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Groundwater chemistry and entropy weighted water quality index of tsunami affected and ecologically sensitive coastal region of India

Balamurali Krishna, V. Sivanandan Achari *

Environmental Chemistry Laboratory, School of Environmental Studies, Cochin University of Science and Technology, Kochi, 682 022, Kerala, India

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ABSTRACT

Quality groundwater is the most essential prerequisite for the better livelihood of the coastal villages and a vital resource for a safe living. Seawater interaction and coastal inundation modify hydro geochemical cycles leading to gross utility as a challenge. Poor quality water intake causes diseases and seriously affects human health. In this study, the suitability of shallow drinking water sources (10–15 *m*) has been studied with a focus on coastal village in south west of India (Alappad coast, Kollam, Kerala) which is a host of huge placer mineral reserve of the country. This coastal stretch has good deposition of Late Quaternary sediments of heavy mineral placers subjected to severe seawater interactions. Mineralogically, garnet and heavy minerals comprises the beaches and most coastal plains of the Alappad. A concerted geological process where moving water and waves causes erosion, leads to lowering of the earth's surface -is prominent in this fragmented land. This study critically evaluates the temporal-spatial impact of these interactions in an age of varying climatic conditions and hence for reference beyond. Water quality index analysis has been attempted using the entropy weighted water quality index (EWQI) method for a total of 45 samples (15 samples season-wise). It aims to ascertain better choices of groundwater sources for domestic uses for isolated settlers endowed with estuaries, and old coastal plains with barrier beaches. Irrigation suitability was evaluated using sodium adsorption ratio (SAR) and Na %. Observed EWQ Indices (38.2 ± 14.5) for post-monsoon (80% samples), (66.1 ± 77.7) for monsoon (66% samples), and (71.4 ± 71.3) for pre-monsoon (53% samples) fall in excellent category. Post-monsoon is most favoured for a better quality groundwater as evidenced by WQI of 80% among the samples tested. Ca–HCO_3 is the dominant hydrochemical type observed. The mean value of iron (0.9 ± 1.3 mg/L) exceeded the permissible limit of 0.3 mg/L during monsoon season due to mineral-water interactions. In pre-monsoon season the parameters Na^+ (95.9 ± 200.7 mg/L), Cl^- (173.4 ± 510.2 mg/L), EC (1559.3 ± 2510.6 μS/cm), and TDS (492.5 ± 629.7 mg/L) were observed in higher ranges. Significant correlation ($p < 0.05$) prevailed between EWQI, and parameters-conductivity (0.75), TDS (0.75), Iron (0.59), Ca^{2+} (0.66), and Mg^{2+} (0.74). Principal component analysis (PCA) on chemical parameters accounted for the total variance of 84.2% in pre-monsoon, 89.9% in monsoon and 82.9% in post-monsoon. Groundwater quality is influenced by geochemical processes, salt intrusion, and human activities like fertiliser application and domestic sewage discharge. Hierarchical cluster analysis (HCA) grouped the samples into three clusters. Cluster 3 represents poor quality water (13%) in pre-monsoon (EWQI ranged 32.2–192.7), and monsoon (EWQI ranged 171.8–309.7). Cluster 3 in post-monsoon (20%)

* Corresponding author.
E-mail address: vsachari@cusat.ac.in (V.S. Achari).

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indicating good water quality (EWQI ranged 51.4–72.6). Ultimate finding is that post-monsoon groundwater is more suitable for drinking and domestic purposes for the selected coastal area.

1. Introduction

Groundwater is vital and essential resource for drinking, agricultural, and industrial requirement of the world. Its availability is crucial to maintain ecological and environmental balance of nature [1–3]. Groundwater is mostly unconfined and in phreatic condition, hence vulnerable to anthropogenic pollution [4,5]. Coastal zones of India are having high density of populations because of numerous activities related to fisheries, agriculture, and the economic activities including harbour trade, port and infrastructure developments. Quality potable freshwater will be a severe limitation in future due to many hydro geochemical/anthropogenic interactions in making, in these coastal barrier islets. Chances of pollution and its effects on water quality are a great threat to human health, economic development and social prosperity [6]. Groundwater is the only dependant source for human consumption in coastal regions where fresh water sources are scarce [7–9]. Once the source water is over contaminated, it is hard to control the health issues and restore the natural quality and harmony of social life. Nevertheless, coastal regions worldwide are having huge wealth of resources always been among the most frequently exploited. Mostly, coastal aquifers are at high risk of contamination from seawater intrusion all over the world [10]. India has a 5700 km long coastline, comprises 590 km coastline of Kerala. Here, the coast is formed with chain of estuaries, and old coastal plains. More marvellously placed with ridge-runnel systems and barrier beaches-regarded as gift of God's own country. These regions are noted as a rare place for many endemic marine organisms and mangrove ecosystems. Estimated that, 44% of people (2934 persons/km^2) live in near the Kerala coast [11], is a relatively high density dwelling reported. Fishermen community of the state are traditionally settled in these coastal villages. More than 80% of the settlers depend on groundwater for their domestic and irrigation needs. Excessive consumption of drinking water having undesirable dissolved ions and traces impacted the health of many in the history. WHO guidelines play a crucial role for the suitability of drinking water sources by a regulatory systems [12]. In this perception, the need of primary data on hydro chemical quality of coastal shallow groundwater and its critical interpretation is significant for the wellbeing and economic stability of the coastal communities of the world.

Most coastal regions are aesthetically attractive, landscaped with cities and architecturally fine-tuned for socio-economic activities. Accordingly, marked by rapid urbanisation and economic growth [13] augmented by coastal resources-groundwater is the prime one. Hydrochemical interferences and salt water intrusion caused by natural, human activities and industrial practices are regularly reported [14]. Beach & mineral sand mining contributed many changes in coastal land environment beyond restoration in the coastal areas of Kerala. According to Central Water Commission (CWC) [15] report of India, 63% of the Kerala coast been eroded, whereas accretion is only 24%. These fragmented coast land alters the quality of water by saline ingress, and become vulnerable to many natural hazards. Alappad coast (9°2′57″N to 9°7′15″N latitude and 76°28′19″E to 76°30′13″E longitude) is a 16 km long stretch of ridge (in Kollam district in Kerala, India). Has been severely devastated by 26^{th} December 2004 by Indian Ocean Tsunami, 149 people died, hugely inundated and flooded the groundwater sources [11,16]. As regards to sustainable water resource security measure [17,18] it becomes important to quantify the quality of these ground waters to devise ways and means to protect it.

Usually, the nature of the aquifer rock, residence time, flow pattern, and recharge source all have a significant role in determining the chemical composition of groundwater. Studies on groundwater chemistry are necessary to develop management plans to protect them from any type of contamination [19]. The coastal groundwater resources is considered to be a complex dynamic system, influenced by various factors like climate, tidal effects, upstream groundwater recharge, natural hazards and human interferences [20, 21].

This study provides baseline information about the recent condition of available groundwater quality of a coastal area, hugely destructed by tsunami disaster and its impacts on ground water resources had been reported earlier [21]. This region is continuously monitored over a period of years since 2005 (after Indian Ocean tsunami on 26th December 2004) to support water resource planning for economic engineering and coastal groundwater chemistry studies [21]. The study area has placer mineral deposits and are home to one of the world's richest black sand minerals. The major constituents among are ilmenite (TiO_2 59%, Fe_2O_3 17% to FeO- 23.5%), zircon-bearing beach sands (ZrO_2 65%), rutile (TiO_2 95%), monazite (ThO_2 8–10%) including radioactive thorium [19,21]. Any change in the water quality of the region by external stress invariably will alter mineral-groundwater equilibrium persisted in shallow aquifer formations over years. Chances of acid mine drains/spillage can bring changes in groundwater chemistry matrices. Analysis of principal components responsible for the groundwater chemistry of the placer mineral enriched and economically significant coastal region of Kerala, India, can bring about new insights.

Groundwater chemistry has been used to forecast water quality criteria and suitability under different ionic environment as an analytical tool of the trade. Many methods are known in literature to assess groundwater quality [22] and ionic equilibrium. WQI is obtained by statistical technique that reduces large amounts of descriptive data to a single value to decide a desired quality for safe drinking/consumption. Mostly, these evaluation models are developed based on the relationship between aquatic environmental quality and evaluation indicators [22]. Weighted arithmetic water quality index, artificial neural network (ANN), fuzzy mathematics, analytical hierarchy process (AHP), topsis (technique for order of preference by similarity to ideal solution) model, multi-criteria decision making model (MCDM) are well known [23–28]. The EWQI is an efficient tool to assess overall water quality using pertinent water quality parameters [29]. In other WQI methods, the weighing factors are decided by according to their expertise and hence enough valuable information gets lost [28]. One of the known advantages of the entropy weighted method (EWM) is – it is truly free from the interference of human factors on the weight of indicators [30]. This enhances the objectivity of the comprehensive evaluation of final results. Further, it become possible to reduce large data set to maximum acceptable level of information and with the meaning is substantially retained [31].

