District. It lies between 78°42′ to 78°59′E longitude and 11°42′ to 11°59′N latitude covering the total area of 497.11 km^2 in which hilly area occupies 187.19 km². Western side the study area covered by Kalvarayan hills (Fig. [1](#page-2-0)) which divide the Salem and Villupuram districts are seen to the extreme west of Kallakurichi taluk. The average annual rainfall of the

study area is 1115 mm bring the groundwater recharge in the area. The study area chiefly consists of hard crystalline rocks of archean age. The flow of water in the river is reduced during the period from February to June, and as a result, in the region depends on groundwater for their use. A major part of the study area covered in the agricultural activities, where sugarcane, paddy, and groundnut are being cultivated.

Geology and Hydrogeology

Upper Manimuktha sub basin comprises the precambrian peninsular gneiss and its retrograded products (Kumar et al. [2009](#page-14-15)) the area mainly underlain by chornockites, fissile hornblende gneiss, hornblende biotite gneiss, and ultrabasic rocks (Deepa et al. [2016\)](#page-13-11). Drainage mainly consisting of dendritic, sub dendritic and radial in nature. 13 kinds of geomorphological features are noticed in the study area, the catchment area covered by ridge type structural hills in the western side and followed by pediplains, lies along the river course side. Some of area spread by inselberg, pediment canal command, water body masks, linear ridge dykes and upper piedmont slope. Weathering is highly erratic and the depth of abstraction structures is controlled by the intensity of weathering and fracturing. The depth of wells varies from 6.64 to 17 m bgl and water levels in observation wells tapping shallow aquifers varied from 0.74 to 9.7 m bgl during premonsoon (2006–2015) and it varies from 0.7 to 4.45 m bgl during postmonsoon (2006–2015). During premonsoon season, the water levels range of > 2 to 5 m bgl in major part of the district, in the range of > 5 –10 m bgl in western and southeastern parts of the district (CGWB 2009).

Materials and methods

Groundwater sample collections and analysis

The base map of the study area was prepared using Survey of India topographic sheets (58E 9 and 13) having a scale of 1:50,000 and digitized using ArcGIS 9.3 software. Forty eight groundwater samples were collected during the January 2014. Figure [1](#page-2-0) shows the locations of the groundwater samples.

The collection, preservation and chemical analysis for major ions of water samples were made following the standard methods are given by the American Public Health Association (APHA [1998\)](#page-13-12). The ionic constituents Ca, Mg, Na, K, Cl, HCO_3 , NO_3 , F and SO_4 and the non-ionic constituents pH, electrical conductivity (EC) and total dissolved solids (TDS) were determined for this groundwater in the study area.The detailed methodology shown in Fig. [2](#page-2-1).

Before analyzing the data, the degree of chemical accuracy was identified as ion balance error or reaction error

Fig. 1 Base map of the Upper Manimuktha sub basin

(RE). The analytical precision for ions was determined by the ionic balances calculated as Eq. [1](#page-3-0).

$$
RE = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum (\text{Cations} + \text{Anions})} \times 100. \tag{1}
$$

RE value greater than 5% would indicate that the accuracy of data is questionable (Metcalf and Eddy [2003](#page-14-16); Freeze and Cherry [1979](#page-13-13)). If RE is in permissive extent, Shapiro–Wilk test should be used to check the normality of data distribution (Shapiro and Wilk 1965). Figure [3](#page-3-1) shows graph of the total sum of cations vs the total sum of anions. The quality of the analysis was documentation by standardization using blank, spike, and duplicate samples. Statistical measures such as minimum, maximum, average, and standard deviation are given in Table [1](#page-3-2).

GIS analysis

Spatial Analyst extension (an extended module of ArcGIS 9.3) was used to interpolate the spatial distribution of the WQI map. Inverse distance weighted (IDW) interpolation technique was used to create different thematic layers. IDW is an algorithm used to interpolate data spatially or estimate values between measurements. Weights are computed by taking the inverse of the distance from observations location to the location of the point being estimated (Burrough and Donnell [1998](#page-13-0)).

WQI model

WQI is a technique that provides the combination of every individual water quality parameters on the overall quality of

Table 1 Statistical measures such as maximum, minimum, average and standard deviation

| Parameter | Unit | | Minimum Maximum Mean | | Std. deviation |
|------------------|------------|-------|----------------------|--------|----------------|
| EC | μ S/cm | 475.0 | 4080.0 | 1392.2 | 632.6 |
| TDS | mg/l | 351.0 | 1572.8 | 889.1 | 292.4 |
| pH | | 6.9 | 8.1 | 7.5 | 0.4 |
| Alkalinity | mg/l | 152.0 | 608.0 | 351.3 | 100.6 |
| TH | mg/l | 136.0 | 748.0 | 409.2 | 134.2 |
| Ca | mg/l | 34.0 | 184.0 | 86.0 | 32.4 |
| Mg | mg/l | 13.0 | 73.0 | 37.5 | 13.8 |
| Na | mg/l | 43.0 | 192.0 | 111.9 | 41.2 |
| K | mg/l | 4.0 | 54.0 | 17.6 | 9.4 |
| NO ₃ | mg/l | 4.0 | 64.0 | 25.2 | 13.5 |
| C ₁ | mg/l | 44.0 | 412.0 | 191.9 | 86.7 |
| F | mg/l | 0.2 | 3.6 | 1.3 | 0.8 |
| SO_4 | mg/l | 8.0 | 150.0 | 56.6 | 29.0 |
| HCO ₃ | mg/l | 164.8 | 555.2 | 346.1 | 95.4 |

Fig. 3 Correlation coefficient between TCC and TCA

water. This study focuses on the development of WQI for human consumption. The calculations are made based on the standards suggested by (WHO [1996](#page-15-5) and; BIS [1991](#page-13-14)). For computing WQI three steps are followed (Vasanthavigar et al. [2010;](#page-15-3) Sadat-Noori et al. [2014\)](#page-14-5). In the first step, each of the 12 parameters (pH, EC, TDS, Ca, Mg, Na, K, HCO₃, Cl, SO₄, $NO₃$ and F) has been assigned a weight (wi) according to its relative importance in the overall quality of water for drinking purposes (Table [2](#page-3-3)). The maximum weight of 5 has been assigned to nitrate due to its major importance in water quality assessment (Srinivasamoorthy et al. [2008](#page-14-17)). The maximum and minimum weightages was given based on their importance in the water quality and their weight given in Table [2](#page-3-3) depending on their importance in water quality determination. In the second step, the relative weight (Wi) is computed from the Eq. [2](#page-3-4):

$$
W_i = \frac{w_i}{\sum_{i=1}^n w_i},\tag{2}
$$

Table 2 Relative weight of chemical parameters

| Parameters | WHO | Weight (wi) | Relative weight (Wi) |
|------------------|-------------|-----------------|----------------------|
| TDS | 500 | 4 | 0.108 |
| pH | $6.5 - 8.5$ | 4 | 0.108 |
| TH | | 2 | 0.054 |
| Ca | 75 | 2 | 0.054 |
| Mg | 30 | 2 | 0.054 |
| Na | 200 | 2 | 0.054 |
| K | 12 | 2 | 0.054 |
| Cl | 250 | 3 | 0.081 |
| F | 1 | 4 | 0.108 |
| NO ₃ | 45 | 5 | 0.135 |
| HCO ₃ | 500 | 3 | 0.081 |
| SO_4 | 200 | 4 | 0.108 |
| | | $\sum w_i = 37$ | $\sum Wi = 1.000$ |

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

In the third step, a quality rating scale (qi) for each parameter is consigned by dividing its concentration in each water sample by its respective standard according to the guidelines laid down in the BIS 10500 (1991) and the result is multiplied by 100:

$$
q_i = (C_i/S_i) \times 100,\tag{3}
$$

where q_i is the quality rating, C_i is the concentration of each chemical parameter in each water sample in milligrams per liter. Si is the Indian drinking water standard for each chemical parameter in milligrams per liter according to the guidelines of the BIS 10500 (1991).

For computing the WQI, the SI is first determined for each chemical parameter based on the Eq. [4,](#page-4-0) which is then used to determine the WQI as per the Eq. [5.](#page-4-1)

$$
SI_i = W_i \times q_i,\tag{4}
$$

$$
WQI = \sum SI_i , \qquad (5)
$$

where SI_i is the Sub-Index of ith parameter, q_i is the rating based on concentration of ith parameter, n is the number of parameters.