The EWM is an important information weight model that has been extensively studied and practiced. Groundwater quality evaluated and reported is known using entropy-topsis method in Azarshahr plain aquifer, east Azerbaijan, Iran. It showed 35% of samples are in excellent quality, 51% falls in moderate quality and groundwater has been mainly in Ca–Cl type [26]. Based on the integrated-weight water quality index (IWQI), the city Xi'an, in China Guanzhong basin reported to have predominantly Ca–Mg–HCO_3 type. Also revealed 9% of groundwater samples was of medium to poor quality and unsuitable for drinking [25]. Information entropy method was applied for the groundwater of lower Ganga basin in a similar study. Reported that, HCO_3^-, Ca^{2+}, SO_4^{2-}, TH, Mg^{2+}, and pH has relatively lower entropy weights (<0.10), and the quality of groundwater varied from excellent to medium [30] quality. The osculating value method and entropy is applied on the groundwater in Beijiao Water Source of Yinchuan revealed 96% of the phreatic water samples are fit for human consumption [32]. Entropy-based groundwater quality of the Ameka Region of Southeast Nigeria

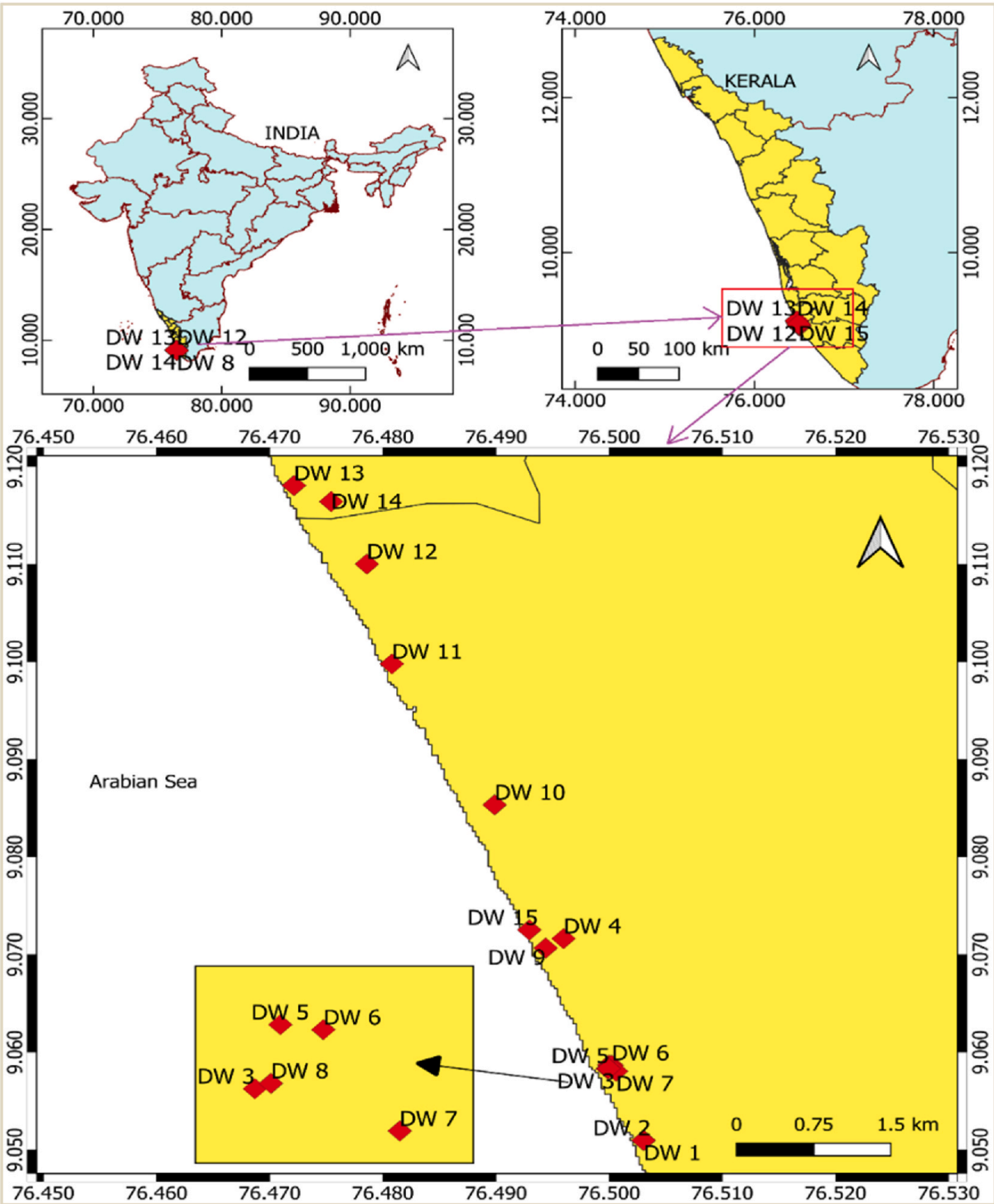

Fig. 1. Location map showing groundwater collection points in study area, Alappad coast, Kollam, Kerala, India.

showed the EWQI range 1448–15329 indicating extremely poor water [33]. Groundwater quality based on EWQI of rural part of Wanaparthy District, Telangana, India revealed 47% of total area has good quality water for drinking purpose [34]. Some of the iimportant studies using information entropy method is summarized in Table S1, Supplementary Material. It is known that, the entropy water quality index (EWQI) is a significant approach involving all physico-chemical parameters of groundwater samples to analyse the water quality [35]. Shannon (1948) introduced the entropy theory to determine the weight of each parameter to reduce the error caused by the ignorance of the weight of parameters [36]. The entropy weighted method evaluates data by measuring the degree of differentiation. It is a water rating scale based on reflecting the influence of various parameters on overall quality of drinking water [31]. The higher the degree of dispersion of the measured value, the higher the degree of differentiation of the index, and more information can be derived [37]. The results of the entropy weighted method are reliable and found effective for a study of hydrological effects of water reservoir in a multi scale entropy analysis [32,38]. Contributions of physicochemical parameters to overall water quality are different in many occasions. Hence, they are represented by assigning different weights, when used for water quality assessment [32]. Entropy weight can be determined by different methods such as the Analytical Hierarchy Method, Delphi Method and the Information Entropy Method [16,39].

The research on the groundwater quality of ecologically fragile coastal environment, having a unique rare earths mineral chemistry, subjected to severe erosion and sensitive to tsunami impacts with seasonally oscillating hydrodynamics with special geochemical setting is a gap area. The dependence on available groundwater by communities for their domestic needs in this populated coastal area is a great concern. Studies on hydro geochemistry and systematic account on quality of drinking water on long term basis will benefit the humanity in many ways for a sustainable living. This study comprehensively determine and reports the suitability of shallow groundwater for drinking purposes using EWQI, weighted arithmetic mean method, and groundwater pollution index. These methods are useful for interpreting water quality data in an understandable manner. The objective of the present study are (1) to evaluate the groundwater chemistry and quality in an ecologically vulnerable coastal phreatic aquifer of India (Alappad coast, Kerala) for drinking purpose. (2) To identify the irrigation suitability of coastal groundwater sources using sodium adsorption ratio (SAR) and percent sodium [40–42]. (3) To report the hydrochemical processes and anthropogenic effects on groundwater sources in a sensitive coastal area of India. Statistical methods and multivariate analysis like principal component analysis (PCA), correlation analysis, and hierarchical cluster analysis (HCA) were used to categorize the spatio-temporal hydrochemistry of the region. Hill-Piper Trilinear Diagram [43], Gibbs Plot [44], and Scatter Diagrams are used to confirm the hydrochemical processes prevalent in this ecologically vulnerable coastal segment.

Table 1
Details of groundwater sampling stations of Alappad coastal region, Kollam, Kerala, India.