The calculation method of WQI is expressed in detail by many authors (Saeedi et al. [2010;](#page-14-18) Vasanthavigar et al. [2010](#page-15-3); Yidana and Yidana [2010](#page-15-6); Jasmin and Mallikarjuna [2014](#page-14-13); Sadat-Noori et al. [2014](#page-14-5); Selvam et al. [2016](#page-14-19); Boateng et al. [2016](#page-13-2); Sakizadeh [2016\)](#page-14-20). WQI values are usually classified into five categories (Table [3](#page-4-2)) such as excellent, good, poor, very poor, and unsuitable for human consumption (Sahu and Sikdar [2008](#page-14-21)).

Statistical techniques

The analytical results of the chemical analysis and the statistical parameters such as minimum, maximum, average and standard deviation are presented in Table [1](#page-3-2). Multivariate statistical analysis was performed by major ions and EC, pH and TDSs. Multivariate statistical analysis was used to reduce and organize large hydrochemical datasets into

Table 3 Categorization of groundwater quality according to WQI

groups with similar characteristics (Srinivasamoorthy et al. [2011;](#page-15-4) Selvam et al. [2016](#page-14-19)). The basic purpose of this analysis was to interpret the relationship of variables. The correlation coefficient (r) commonly used to examine the degree of correlation between the different chemical parameters, which influence the quality of groundwater. It is a simple assess to reveal how well one variable predicts the other (Kurumbein and Graybill [1965](#page-14-22)).

Analytical data was processed using SPSS version 16.0 software. Factor analysis was performed by varimax rotation (Howitt and Cramer [2005\)](#page-13-15), which minimized the number of variables with a high loading on each component, thus facilitating the interpretation of PCA results. The main advantage of principal component analysis (PCA) is that it identifying patterns by compressing the data by reducing the numbers of dimensions without much loss of information (Irawan et al. [2009;](#page-13-16) Kazi et al. [2009](#page-14-23); Srinivasamoorthy et al. [2011](#page-15-4); Selvam et al. [2016;](#page-14-19) Boateng et al. [2016\)](#page-13-2). The spatial variability of groundwater was determined by the Cluster Analysis (Shanmugasundharam et al. [2015\)](#page-14-24). Two different methods can be applied to identify clusters, including R- or Q-modes. R mode is usually applied to water quality variables to reveal the interactions between them, while Q-mode reveals the interactions between the studied samples.

For this study R mode was used for Fourteen hydrochemical measured variables (EC, TDS, pH, Alkalinity, Total Hardness (TH), Ca, Mg, Na, K, NO₃, Cl, F, SO₄ and HCO₃) were utilized in this analysis. As there is no test to determine the optimum number of groups in the dataset (Guler et al. [2002](#page-13-17)), the visual inspection is the only criteria to select the groups in the dendrogram.

Result and discussion

pH, EC and TDS

pH of the groundwater samples in the study area ranges from 6.9 to 8.1 the average pH was found to be 7.5. The electrical conductivity (EC) of the groundwater ranges from 475 to 4080 µS/cm, the average EC was found to be 1392.2 µS/cm indicates the groundwater had slightly salinity nature. TDS values are considered as important values in determining the usage of water. The concentration of total dissolved solids (TDS) ranges from 351 to 1572.8 mg/l, the average TDS was found to be 974.56 mg/l indicating well for drinking purpose but few samples fall in the not potable limit.

Major anions

The bicarbonate measured in the groundwater ranges from 164.8 to 555.2 mg/l, the average was found to be 346.1 mg/l it does not exceed above the desirable level (Table [1](#page-3-2)). The sulfate concentration of study area ranges from 8 to 150 mg/l, the average was found to be 56.6 mg/l and it is under the permissible limit.

The concentration of nitrate in groundwater varies from 4 to 64 mg/l, the average of the nitrates 25.2 mg/l does not exceed above the potable limit only three groundwater samples fall in the not potable limit. Nitrate is also an indicator of pollution. A large amount of Fertilizers usage in the agricultural land leads to the nitrate content in groundwater is increasing all over the world. Nitrate and nitrite are hazardous to human health (USEPA [2002](#page-15-7)). The chloride concentration of study area ranges from 44 to 412 mg/l, the average was found to be 191.9 mg/l and it does not exceed above desirable limit only one sample fall in the not potable limit. Fluoride is an essential for maintaining normal development of teeth and bones. The concentration of fluoride ranges from 0.2 to 3.6 mg/l, the average of fluoride 1.3 mg/l. Such a higher concentration may be attributed to the percolation of phosphatic fertilizers from the irrigational runoff from the nearby lands. Discharge of domestic waters and the wastes from the surrounding industries can also increase the fluoride values (Singh et al. [2011\)](#page-14-25). The fluoride contaminations in the groundwater indicate the presence of fluoride bearing minerals (Kumar et al. [2011](#page-14-26); Ramachandramoorthy et al. [2010](#page-14-27)).

Major cations

The calcium concentration in the groundwater ranges from 34 to 184 mg/l, the average of calcium 86 mg/l not exceeds the allowable limit and all samples fall in acceptable and allowable limits. The magnesium concentration in the groundwater ranges from 13 to 73 mg/l and average of magnesium 37.5 mg/l not exceed the allowable level and maximum samples fall in the potable, allowable limit. The concentration of Ca and Mg in the groundwater is most probably derived from leaching of carbonate minerals such as calcite and dolomite. The concentration of sodium in the groundwater ranges from 43 to 192 mg/l and average of the sodium is 111.9 mg/l it does not exceed potable limit. Sodium and potassium were the most important elements occurring naturally. Potassium ranges from 4 to 54 mg/l, the average of the potassium 17.6 mg/l, it exceeds above the potable category, maximum sample falls in the not potable limit. The excess amount of potassium present in the water sample may lead nervous and digestive disorder (Tiwary [2001\)](#page-15-8).

Box plot

Box plot one of the easiest plot and gives better illustration about the anions and cations dominance (Taheri and Voudouris [2008](#page-15-9); Srinivasamoorthy et al. [2014\)](#page-15-10). Box plots were used to represent temporal concentration and dominance of the major ions (Fig. [4\)](#page-5-0). The upper and lower quartiles of the

constituents

data define the top and the bottom of a rectangle box. The line inside the box represents the median value and the size of the box represents the spread of the central value (Srinivamoorthy et al. 2014).

This plot reveals groundwater samples were are dominated by the order of $Na > Ca > Mg > K$ for cations and $HCO_3 > Cl > SO_4 > NO_3$ in anions. The plot shows remarkable variation in mean, median and standard deviation values of hydrochemical parameters indicating study area is wideranging of process influenced in the groundwater for various complex contaminant sources.

Base exchange indices

Base Exchange Indices is a process for determine the groundwater type of the study area. It mainly depending the sodium, chloride and sulfate ions. The Base Exchange Indices (Soltan [1999\)](#page-14-28) determined by using the Eq. [6](#page-6-0);

$$
r1 = Na - Cl/SO_4,\tag{6}
$$

where r1 is in milliequivalents per liter.

Table [4](#page-6-1) gives details of the groundwater can be grouped as Na-HCO₃ type if $r1 > 1$ and Na-SO₄ type with $r1 < 1$. In the study region all the samples fall in Na-HCO₃ type, except one sample fall $(Na-SO₄)$ (Fig. [5\)](#page-6-2).

Meteoric genesis index (r2) is to determine the groundwater sources as shallow or deep meteoric in the groundwater. This index dervied by sodium, potassium, chloride and sulfate ions concentration in the groundwater. Meteoric genesis index is calculated by Soltan [\(1999\)](#page-14-28) Eq. [7.](#page-6-3)

$$
r2 = ((K + Na) - Cl)/SO_4,
$$
 (7)

where r2 is in milliequivalents per liter.

Figure [6](#page-6-4) show maximum of the groundwater samples (79%) were deep meteoric percolation type (Table [4\)](#page-6-1).

Table 4 Classification of groundwater samples by Soltan (1998)

| Parameters | Ranges | Type of water | No. of samples |
|-----------------------|--------------------------------------|-------------------------|----------------|
| TDS | < 1000 mg/l | Fresh water | 28 |
| | > 1000 mg/l | Brackish water | 20 |
| Chloride | < 15 meq/l Normal Chloride type | | All samples |
| | >15 meg/l | | |
| SO_{4} | < 6 meq/l | Normal sulfate type | All samples |
| | > 6 meq/l | | |
| HCO ₃ | $2-7$ meg/l | Normal Bicarbonate type | 28 samples |
| | >7 meg/l | | 20 samples |
| Base exchange indices | | | |
| r1 | < 1 | $Na-HCO3$ type | 47 samples |
| | >1 | $Na-SO4$ type | 1 samples |
| r ₂ | < 1 | Deep meteoric water | 38 samples |
| | >1 | Shallow meteoric water | 10 samples |

 $r1 = r$ 1.00 r1 Index 0.50 Zero line 0.00 -0.50 0.00 10.00 20.00 30.00 40.00 50.00 S.Nos.