Stations	Station Description (Dug Wells)	Latitude	Longitude	Height of water column (cm)			Remarks
				Pre-Monsoon	Monsoon	Post-Monsoon	
DW 1	Cheriyazheekkal Bagavathi temple well	9°03′03.20″N	76°30′9.25″ E	33	29	25	Used for drinking purpose
DW 2	Kashinathan Temple well	9°03′03.20′N	76°30′10.90″ E	60	28	88	Not used for drinking purpose
DW 3	Vidyadharan (house owner)	9°03′03.49″ N	76°30′10.91″ E	75	40	20	Irrigation use only
DW 4	Rajappan Kadayil - (house owner)	9°03′29.88″ N	76°29′59.49″ E	50	98	32	Not used for drinking purpose
DW 5	Kuttiyedath Chandrababu (house owner)	9°04′17.90″ N	76°29′45.45″ E	50	52	20	Irrigation use only
DW 6	Harisree (house owner)	9°03′31.24″ N	76°29′59.96″ E	86	75	35	Used for Irrigation and washing purposes
DW 7	Joy Cherukarayil (house owner)	9°03′31.14″ N	76°30′0.75″ E	41	93	62	Irrigation purpose only
DW 8	Usha Kaithoppil (house owner)	9°03′28.98″ N	76°30′2.16″ E	33	40	25	Not used for drinking purpose
DW 9	Sree Subrahmanya swami Temple well	9°03′30.20″ N	76°29′58.2″ E	35	73	30	Used for drinking purpose
DW 10	Parayakkadav Ponna Bhagavathy Temple well	9°04′14.41″ N	76°29′39.76″ E	30	35	90	Used for drinking purpose
DW 11	Srayikkadu Temple well	9°05′7.26″ N	76°29′23.53″ E	48	56	48	Used for drinking purpose
DW 12	Azheekkal Subrahmanya Temple well	9°05′59.20″ N	76°28′50.84″ E	38	74	98	Used for drinking purpose
DW 13	Kurikkasseril Temple well	9°06′59.07″ N	76°28′31.54″ E	40	44	60	Used for drinking purpose
DW 14	Kurissadi (Pochayil house well	9°06′36.0″ N	76°28′44.22″ E	44	76	65	Used for drinking purpose
DW 15	Lakshmi (house owner)	9°07′4.98″ N	76°28′19.70″ E	24	56	142	Irrigation purpose only

2. Study area

2.1. Location of the study area

The study area is a coastal land located in the southwest of the Indian state of Kerala with an altitude of 0–7.5 *m*. This Alappad coast (9°2′57″N to 9°7′15″N latitude and 76°28′19″E to 76°30′13″E longitude) is 16 km long fishing village in south west of Kollam district (Kerala state). It is a narrow strip of land sandwiched between the Arabian Sea and the TS (Trivandrum - Shoaranur) canal (Fig. 1). The study area was flooded in 26th December 2004 b y Indian Ocean Tsunami, 149 people died [11,16]. Saline intrusion is a common phenomenon in the entire stretch. Dug wells are the only dependable source for the domestic water usage for the people in this region. The groundwater sampling points are located in residential area near to the seashore of Alappad coast. The latitude and longitude of the sampling location is given in Table 1. According to Census 2011 information, the Alappad village has the total population of 21,655 peoples (10,689 males and 10,966 females) and population density 2934 persons per square km [11].

2.2. Climate of the study area

The area enjoys a humid equatorial tropical climate with two rainy seasons they are south west monsoon from June–September and north east monsoon/post-monsoon from October–December. Pre-monsoon (a hot summer) persists from January–May and this area receives an average rainfall of 1934 mm [19]. Monsoon period (South west monsoon, June–September) contributes 65% of the rainfall and the Post-monsoon (northeast monsoon, October–December), contributes only 20%, is considered crucial in recharging the groundwater system and also in maintaining the stream flow to last the leaner summer months.

2.3. Geological setup

The coastal plains of Kerala include areas between Lakshadweep Sea in the west and elevations of 6 *m* above mean sea level in the east. The geologyof this area mainly consists of coastal sands and alluvium of recent age and sedimentary rocks [19]. The thickness of the coastal alluvial formation in the Kerala coast varied from few meters to above 100 *m* and depth to water level ranges from <1 to 6 *m* below ground level [19,21]. The coastal region has tertiary sediments of Alleppey, Vaikom, Quilon and Warkali beds, overlain by 10–15 *m* thick alluvium. The alluvial material composed of mainly clay and sand. Laterite layer is seen below the alluvial formations. The Warkali beds form the youngest formation of the tertiary sediments of Kerala. These attain maximum thickness of 140 *m* around Alappuzha. These layer consists of fine to medium grained sand with clays and thin bands of lignite [19]. Quilon beds underlying the Warkali beds with compact and ash grey limestone, calcareous clay and marl having the thickness 6–100 *m*. Vaikom beds seen underlying the Quilon beds and extends the sedimentary basin consists the lithology of sandstone with pebbles, gravel beds, clay and thin bands of lignite. More details on the hydrogeological set up in the study area are depicted in Figs. S1 and S2, Supplementary Material. The groundwater sources are in phreatic condition. The handmade dug wells are the source for domestic needs along the low land coastal regions.

3. Methodology

3.1. Sample collection procedure

Coastal shallow groundwater sampling survey were conducted during the pre-monsoon (March), monsoon (August) and post-monsoon (December) seasons of 2018. A total of 45 groundwater samples were collected from 15 sampling stations in the coastal region. These are the only available source of groundwater for domestic purposes for a large number of settlers in the islet. The geographical position of the sampling stations (sites) was recorded with the use of the Geographical Position System GPS. Samples were collected in 2.5 L polyethylene containers. The bottles were rinsed in 0.1 N HNO_3 after then washed with double distilled water. The washed bottles were oven dried at 60 °C and rinsed with sample water before filling the samples. Samples were labelled and sealed properly and stored in an ice box to carry Environmental Chemistry Laboratory of School of Environmental Studies, Cochin University of Science and Technology, Kochi-682 022, for immediate analysis.

3.2. Laboratory analysis methods and equipment used

Groundwater temperature, pH, Eh, EC and TDS were recorded at the collection point using calibrated multi-parameter water analyser (Eutech, PCD 650, Serial No. 2656947). Water sampling (Part 1060), preservation (Part 1060 C), and analysis (Part 2000) were performed as per the recommendation employed by American Public Health Association (APHA)-Standard Methods [45]. Reagent blanks (Part 1080) and analytical grade reagents were used for all analyses. Calibration of instruments (Part 1020 B) was performed with standards before testing samples. Alkalinity (Part 2320 B) was determined by titrating sample (50 ml) against HCl solution (0.01 N). Total hardness and Ca^{2+} were measured by EDTA titration (Part 2340 C); Chloride was estimated by argentometric titration (Part 4500 B). Na^{+} and K^{+} (Part 3500 B) were determined by flame photometry (ELICO CL378 Flame Photometer). Mg^{2+} (Part 3500-Mg^{2+} B) were determined using the calculation method (Eq. S1, Supplementary material). NO_3^- was analysed by UV-screening method (Part 4500-NO_3^- B), SO_4^{2-} determined by turbidimetric method (Part 4500- SO_4^{2-} E) and PO_4^{3-} was analysed by ascorbic acid method using double beam spectrophotometer (Part 4500-P E). A blank was run for every laboratory analysis event. Samples analysed in triplicate and the mean values are recorded. The accuracy of the analysis was verified by calculating the ion-balance errors (%Error), taking the relationship between the total cations and the total anions for each season. Where the ∑Cations and ∑Anions, are the sum of major cations and anions in meq/L. The error percentage (%E) of all the water samples in all the seasons observed within the acceptable limit of ±5% (Part 1030 E). In addition, Hill-Piper Trilinear diagram [43], Gibbs diagram [44], and mixing plots were used for the identification of hydrochemical process and natural controlling factors of groundwater sources. Piper diagram was prepared using Aquachem 2014.2 software, the data analysis was performed using IBM SPSS version 20. Further, the irrigation water quality was evaluated by calculating the sodium ion percent (Na%) and sodium adsorption ratio (SAR) of the shallow coastal groundwater sources [40,41].

3.3. *Analysis of groundwater for drinking and domestic purposes*

EWQI, regarded as one of the most acceptable methods [46], weighted arithmetic mean water quality index (WQI), pollution index of groundwater (PIG) followed for the evaluation of analytical data for meeting criteria for drinking purposes. These were applied stepwise accordingly.

3.3.1. *Computation method of entropy-weighted water quality index (EWQI)*

The information entropy method was employed for WQI determination in the present study. For EWQI computation, three steps were followed [47]. Step 1: the weight values of individual indicators are determined by calculating the entropy and entropy weight. The entropy weight reflects the influences of various pollutants. Entropy weight was calculated and assigned to each parameter. Considering, if there are ‘**z**’ water samples (***i*** = 1, 2, 3, 4, …., z), each water sample has ‘***t***’ water quality parameters (***j*** = 1, 2, 3, 4, ….,t) [22,37,48]. Then the Eigen value matrix is constructed as shown in below equation (1).

$$X = \begin{bmatrix} x_{11} & x_{12} & . & . & . & x_{1t} \\ x_{21} & x_{22} & . & . & . & x_{2t} \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ x_{z1} & x_{z2} & & . & & x_{zt} \end{bmatrix} \tag{1}$$

According to the attribution of every index, the feature index may be divided into four types; efficiency type, cost type, fixed type and interval type [30,49]. For the efficiency type, the construction function of normalization (y_{ij}) is given in equation (2).

$$y_{ij} = \frac{x_{ij} - (x_{ij})_{min}}{(x_{ij})_{max} - (x_{ij})_{min}} \tag{2}$$

After transformation, the standard-grade matrix y can be obtained as shown below (3):

$$y = \begin{bmatrix} y_{11} & y_{12} & . & . & . & y_{1t} \\ y_{21} & y_{22} & . & . & . & y_{2t} \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ y_{z1} & y_{z2} & & . & & y_{zt} \end{bmatrix} \tag{3}$$

The standardised value of the jth index in ith sample is denoted as P_{ij} and it is calculated using the following equation (4).

$$P_{ij} = \frac{y_{ij}}{\sum_{i=1}^{z} y_{ij}} \tag{4}$$

The information entropy can be determined by formula (5) below:

$$e_j = -\left(\frac{1}{\ln Z}\right) \times \sum_{i=1}^{z} P_{ij} ln P_{ij} \tag{5}$$

If the smaller the value of ‘e_j’ is, the bigger the effect of ‘j’ index. When the entropy value is large shows that there is a small amount of information and the weight value is small [22,31]. Then the entropy weight (ω_j) can be calculated using equation (6).

$$\omega_j = \frac{1 - e_j}{\sum_{j=1}^{t} (1 - e_j)} \tag{6}$$

where, ω_j is the entropy weight of j parameter.