Fig. 5 Base exchange index plot (r1)

 1.50

Because of high rainfall situation and also the continuous exploitation of groundwater resultant in steep fall in water levels might have led to more of deep meteoric percolation type of water (Rao et al. [2013;](#page-14-29) Machender et al. [2014\)](#page-14-30).

Hydrochemical processes

The major ion chemistry of groundwater is a powerful tool because of dealing with groundwater evolution as a result of water–rock interaction leading to the dissolution of carbonate minerals, silicate weathering and ion exchange processes (Herczeg et al. [1991](#page-13-18); Elliot et al. [1999;](#page-13-19) Edmunds and Smedley [2000](#page-13-20); Kumar et al. [2006\)](#page-14-31). From the resultant average ratio of $(Ca + Mg)/\text{total cations varied from } 0.4$ to 0.66 in the study region.

The Figure [7](#page-7-0) shows $Ca + Mg$ vs total cations, that all the points lies above the aquiline signifying the condition of alkalis to the major ions, which resulting from silicate weathering and alkaline earth silicates. This plot also reveals increasing contribution of Na and K with increasing total dissolved solids.

The average ratio of $(Na + K)/total$ cations varied from 0.3 to 0.5. Figure [8](#page-7-1) show (Na + K) vs total cations of that samples fall along the aquiline, signifying that the cations in groundwater might have been derived from silicate weathering in the geochemical processes, which contributes mainly

Fig. 6 Meteoric genesis index plot (r2)

Fig. 7 Ca+Mg versus total cation plot

Fig. 8 Na+K versus total cation plot

Fig. 9 Na/Cl ration versus EC plot

sodium and potassium ions to the groundwater (Stallard and Edmond [1983\)](#page-15-11).

The Na-Cl relationship is mostly used to identify mechanisms related to salinity in semi-arid regions (Ganyaglo et al. [2011;](#page-13-21) Nematollahi et al. [2016](#page-14-32)). Figure [9](#page-7-2) shows the Na/Cl ratio decreasing trend with increasing EC, indicating Na released from silicate weathering process. In the plot (Fig. [8\)](#page-7-1) shows 32 samples have Na/Cl ratio below one and 16 groundwater samples above the one in the study area, indicating that maximum of halite dissolution and some places controlled by silicate weathering processes respectively.

The Na vs Cl (Fig. [10\)](#page-7-3) plot indicates the increasing trend of Na with Cl and also most of the samples lie above the aquiline representing the excess of Na is attributed to silicate

Fig. 10 Na versus Cl plot

Fig. 11 Ca/Mg versus sample nos. plot

weathering (Stallard and Edmond [1983](#page-15-11)) whereas some samples lay below it, indicating that the addition of Cl may be due to water level rise which causes more salt dissolution from the soil (Rao et al. [2013](#page-14-29)).

The Ca/Mg ratio of 1 specify dissolution of dolomite and of >2 revealed an effect of silicate minerals on the groundwater chemistry; it also suggested dolomite dissolution for Ca-Mg concentration in groundwater (May and Loucks [1995\)](#page-14-33). Ca/Mg ratio of 93.7% samples ranges from 0.78 to 1.94 indicates dolomite dissolution responsible for Ca–Mg contribution (Fig. [11](#page-7-4)).

The sources of the dissolved constituents in ground water can also be evaluated from the relative abundance of individual ions and inter-elemental correlation (Singh et al. [2011](#page-14-25)). The plot of $(Ca+Mg)$ vs $(HCO₃+SO₄)$ will be close to 1:1 line in case of dissolution of calcite, dolomite and gypsum. Ion exchange tends to shift the plotted points towards right due to a large excess of (HCO_3+SO_4) and towards the left in case of reverse ion exchange and dominance of $(Ca+Mg)$ over $(HCO₃+SO₄)$ (Cerling et al. [1989;](#page-13-22) Fisher and Mulican [1997](#page-13-23)). (Ca+Mg) vs $(SO₄+HCO₃)$ for groundwater samples indicate in Fig. [12](#page-8-0) that majority of the groundwater samples falls near and along the aquiline, it reveals both ion exchange and reverse ion exchange were responsible for hydrochemical process in the study area. If bicarbonate and sulfate are dominating than calcium and magnesium, it reflects that silicate weathering and ion exchange process were dominating

Fig. 12 Ca/Mg versus $SO_4 + HCO_3$ plot

to responsible for the increase in the concentration of $HCO₃$ in groundwater.

WQI of the Upper Manimuktha sub basin

Water quality types were determined on the basis of WQI. The computed WQI values range from 45.8 to 225.1. According to the WQI values for 2 samples were located in Excellent classification, 22 samples to be found in Good water classification, 23 samples placed in poor water and 1 sample located in the very poor water. Based on the WQI, 50% of the samples not good for drinking purposes. Figure [13](#page-8-1) indicates that the central part of the study area covered by good WQI. The groundwater quality decreases in the northern and southern side of the sub basin. This is mainly due to the effects of the hydraulic gradient (Sadat-Noori et al. [2014](#page-14-5)) and the domestic pollution; anthropogenic activities such as fertilizer usage for agricultural land mainly affect the groundwater of southern and northern side of the

Fig. 13 Spatial distribution of WQI

study area. As well as the area with deep groundwater is also the main reason for poor water quality of the study area (Vasanthavigar et al. [2010](#page-15-3)).

Calculation of WQI for every sample are represented in Table [5](#page-9-0). Groundwater samples represent 4.2% of samples within the "excellent water", 45.83% indicate "good water", 47.91% shows "poor water", and 2.1% shows "very poor

Table 5 Groundwater classification in the study area based on WQI

| WQI | Classification | S. No. | WQI | Classification |
|-------|-----------------|--------|-------|------------------------|
| 75.0 | Good water | 25 | 86.5 | Good water |
| 63.2 | Good water | 26 | 152.6 | Poor water |
| 113.6 | Good water | 27 | 84.0 | Good water |
| 126.3 | Poor water | 28 | 100.7 | Poor water |
| 123.3 | Poor water | 29 | 115.0 | Poor water |
| 66.2 | Good water | 30 | 97.4 | Good water |
| 93.1 | Good water | 31 | 82.7 | Good water |
| 124.3 | Poor water | 32 | 66.8 | Good water |
| 80.9 | Good water | 33 | 89.7 | Good water |
| 225.1 | Very poor water | 34 | 125.8 | Poor water |
| 109.0 | Poor water | 35 | 175.4 | Poor water |
| 56.3 | Good water | 36 | 59.3 | Good water |
| 112.4 | Poor water | 37 | 132.7 | Poor water |
| 138.0 | Poor water | 38 | 111.7 | Poor water |
| 98.0 | Good water | 39 | 132.1 | Poor water |
| 86.5 | Good water | 40 | 119.8 | Poor water |
| 146.1 | Poor water | 41 | 124.8 | Poor water |
| 111.1 | Poor water | 42 | 127.7 | Poor water |
| 166.4 | Poor water | 43 | 50.0 | Excellent water |
| 87.5 | Good water | 44 | 70.2 | Good water |
| 88.2 | Good water | 45 | 96.4 | Good water |
| 82.9 | Good water | 46 | 104.7 | Poor water |
| 72.7 | Good water | 47 | 85.9 | Good water |
| 149.2 | Poor water | 48 | 45.8 | Excellent water |
| | | | | |

water". This may be due to effective leaching of ions, overexploitation of groundwater, direct discharge of effluents and agricultural impact (Sahu and Sikdar [2008\)](#page-14-21).