Step 2. For calculating WQI, it is required to assign the quality rating scale (q_j) for each parameter. The q_j can be calculated by using the following equation (7).

$$q_j = \left(\frac{C_j}{S_j}\right) \times 100 \tag{7}$$

In equation (7), *Cj* is the concentration observed for each chemical parameter (*j*) in mg/L in each water sample, *Sj* is the permissible limit of each observed parameter. In this study, the standard for drinking water chemical parameters recommended by Bureau of Indian Standard (BIS) [50] and world health organisation's (WHO) guideline [12] were used for the water quality index computations.

The final step is to calculate the water quality index (WQI) using equation (8) given below.

$$\text{WQI} = \sum_{j=1}^{t} \omega_j q_j \tag{8}$$

Based on EWQI results, groundwater is classified into Five Ranks, if EWQI<50 water belongs to 'Excellent' quality, EWQI in between 50 and 100 reveals 'Good' quality water, 100–150 belongs to 'Average' water, 150–200 is 'Poor' quality of water and EWQI>200 is 'Extremely Poor' water. The rank classification standards are given in Table S2 Supplementary Material.

3.3.2. *Weighted arithmetic mean water quality index (WQI) method*

The water quality index (WQI) is an important parameter for identifying the water quality and its suitability for drinking purposes [51]. The overall quality of groundwater is represented numerically for drinking and domestic purposes using the water quality index method. In the present study, 15 parameters (pH, DO, EC, TDS, Alkalinity, Total Hardness, Chloride, Iron, SO_4^{2-}, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and biochemical oxygen demand-BOD) were considered for the calculation of WQI for identifying drinking utility. In the weighted arithmetic mean method, a weighing factor (W_i) is determined. These factors were multiplied by all the quality ratings of each parameter and an aggregate was taken to the final result (Equation (9)).

$$\text{Water quality index (WQI)} = \frac{\Sigma W_i q_i}{\Sigma W_i} \tag{9}$$

Where, $q_i = 100*[V_o\text{-}V_i]/[S_i\text{-}V_i]$; $W_i = K/Si$; Where q_i is the quality rating for the *i*th water quality parameters ($i = 1, 2, 3, 4 \ldots N$); V_o = observed value or mean of the observed values of any parameter; V_i = ideal value of that particular parameter, zero for all parameter except pH and DO. V_i for pH = 7 and for DO = 14.6 mg/L; *Si* = standard permissible value of particular parameter, determined by WHO. The standard permissible value and W_i calculated for each parameter for the calculation of WQI are presented in Table S3, Supplementary material. These values are used for the computation of quality rating (*qi*) for each parameter.

The water is classified into five according to the level of WQI values. 0–25 belongs to Excellent water quality with '*A*' grade. 25–70 belongs to the 'Good' category with '*B*' grade. 51–75 is Poor with '*C*' grade, 76–100 is Very Poor water quality with '*D*' grade; WQI >100 is Unfit for drinking purposes with '*E*' grade.

3.3.3. *Pollution index of groundwater (PIG)*

The pollution index of groundwater (PIG) was proposed by Subba Rao (2012) [52]. Drinking water quality is assessed using this PIG method. Five steps are involved in the computation. The first step (1), is to find relative unit weight (*Rw*) on a scale of 1–5. The values can be assigned based on their impact on human health. The unit weight of each parameter and corresponding BIS values are given in Table 2.

The second step (2), is to evaluate the weight parameter (*Wp*) of each to assess their relative contribution to the groundwater quality. It is the ratio of *Rw* and $\sum Rw$ as shown in equation (10).

In the third step (3), estimated the status of concentration (*Sc*) by dividing the result of each water quality parameter (*C*) in each of the water samples by their respective standard limits D_S (Equation (11)). In this study, permissible limits of water quality parameters recommended by BIS [50] and WHO [12] were used for the PIG assessment. In the fourth step (4), the overall quality of the groundwater (*Ow*) was computed by multiplying the *Wp* with the *Sc*, as shown in equation (12).

The final step in the PIG assessment involved the summation of all the *Ow* values per sample (Equation (13)).

Table 2
Components used for PIG computation.

Parameters (C)	Unit	Relative Weight *(Rw)*	Weight Parameter *(Wp)*	Standard Value *(Ds)*
pH	–	3	0.08	8.5
TDS	mg/L	5	0.14	500
Cl^-	mg/L	4	0.12	250
Iron	mg/L	4	0.12	0.3
SO_4^{2-}	mg/L	5	0.14	200
NO_3^-	mg/L	5	0.14	45
Na^+	mg/L	4	0.12	200
K^+	mg/L	1	0.03	12
Ca^{2+}	mg/L	2	0.05	75
Mg^{2+}	mg/L	2	0.05	30
		$\sum R_W = 35$	$\sum W_P = 1.00$	

Table 3
Summary of physico-chemical parameters in the study are Alappad Coast, Kollam, Kerala, India.

Parameters	Minimum			Maximum			Standard deviation			BIS (2012) limit	WHO (2017) limit
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon		
Temperature (°C)	27.9	25.5	24.9	32.5	31.0	30.7	1.2	1.4	1.6	–	–
pH	7.0	6.9	7.2	8.4	8.3	8.6	0.4	0.4	0.4	6.5–8.5	6.5–8.5
Eh (mV)	−82.0	−77.0	−90.0	−2	9.0	−10.0	25.4	25.3	21.0	–	–
EC (μS/cm)	150.0	420.0	410.0	10510.0	3540.0	2020.0	2510.0	771.4	413.5	–	1500.0
Turbidity (NTU)	0.0	0.0	0.3	2.2	70.0	2.8	0.6	17.7	0.7	5.0	5.0
TDS (mg/L)	45.0	105.0	103.0	2660.0	864.0	521.0	629.7	189.8	105.1	500.0	1000.0
DO (mg/L)	0.4	0.8	1.2	7.7	8.3	6.6	2.5	2.6	1.9	–	–
BOD (mg/L)	0.0	0.0	0.0	6.0	3.8	9.9	1.3	1.2	2.4	–	–
Alkalinity (mg/L)	50.8	90.9	92.7	375.6	292.9	298.7	87.6	62.0	67.1	200	–
HCO_3^- (mg/L)	61.9	110.9	113.1	458.2	357.4	364.4	106.9	75.7	81.8	–	–
Hardness (mg/L)	49.0	39.2	70.6	2250	460.6	539.0	542.9	124.9	115.7	600	100
Cl^- (mg/L)	11.7	7.7	3.9	2014.7	549.6	43.4	510.2	136.2	11.0	250	250
Iron (mg/L)	0.0	0.0	0.0	0.98	5.1	0.2	0.4	1.3	0.1	0.3	0.1
SO_4^{2-} (mg/L)	0.0	0.0	0.0	432.8	202.5	174.3	129.8	51.4	54.0	200	400
PO_4^{3-} (mg/L)	0.0	0.0	0.0	1.13	1.4	1.9	0.3	0.5	0.5	–	–
NO_3^- (mg/L)	−0.1	0.0	0.0	3.8	5.3	1.3	1.2	1.3	0.4	45	50
Na^+ (mg/L)	11.8	11.8	30.4	818.0	415.5	100.1	200.7	101.4	21.9	–	200
K^+ (mg/L)	1.3	1.9	2.8	21.9	19.6	24.1	5.2	5.2	5.4	–	12
Ca^{2+} (mg/L)	7.9	10.2	13.3	489.6	156.8	180.3	117.9	36.3	39.8	75	200
Mg^{2+} (mg/L)	3.6	3.3	3.3	248.3	75.9	21.3	61.4	18.3	5.9	30	150

$$\text{Wp} = \frac{\text{Rw}}{\sum \text{Rw}} \tag{10}$$

$$\text{Sc} = \frac{\text{C}}{\text{Ds}} \tag{11}$$

$$\text{Ow} = \text{Wp x Sc} \tag{12}$$

$$\text{PIG} = \sum \text{Ow} \tag{13}$$

The final PIG values are classified into Five Groups. If $PIG < 1$ indicates Insignificant Pollution (IP); $1.0 < PIG < 1.5$ indicates Low Pollution (LP); $1.5 < PIG < 2.0$ signifies Moderate Pollution (MP); $2.0 < PIG < 2.5$ indicates High Pollution (HP); and $PIG > 2.5$ indicates Very High Pollution (VHP).

3.4. Statistical analysis

3.4.1. Principal component analysis

The principal component analysis is used to explain the variance of interrelated variables for reducing the dimensionality of a large data set [34]. Multivariate statistics can identify hidden relationships between variables [53]. The analysed physico-chemical parameters were used for the principal component analysis using IBM SPSS version 20, software. The Varimax rotation with Kaiser Normalization [54] method was applied to extract the principal components. Principal components having eigen values > 1 is considered as the significant influential water quality parameters of the data set. PCA loadings with total variance and percentage cumulative variance of each component were determined. The parameters having greater absolute loadings are considered to have higher significance within the same component.

3.4.2. Hierarchical cluster analysis (HCA)

Hierarchical cluster analysis (HCA) also performed as a data reduction technique, without losing much information. Cluster analysis creates groups among the variables have similar characteristics [55]. HCA illustrated by a tree diagram or dendrogram which provide the information on similarities among a large set of data. The statistical package for social sciences (SPSS) were used to perform the cluster analysis. The standardised z-scores was applied for R-mode (to group the parameters) and Q-mode (to group the sampling stations) hierarchical cluster analyses based on their similarities and differences in various seasons [56].

3.4.3. Pearson's correlation

Pearson's correlation matrix was constructed for the three seasons (pre-monsoon, monsoon, and post-monsoon) using SPSS, IBM statistics-version 20 package. The correlation coefficient is the strength and direction of the linear relationship between the water quality parameters and analysed WQI. The correlation coefficient r can be determined by the following equation (14) [57].

$$\text{r} = \frac{n\sum xy - (\sum x)(\sum y)}{\sqrt{\left[n(\sum x^2) - (\sum x)^2\right]} \times \sqrt{\left[(n(\sum y^2) - (\sum y)^2\right]}} \tag{14}$$

where x and y are the variables to be compared, n is the number of variables. The correlation coefficient 'r' is determined by using equation (14). Where x and y are the variables to be measured and n is the number of variables or parameters. If the correlation coefficient $r > 0.8$ is considered a strong positive correlation, $r < 0.5$ indicate a weak correlation.

4. Results and discussion

4.1. Hydrochemical characteristics

The phreatic groundwater was the only main source of drinking water for the communities in the study area before Indian Ocean tsunami (26 December 2004). After this disaster, due to extensive inundation by giant waves with high run up, shallow groundwater resources were underutilised for the drinking and domestic purposes. In this context, seasonal variation of groundwater of the coastal phreatic aquifer is assessed. Overall water quality condition is explained with various physico-chemical parameters and computed the water quality index (See Tables S5–S7, Supplementary material). The permissible limits prescribed by WHO [12] and BIS [50] are chosen as the basis to determine the suitability of groundwater for drinking purposes. The descriptive summary of physico-chemical parameters are presented in Table 3. The pH value of groundwater is in the range of 7.0–8.4 in pre-monsoon (mean 7.8 ± 0.4), 6.9–8.3 in monsoon (mean 7.7 ± 0.4) and 7.2–8.6 during post-monsoon (mean 7.8 ± 0.4) revealed that groundwater is alkaline nature in this area [39] and within the permissible limit of 6.5–8.5. Drinking water having pH > 8 causes gastro-intestinal problems and acidic pH causes corrosion effect.

Electrical conductivity (EC) in pre-monsoon ranged 150.0–10510.0 μS/cm (mean 1559.3 ± 2510.6 μS/cm). EC ranged 420.0–3540.0 μS/cm in monsoon (mean 1044.0 ± 771.4) and 410.0–2020.0 μS/cm in post-monsoon (mean 1023.3 ± 413.5 μS/cm). EC in sampling sites DW8 (10510.0 μS/cm) and DW11 (1740.0 μS/cm) during the pre-monsoon season was observed above the permissible limit of 1500 μS/cm of WHO [12]. In monsoon, DW8 (3540.0 μS/cm) and DW11 (1710.0 μS/cm) showed EC above the permissible limit. During the post-monsoon period, DW11 showed high EC (2020.0 μS/cm) than the permissible standard limit [12]. High conductivity in this station indicates the presence of high inorganic pollutants such as dissolved salts, sewage water, agricultural run off and seawater intrusion. Groundwater in the study area showed turbidity within the permissible limit of 5 NTU of BIS [50], except for samples DW2 (70.0 NTU), DW8 (11.0 NTU) and DW11 (6.0 NTU) in the monsoon season. It may be due to the effect of southwest monsoon rain fall during the period, altered the sediment chemistry in the bottom of the dug well that noted during sample collection.

Coastal fisherman settlers along this area are socially and economically backward and depend on well water for their domestic needs throughout the year. Rainwater is an alternative source of water for domestic uses, hence communities in the study area are less dependent on dug wells during the monsoon period (southwest-northeast monsoon and the beginning of post-monsoon). Total dissolved solids originated as a result of the chemical weathering and dissolution of soil and sediment matter in contact with the groundwater [42]. During the pre-monsoon season, TDS was observed higher than the other two seasons. The permissible acceptable limit of TDS in drinking water is 500 mg/L [50]. High TDS concentration in drinking water affects the kidney functioning and heart diseases [39].

Alkalinity in water is due to the presence of dissolved bicarbonates and hydroxide compounds of calcium, sodium and potassium [58]. It is the ability of water to neutralise acids. Alkalinity ranged from 50.8 to 375.6 mg/L with mean (258.4 ± 106.9 mg/L), 90.9–292.9 mg/L, mean (177.8 ± 62.0 mg/L), and 92.7–375.6 mg/L, mean (189.5 ± 67.1 mg/L) for pre-monsoon, monsoon and post-monsoon seasons respectively. The alkalinity of 73% of groundwater in pre-monsoon season is above the permissible limit of 200 mg/L of BIS 2012 [50]. Monsoon and post-monsoon seasons (33%) observed higher alkalinity than the permissible limit [12].

Total Hardness ranged from 49.0 to 2250.0 mg/L (mean 355.0 ± 542.9 mg/L) in pre-monsoon and 32.9–460.6 mg/L during monsoon (mean 191.6 ± 124.9 mg/L) and 70.6–539.0 mg/L in post-monsoon seasons (mean 199.4 ± 115.7 mg/L). Total hardness concentration in 27% samples showed higher than the permissible limit of BIS [50] during pre-monsoon (DW5, DW6, DW11, DW9, DW13) and three samples (DW5, DW8, DW11) in monsoon periods (20%). The elevated hardness in the study area is presumed to have the presence of dolomite. Post-monsoon (ranged 70.6–539.0 mg/L) has reported total hardness of all the samples, is well below the standard permissible limit of 600 mg/L (Fig. S3, and Table S4 Supplementary material), except DW 11 (539.0 mg/L). Hardness of drinking water having above prescribed limit of 600 mg/L of BIS [50], causes adverse health effects like cardio vascular mortality, diabetes, growth retardation, neural disease, renal dysfunction and reproductive failure [12].

Chloride concentration in groundwater sources showed all the samples belongs to the permissible limit of 250 mg/L [50] except DW 8 (Cl^- 2014.7 mg/L). Cl^- in pre-monsoon (ranged 11.7–2014.7 mg/L, mean 173.4 ± 510.2 mg/L), monsoon (ranged 7.7–549.6 mg/L, mean 59.3 ± 136.2 mg/L) and post monsoon (ranged 3.9–43.4 mg/L, mean 23.3 ± 11.01 mg/L) observed within the permissible limit. Drinking water should maintain acceptable limit of Cl^- content otherwise, continuous intake of high chloride containing water adversely effects on digestion system and heart and kidney functions [12].

Sulphate occurs naturally in water due to the leaching from gypsum and other common minerals [59]. Sulphate content changes significantly with time during rainfall and infiltration of groundwater. Excess amounts of sulphate in drinking water caused a laxative effect on the humans [60]. DW 8 (317.0 mg/L) and DW 11 (432.8 mg/L) showed sulphate concentrations above the permissible limit during the dry period. Sulphate ranged from 0.0 to 432.8 mg/L and mean 61.0 ± 129.8 mg/L during pre-monsoon. Sulphate content in monsoon period ranged 0.0–202.5 mg/L, mean 18.7 ± 51.4 mg/L. Post monsoon revealed (range 0.0–174.3 mg/L, with mean 27.6 ± 54.0 mg/L) that all the samples are within the permissible limit of 200 mg/L [50]. Excess SO_4^{2-} in drinking water causes cathartic effects in infants [12]. Sampling station DW8 was situated on the seaward side of the study area and showed occurrence of higher electrical conductivity (EC), TDS, Cl^-, SO_4^{2-} and Na^+. In monsoon season, except for turbidity (7.0 ± 17.7 NTU), all the parameters belong to the permissible standard limit [50]. During post-monsoon season mean values of all the water quality parameters are within the permissible limit of WHO [12] and BIS [50] with less spatial variation.