Multivariate statistical analysis

The Pearson's correlation matrices (Swan and Sandilands [1995](#page-15-12)) are used to find the relationships between two or more variables, where the correlation matrices between 13 chemical parameters were computed and presented in Table [6.](#page-9-1)

Based on the Pearson's correlation, significant and high positive correlation $(r>0.7)$, majority of the parameters were found to tolerate statistically significant correlation with each other representing close association of these parameters with each other except pH and F. Strong significant correlation of TDS between all the elements except pH, F. The pH was negatively correlated with all the physicochemical parameters and also the strong significant correlation of alkalinity with all the elements except pH, F, SO4. The strong significant correlation of Total hardness with Na, K, NO₃, Cl, SO₄, HCO₃ and moderately correlated with Ca, Mg. Table [6](#page-9-1) indicates all the constituents highly correlated with one another except pH and F. This reflects that the groundwater in the area has been contaminated due to application of excess amount of fertilizer, over exploitation, and anthropogenic activities. The variation of these relationships may indicate the complexity of the hydrochemical components of groundwater where natural water always contains dissolved and suspended substances of mineral origin (Elkrail and Obied [2013](#page-13-24)). Sodium also highly correlated with Cl and then $NO₃$, $HCO₃$, K. High positive correlation coefficient between Na and Cl suggests the predominance of chemical weathering and dissolution of chloride salts (mostly halite) in the study area. This means that Base Exchange and dissolution of sodium salts during movement of the groundwater through sediments might lead to high

sodium concentration (Nematollahi et al. 2016). The NO₃ ion was strongly correlated with Cl it indicates a possibility of contamination from fertilizers, municipal wastewaters, septic systems, and sometimes the cultivation of grasslands. Weathering processes and anthropogenic inputs are the two main contributors for changing the geochemical composition of the groundwater (Chan [2001](#page-13-25)). Potassium also first of all highly correlated with $NO₃$ then only the Cl, it also indicate wherever $NO₃$ high that mainly correlated with K. The weak correlation of F and pH with others, indicate these not influence of other constituents in the study area.

Negative correlation relation between parameters

The correlation analysis mainly deals with correlation between elements and another one main thing it also indicate a opposite relation with element as pH is negatively correlated with TDS, alkalinity, calcium, magnesium, potassium, nitrate, chloride and fluoride. It indicate that wherever pH ranges going to decreases with also TDS, alkalinity, calcium, magnesium, potassium, nitrate, chloride and fluoride increased. It clearly explains the acidic nature of groundwater mainly rich with anions and cations.

Factor analysis explain observed relation between numerous variables in terms of simpler relations. It is also a way of classifying manifestation of variables (Kumar et al. [2006](#page-14-31)). The concentration of each compound is separated in two partial contributions, one related to weathering reactions, and the other related to pollution. Factor analysis was applied to distinguish the partial contributions (Rao et al. [2013\)](#page-14-29). An Eigenvalue provides assess of the significance of the factor: the factors with the highest Eigenvalues are the most significant. Eigenvalues of 1.0 or greater are considered significant. Liu et al. ([2003](#page-14-34)) classified the factor loadings as 'strong', 'moderate' and 'weak', resultant to the absolute loading values of > 0.75 , 0.50 to 0.75 and 0.30 to 0.50, respectively. The results of the analysis discovered in the Table [7](#page-10-0), three factors accounted for 84.14% of the total variance. Based on the distribution of the Eigenvalues, factor 1 alone explained 69.04% of the variance. Figure [14](#page-10-1) clearly reveals all the constituents were strongly correlated with factor 1 except pH and F. Factor 1 source mainly attributed to weathering and leaching of host rocks and as well as natural sources. From the factor 1 natural process is the important process in ions concentration in the groundwater. Factor 2 which describes 8.96% of the total variance has high positive loading for F. This factor could be mainly attributed to the gypsum and silicate weathering processes and cation exchange processes at soil–water interfaces. pH was strongly correlated with factor 3. Factor 3, therefore, could be said to reflect the influence of anthropogenic activities. Because the third factor mainly indicate the groundwater acidic and basic nature may be contribute by the anthropogenic activities such high amount

Table 7 Factor-loading matrix, eigenvalues

| Parameters | Factor 1 | Factor 2 | Factor 3 |
|------------------|----------|----------|----------|
| EC | 0.93 | 0.16 | -0.07 |
| TDS | 0.99 | 0.08 | -0.02 |
| pH | -0.03 | -0.13 | 0.97 |
| Alk | 0.85 | -0.04 | -0.11 |
| TH | 0.80 | 0.33 | 0.16 |
| Ca | 0.92 | -0.03 | 0.01 |
| Mg | 0.88 | 0.06 | -0.16 |
| Na | 0.92 | 0.17 | 0.10 |
| K | 0.88 | 0.17 | -0.18 |
| NO ₃ | 0.94 | 0.09 | 0.00 |
| Cl | 0.96 | 0.08 | 0.03 |
| F | 0.09 | 0.97 | -0.14 |
| SO_4 | 0.68 | 0.04 | 0.11 |
| HCO ₃ | 0.90 | 0.05 | -0.12 |
| Total | 9.66 | 1.25 | 0.86 |
| % of Variance | 69.04 | 8.96 | 6.15 |
| Cumulative % | 69.04 | 77.96 | 84.14 |
| | | | |

Fig. 14 Factor analysis results

of fertilizer usage, the dumping of organic and inorganic waste at or near the lakes.

According to Massart and Kaufmann ([1983](#page-14-35)) the multivariate statistical analysis mainly based on the similarity and dissimilarity of variables and cases. Hieratical cluster analysis performed using Ward method. The results of parameters are shown three groups in Fig. [15](#page-11-0). Most of the samples were classified in cluster 1 with similarity between major ions $(F, K, NO₃, Ca, Mg, Na, SO₄, Cl and pH)$ which indicated the same source of origin of charnockitic terrain. Because the study area mainly underlain by charnockite. Cluster 2 demonstrate, total hardness (TH), bicarbonate and alkalinity were associated based on their amount of concentration were correlated with one another. The third cluster shows the similarity between EC and TDS also the amount of contribution is more or less same.

Another one way also illustrates quality of groundwater that is case wise classification of dendrogram. From Fig. [16](#page-12-0) consists two classes as good water and polluted water of the **Fig. 15** Dendrogram for the groundwater assemblage with respect to their physico-geochemical parameters

study area. From this dendrogram analysis polluted water mainly in the northern and southern part of the study area. From the Table [5,](#page-9-0) polluted and unpolluted area matches with the Fig. [16.](#page-11-0) Polluted water is characterized by high amount of TDS, EC and as well as anions and cations. These 2 groups were alienated based on the increasing order of concentrations of variables in groundwater samples from above to below of the dendrogram.

Correlation between case wise Dendrogram and WQI

Cluster analysis results communicate with the WQI, therefore cluster analysis one of the main study to correlate with WQI and also validate the exactness of the WQI. From the dendrogram (Fig. [16](#page-12-0)) each and every sub cluster correlated with WQI. Figure [17](#page-13-26) indicates every dendrogram wise samples align an ascending manner. It illustrate that the WQI also increase with the order of dendrogram samples wise.

Conclusion

Groundwater quality incorporate with WQI, GIS and the multivariate statistical analysis were carried out to conclude the geochemical processes accountable for quality deterioration in the study area. Based on this study EC, TDS, sodium, potassium, nitrate, chloride and fluoride were some of the locations exceeded the WHO permissible limits for drinking water. The groundwater samples were dominated by $Na > Ca > Mg > K$ for cations and $HCO_3 > Cl > SO_4 > NO_3$ in

anions. Maximum of the study area underlain by charnockite rock, it is one of the main reason for dominant of sodium. WQI indicate northern and southern side of 23 sam-

ples fall in the poor water and one samples fall in the very poor water in the Kadavanur reserve forest. These locations mainly lie in charnockite and fissile hornblende biotite gneiss type of rocks. It reveals lithology also major reason for contamination of ground water in the study area. Maximum of lakes located in northern side of the study area also indicate poor quality, because of the contamination of waste water at or near the lakes such as organic as well as the inorganic waste migrate in the groundwater. As well as this area mainly fall the shallow groundwater it indicates the domestic, agricultural waste also contributed the groundwater impurity. The quality of groundwater was establish to be fit for drinking in spite a southern and northern parts of the study area. Correlation between WQI and Dendrogram analysis to prove this was able to correlate and appropriate study to gives proper result. Based on the result the correlation gives dendrogram cases and WQI S.No. aligned in a increasing order. From the correlation between stream wise analyses indicate element concentration changes random manner while mainly decreasing by the linear approach from the location to location upto the reservoir of the study area. This study also gives a better idea between the relation to case wise dendrogram and WQI. The overall geochemistry of groundwater in the study area is controlled by natural geochemical processes like rock water interaction and some places anthropogenic tempt activities like overexploitation of aquifers, fertilizer influences and agricultural return flow.

Fig. 17 Correlation between case wise Dendrogram and WQI

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