Total iron concentration in groundwater sources of the study area during pre-monsoon varied from 0.0 to 0.98 mg/L (0.3 ± 0.4 mg/L) and showed five stations (33%) are above the permissible limit of 0.3 mg/L of BIS & WHO [12,50]. In monsoon period, 47% samples showed iron concentration above the permissible limit (range 0.0–5.1 mg/L, mean 0.9 ± 1.3 mg/L). During the post-monsoon period (range 0.0–0.2 mg/L, mean 0.02 ± 0.07 mg/L), most samples showed below the detectable limit of iron content.

Calcium (Ca^{2+}) in the groundwater sources varied from 7.9 to 489.6 mg/L in pre-monsoon with average 89.3 ± 117.9 mg/L. Monsoon (range 10.2–156.8 mg/L, mean 55.4 ± 36.4 mg/L) and post-monsoon seasons (range 13.3–180.3 mg/L, mean 64.3 ± 39.8 mg/L) showed lower calcium ion concentration than the pre-monsoon period. Excess intake of calcium leads to bladder stone and rickets [12].

Bicarbonate (HCO_3^-) showed elevated concentration during pre-monsoon season varied from 61.9 to 458.2 mg/L with mean of 258.4 ± 106.9 mg/L. Monsoon (range 110.9–357.4 mg/L) and post-monsoon (range 113.1–364.4 mg/L) showed mean 216.9 ± 75.7 mg/L and 231.2 ± 81.8 mg/L respectively. The order of ionic dominance in groundwater is in the decreasing order $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ for cations in pre-monsoon and $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ for the monsoon and post-monsoon seasons. The abundance of anion during pre-monsoon was in the decreasing order $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > PO_4^{3-}$. The concentration of NO_3^- was slightly higher (0.9 ± 1.2 mg/L) in pre-monsoon than monsoon (0.7 ± 1.3 mg/L) and post-monsoon (0.5 ± 0.4 mg/L). The dominance of anions in monsoon period became in the order $HCO_3^- > Cl^- > SO_4^{2-} > PO_4^{3-} > NO_3^-$. Sulphate content was observed higher (61.0 ± 129.8 mg/L) in pre-monsoon season than the monsoon (18.7 ± 51.4 mg/L) and post-monsoon (27.6 ± 54.0 mg/L) seasons. The order of dominance of anions are $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > PO_4^{3-}$ are confirmed.

A desirable amount of sodium is essential to maintain human health. Whereas, an excess sodium intake will cause adverse health risks such as hypertension and osteoporosis [7]. A higher concentration of Na^+ may risk persons suffering from cardiac, renal and artery diseases [44]. Higher sodium content in groundwater is observed in pre-monsoon season (96.0 ± 200.7 mg/L). Closeness of Arabian Sea near to the study area and possible saline water intrusion could contribute. The fresh water is constantly susceptible to contamination from salt ingress because coastal resources are directly adjacent to the ocean [10,61]. Sodium content in monsoon and post-monsoon showed 50.8 ± 101.4 mg/L and 59.8 ± 21.9 mg/L respectively (Text S1, Supplementary material). Mean of electrical conductivity (1559.3 ± 2510.6 μS/cm), hardness (355.0 ± 542.9 mg/L) and calcium (89.3 ± 117.9 mg/L) in pre-monsoon (See Tables S5–S7, Supplementary material), are above permissible limits of BIS and WHO [12,50].

4.2. Groundwater quality assessment by EWQI method

The calculation of entropy weighted water quality index (EWQI) were carried out for all the samples in the study area for the three seasons. A total of 45 samples (15 samples seasonally) were analysed for the computation of WQI by entropy weighted method. The information entropy and entropy weight of each water quality parameter was determined (Table S8, Supplementary material). The quality rating of each parameter is obtained with the percentage ratio of the observed value of each parameter and the standard value. Finally, the sum of the product of entropy weight and quality rating of each parameter was performed to obtain the overall EWQI. The entropy weighted water quality index and quality rank for each water sample was calculated and presented in Table 4. As per EWQI the groundwater is classified into five ranks (excellent, good, medium, poor, extremely poor).

The entropy weight (ω_i) of Cl^- ($\omega_i = 0.16$), SO_4^{2-} ($\omega_i = 0.11$) Na^+ ($\omega_i = 0.10$), and Fe ($\omega_i = 0.10$) observed higher values than other parameters signifies the major contributor as pollutant in the groundwater sources during pre-monsoon season. Iron observed as the significant pollutant, showed the mean concentration 0.3 ± 0.4 mg/L in pre-monsoon, and 0.9 ± 1.3 mg/L in monsoon seasons. In monsoon season higher values for entropy weight was observed for turbidity ($\omega_i = 0.12$), Cl^- ($\omega_i = 0.12$), SO_4^{2-} ($\omega_i = 0.14$), Na^+ ($\omega_i = 0.12$) and Fe ($\omega_i = 0.10$). In post-monsoon season higher entropy weights observed for turbidity ($\omega_i = 0.11$), Fe ($\omega_i = 0.21$) and SO_4^{2-} ($\omega_i = 0.16$) and Na^+ ($\omega_i = 0.10$). Entropy weight less than 0.1 indicating relatively less contributors to groundwater contamination [25].

Based on the entropy weight the parameters are arranged in their following decreasing order $Cl^- > SO_4^{2-} > Na^+ > Mg^{2+} >$ Iron > hardness > EC > NO_3^- > TDS > $Ca^{2+} > K^+ >$ DO > pH > Alkalinity > BOD for pre-monsoon season. Monsoon seasons observed the decreasing order of entropy weight (ω_i) are as follows SO_4^{2-} > Turbidity > $Cl^- > Na^+ > Mg^+ > NO_3^-$ > Iron > TDS > EC > K^+ > DO > TH > Ca^{2+} > BOD > Alkalinity > pH and post-monsoon season showed the order Iron > SO_4^{2-} > Turbidity > BOD > Na^+ > TH > Mg^{2+} > DO > NO_3^- > pH > $K^+ > Ca^{2+}$ > Alkalinity > TDS > EC > Cl^- respectively.

According to Shannon (1948) the summation of entropy weight is always unity [30,36]. Therefore, the computed relative weights (ω_j) are free from subjective judgments. Many researchers observed that the computed information entropy (e_j) and entropy weights (ω_j) are inversely related. For smaller value of e_j, higher the information contents provided by the j^{th} index of parameters (j index) [22, 25,28,34,62]. In this study, iron content in post-monsoon season has value below the permissible level. Information entropy and entropy weight for iron observed almost similar values. This is because, the measured values are below the detectable level (BDL) in most of the stations (hence $pij = 0$). In the calculation process of the entropy weight, when the normalized value $pij = 0$, then the $pij \times ln$

Table 4
Classification of groundwater sources based on EWQI ranking in various seasons in the study area- Alappad Coast, Kollam, Kerala, India.

Seasons	EWQI Category	Water Quality	No. of Samples	% samples	Station ID
Pre-monsoon (PRM)	<50 (Rank 1)	Excellent	8	53	DW1, DW2, DW3, DW7, DW10, DW12, DW13, DW15
	50–100 (Rank 2)	Good	5	33	DW4, DW5, DW6, DW11, DW14
	100–150 (Rank 3)	Average	0	0	–
	150–200 (Rank 4)	Poor	1	7	DW9
	>200 (Rank 5)	Extremely poor	1	7	DW8
Monsoon (MON)	<50 (Rank 1)	Excellent	10	66	DW1, DW3, DW6, DW7, DW9, DW10, DW12, DW13, DW 14, DW 15
	50–100 (Rank 2)	Good	3	20	DW4, DW5, DW11
	100–150 (Rank 3)	Average	0	0	–
	150–200 (Rank 4)	Poor	1	7	DW8
	>200 (Rank 5)	Extremely poor	1	7	DW2
Post-monsoon (POM)	<50 (Rank 1)	Excellent	12	80	DW1, DW3, DW4, DW6, DW7, DW8, DW9, DW10, DW12, DW13, DW14, DW15
	50–100 (Rank 2)	Good	3	20	DW2, DW5, DW11
	100–150 (Rank 3)	Average	0	0	–
	150–200 (Rank 4)	Poor	0	0	–
	>200 (Rank 5)	Extremely poor	0	0	–

pij become zero [25]. This zero values led to low entropy and high weight for iron. Hence, entropy weight of iron represents 20% of the contribution towards the groundwater chemistry of the region.

EWQI analysis for each groundwater sample revealed that, eight groundwater samples (53%) were ranked "excellent" (rank 1) category, and found suitable for drinking (Table 2) during the pre-monsoon season. Those stations are DW1, DW2, DW3, DW7, DW10, DW12, DW13 and DW15 belong to the northern part and southern most end of the study area. Groundwater samples DW4, DW5, DW6, DW11, and DW14 are placed "good" (rank 2) quality (33%), which are suitable for drinking purpose. Samples DW9 observed "poor" (7%) and station DW8 recorded "extremely poor" quality (7%) are 'not suitable' for drinking purpose during the pre-monsoon season.

Monsoon season showed 66% samples placed "excellent" (rank 1), 20% samples had "good" (rank 2) water quality and these groundwater is suitable for drinking. Sample DW 8 has "poor" (rank 4) water quality, are 'not suitable' for drinking. DW2 belongs to "extremely poor" (7%) (Rank 5) water quality during monsoon season in 2018. However, in the post-monsoon, groundwater showed "good" to "excellent" quality. Eighty percentage (80%) of samples (DW1, DW3, DW4, DW6, DW7, DW8, DW9, DW10, DW12, DW13, DW14 and DW15) has "excellent" (ranked 1) water quality. Samples DW2, DW5 and DW11 belong to "good" water quality (20%). The seasonal variation of computed EWQI were presented in Table 4. The EWQI varied 22–281 in pre-monsoon, 20–310 in monsoon and 20–73 in post-monsoon seasons.

The EWQI values less than 100 are considered as 'good' for domestic and drinking uses. The EWQI of samples DW1, DW3, DW7, DW10, DW12, DW13 and DW15 had placed excellent water quality during the three seasons (Fig. 2). These groundwater sources are suitable for drinking purposes according to entropy weighted water quality index (Table 4). Results showed that seasonal mean of EWQI (71.4 ± 71.3) in pre-monsoon was 'good' quality; monsoon (66.1 ± 77.7) and post-monsoon (38.2 ± 14.5) observed 'good' and 'excellent' respectively. Groundwater having EWQI greater than 100 is unsuitable for human health and threat to normal body physiology. Station DW8 observed 'extremely poor' quality in pre-monsoon and 'poor' quality in monsoon. During pre-monsoon, DW8 has TDS (2250.0 mg/L), Na^+ (818.0 mg/L) and Cl^- (2014.7 mg/L) were observed in elevated concentrations. Drinking water having TDS higher than the recommended limit of 500 mg/L causes human kidney failure. The distribution maps of calculated EWQI were drawn using the Geographic information system (GIS) technique is illustrated in Fig. 6a–c.

4.3. Groundwater quality using weighted arithmetic mean WQI method

The weighted arithmetic water quality index was calculated to represent the groundwater purity for drinking purpose. The guideline values of WHO [12] were used for the computation of WQI for the study area. WQI values showed that the quality of water decreases in pre-monsoon and monsoon seasons (See Table S9, Supplementary material). The mean WQI values are 93.4 ± 100.4 (pre-monsoon), 241.5 ± 356.0 (monsoon) and 27.1 ± 26.3 (post-monsoon). Based on weighted arithmetic water quality index 33% of samples in pre-monsoon, 47% in monsoon season are unsuitable for drinking purpose. Which is attributed by the high hardness content in pre-monsoon (2250 mg/L in DW8) and elevated concentration of dissolved iron in monsoon season (0.9 ± 1.3 mg/L). The reverse ion exchange process is the reason for the increased hardness content in groundwater sources of coastal alluvium [63]. Reverse softening (reverse ion exchange) occurring in the study area can be expressed as:

$$2Na^+ + Ca - Clay \rightarrow Ca^{2+} + Na_2 - Clay \qquad (15)$$

in shallow phreatic aquifers, the calcium and magnesium ions in the aquifer matrix exchanged with the excess sodium ions in the groundwater. Based on the physico-chemical parameters, the average values of chloride content is greater than the sodium concentration in groundwater ($Cl^- > Na^+$). This may be due to the dissolution of ions, such as Ca^{2+}, Mg^{2+}, K^+ and iron from aquifers in exchange of Na^+. The seawater ingress or saline water from the coast of Arabian Sea contribute the chloride content in groundwater.

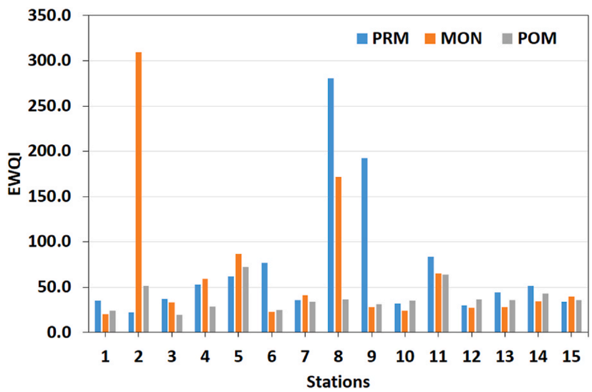

Fig. 2. Seasonal variation of EWQI in the study are Alappad Coast, Kollam, Kerala, India.

Table 5
Varimax rotated principal component factors for various seasons.

Parameters	**Pre-monsoon**				**Monsoon**					**Post-monsoon**				
	Factor				Factor					Factor				
	1	2	3	4	1	2	3	4	5	1	2	3	4	5
pH	0.01	−0.04	0.08	**0.97**	0.41	−0.13	−0.43	**0.67**	−0.15	0.07	0.06	**0.87**	−0.18	0.00
Eh	−0.02	0.07	0.00	**0.95**	0.03	0.17	0.13	**0.94**	0.06	−0.01	0.03	**0.93**	0.16	0.04
EC	0.97	−0.04	−0.07	0.11	**0.88**	0.15	0.41	0.03	0.07	**0.92**	0.17	−0.03	0.22	−0.06
Turbidity	−0.27	**0.80**	−0.29	0.24	0.04	**0.91**	0.16	0.22	0.12	−0.08	−0.08	0.03	0.36	**0.85**
TDS	**0.95**	0.08	0.20	0.09	**0.81**	0.07	**0.53**	−0.02	0.20	**0.96**	0.13	0.00	0.14	−0.09
DO	−0.03	−0.76	−0.19	**0.51**	−0.25	−0.12	−0.38	**0.79**	0.18	0.12	−0.32	**0.80**	−0.29	0.01
BOD	0.15	0.46	0.04	0.49	0.22	0.18	−0.05	0.12	**−0.91**	−0.01	**0.84**	0.19	0.04	−0.19
Alkalinity	0.24	**0.58**	**0.70**	0.06	0.38	0.03	**0.84**	−0.20	−0.23	0.37	**0.50**	0.04	0.02	**−0.53**
HCO_3^-	0.23	**0.58**	**0.71**	0.06	0.37	0.11	**0.86**	−0.14	−0.13	0.34	**0.58**	0.03	0.18	**−0.56**
Total hardness	−0.06	0.00	**0.97**	0.07	**0.57**	−0.30	**0.69**	0.00	0.26	**0.91**	0.27	0.03	−0.12	−0.16
Cl^-	**0.93**	−0.06	−0.13	−0.09	**0.87**	0.18	0.13	−0.18	−0.19	0.14	−0.49	−0.32	**0.63**	−0.23
Iron	−0.38	0.11	−0.21	−0.54	0.01	**0.89**	−0.02	−0.13	−0.27	0.16	**0.73**	−0.27	0.15	0.07
SO_4^{2-}	**0.56**	−0.64	0.06	0.20	0.27	0.14	−0.09	0.35	**0.81**	**0.82**	−0.26	0.25	−0.15	0.29
PO_4^{3-}	0.05	**0.92**	−0.03	0.08	0.37	**0.89**	−0.13	0.06	−0.06	−0.20	0.14	−0.04	**0.75**	0.27
NO_3^-	0.09	**0.90**	0.20	−0.02	**0.86**	0.17	0.29	0.17	0.08	**0.56**	0.10	0.47	−0.18	**0.51**
Na^+	**0.96**	−0.06	−0.05	0.03	**0.83**	0.33	0.06	0.22	−0.14	−0.02	0.12	−0.09	**0.91**	0.11
K^+	**0.86**	0.21	0.15	0.11	0.39	**0.73**	−0.13	−0.11	0.13	−0.06	0.09	0.05	0.01	0.15
Ca^{2+}	−0.12	0.08	**0.95**	0.10	0.25	−0.51	**0.74**	0.01	0.31	**0.91**	0.06	0.05	−0.26	−0.12
Mg^{2+}	0.06	−0.23	**0.87**	0.00	**0.86**	0.05	0.23	−0.08	0.02	**0.51**	0.63	−0.12	−0.16	−0.12
Eigenvalues	5.45	7.73	3.2	2.6	7.46	4.02	2.77	1.7	1.16	5.89	6.34	2.43	2.03	1.75
% Variation	28.7	24.9	16.8	13.7	39.3	21.1	14.6	8.9	6.1	30.9	19.2	12.8	10.7	9.2
Cum. % Variation	28.7	53.65	70.5	84.2	393	60.4	74.9	83.9	89.9	30.9	50.2	62.9	73.6	82.9

4.4. Groundwater quality based on pollution index of groundwater (PIG)

In the present study, the evaluation of groundwater samples by pollution index of groundwater showed the majority of the stations belong to an insignificant pollution condition. Quantitatively (87%) in pre-monsoon (mean 0.6 ± 0.6), (73%) in monsoon (mean 0.6 ± 0.6), and (100%) in post-monsoon (0.3 ± 0.1) showed insignificant pollution. DW8 showed very high pollution (PIG = 2.5) in pre-monsoon and moderate pollution index for DW8 (PIG = 1.6) in monsoon season (See Table S10, Supplementary material). Pollution by salt ingress is a problem in the coastal aquifers of Kerala [21]. Station DW8 is situated almost 15 m away from the sea shore (Arabian Sea). Frequently occurring high tide and salt ingress polluted the groundwater. The groundwater from this dug well is only used for washing and gardening purposes as a practice followed.

4.5. Principal component analysis (PCA)

Principal component analysis is a commonly applied multivariate method which helps to find the relationship among different variables in a large data [64]. The log-transformed normalized data computed for the principal component analysis are presented in Table 5. Factor extraction was carried out by principal components on the normalized data sets of 19 variables (pH, Eh, EC, turbidity, TDS, DO, BOD, alkalinity, HCO_3^-, total hardness, Cl^-, Iron, SO_4^{2-}, PO_4^{3-}, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}) separately for pre-monsoon, monsoon and post-monsoon seasons. Factor loading is classified into strong (>0.75), moderate (0.50–0.75) and weak (0.30–0.50) corresponding to the absolute loading values [64]. Depending upon the eigen-values which are more than 1 is considered as the principal components [22].

PCA in pre-monsoon season yields four factors with 84.2% of total variance. PC1 accounted for 28.7% of the total variance, exhibits significant positive loadings on TDS (0.95), Cl^- (0.93), SO_4^{2-} (0.56), Na^+ (0.96) and K^+ (0.86). These high positive loadings of the quality parameters [TDS (0.95), Cl^- (0.93), & Na^+ (0.96)] imply the prominence of salinity caused by the seawater interaction. This component is highly related to the rock weathering and dissolution, since it consists of positive loadings on ions primarily derived from rock minerals [5]. The second component explains 24.9% of total variance and dominated by the turbidity (0.79), PO_4^{3-} (0.92), NO_3^- (0.89), alkalinity (0.58) and bicarbonate (0.58). The positive loading in PO_4^{3-}(0.92), & NO_3^- (0.89) indicate the influence of agricultural and human activities. PC3 represents the correlation between the hardness parameters. Showed that, total variance of 16.9%

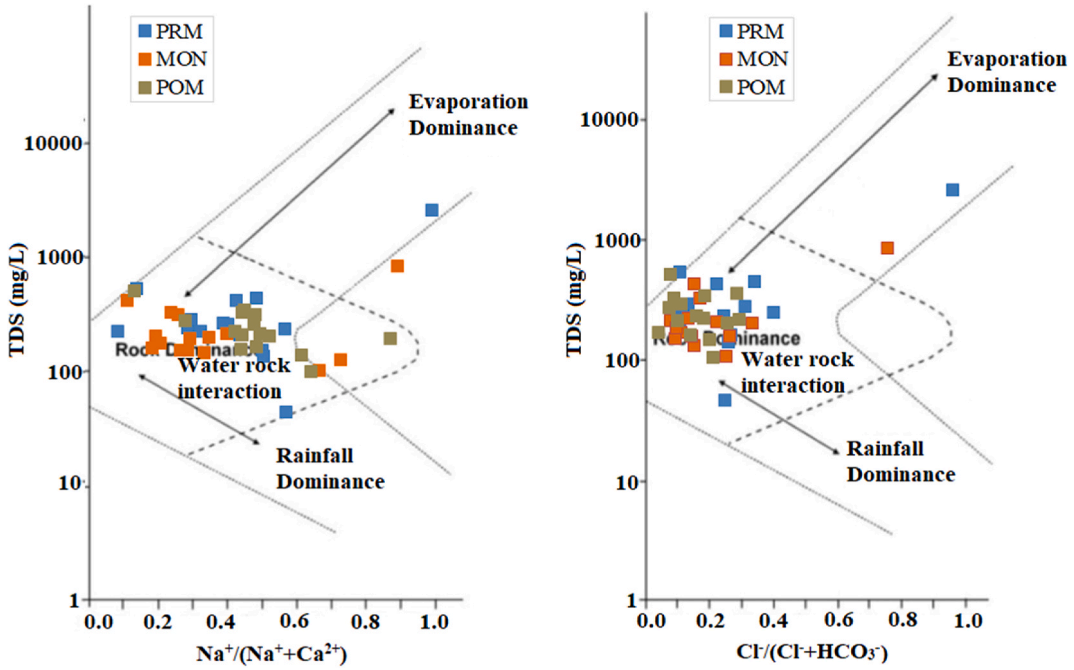

Fig. 3. Gibbs diagram for cations (Na^+/Na^++Ca^{2+}) and anions ($Cl^-/Cl^- + HCO_3^-$) indicating the predominant geochemical process in the study area, Alappad Coast, Kollam, Kerala, India.
Gibbs diagram represents the weight ratios of $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ as a function of TDS is presented to assess the functional sources of dissolved chemical constituents derived from precipitation, weathering and evaporation processes [44,66]. The samples having low TDS (<10 mg/L) and $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ are >0.5, indicate the rainfall dominance. TDS between 70 and 300 mg/L and $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ <0.5 mg/L represents rock dominance. TDS >300 mg/L and $Na^+/(Na^++Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ values between 0.8 and 1.0 shows the dominance of evapocrystallisation [66,67]. The distribution of sample points on the diagram revealed that, chemical weathering of rock forming minerals, dissolution and evaporation are the dominant process influencing the groundwater chemistry. Marine ions carried out by the atmospheric circulation enhance the solute concentration in open groundwater sources along the coastal area [68].

in relation with total hardness (0.97), Ca^{2+} (0.95), Mg^{2+} (0.87), alkalinity (0.70) and bicarbonate (0.71).

In monsoon season 89.9% of groundwater chemistry is controlled by five factors. First Factor (PC1), that explains 39.3% of total variance in relation with TDS (0.81), EC (0.88), Cl^- (0.87), Na^+ (0.83), Mg^{2+} (0.86) and NO_3^- (0.86). The sampling locations are geologically situated in coastal alluvium deposits of the south west coast of India. Alluvial aquifer and sediments usually contains Ca^{2+} and Mg^{2+} resulting elevated content in groundwater. The second factor (PC1) explains 21.13% of total variance with positive correlations in turbidity (0.91), iron- Fe (0.89), PO_4^{3-} (0.89), and K^+ (0.73). Third Factor (PC3) represents significant positive correlation in alkalinity (0.84), HCO_3^- (0.86), TDS (0.53), total hardness (0.69) and Ca^{2+} (0.74). Fourth Factor (PC4) showed positive loadings on pH (0.67), Eh (0.94) and DO (0.79) with total variance contribution of 8.9%. The fifth factor (PC5) represents positive loadings on SO_4^{2-} (0.81) and total variance contributed only 6.1%.

In post-monsoon 82.9% of changes in groundwater quality is explained by five factors indicating high seasonal variation of the water quality parameters. First factor (PC1) explains 31.0% of total variance in relation with EC (0.92), total hardness (0.91), Ca^{2+} (0.91), Mg^{2+} (0.51), SO_4^{2-} (0.82) and NO_3^- (0.56). Second factor (PC2) explains 19.2% of total variance with positive significant loadings on BOD (0.84), alkalinity (0.50), and HCO_3^- (0.58). Third factor (PC3) explains 12.8% of total variance, and is positively influenced by pH (0.87), Eh (0.93) and DO (0.80). Fourth factor (PC4) explains 10.7% of total variance with positive loadings on Na^+ (0.91) and Cl^- (0.63) and PO_4^{3-} (0.75). High loading in PO_4^{3-} (0.75) and NO_3^- contribute pollution from agricultural field and anthropogenic activities. The salinity in groundwater is occurred from the salt ingress from the Arabian Sea, as the sampling locations are situated only a few meters away. The sea water intrusion is a constant threat affected mostly in coastal regions of all over the world [65]. Weathering and leaching of minerals are the common natural process because of the water-rock interactions, and this leads to elevated mineral constituents in coastal groundwaters. Gibbs diagram [44] is plotted to identify the natural process controlling the groundwater chemistry of the coastal region (Fig. 3) for further inferences. The fifth factor (PC5) represents 9.2% of total variation, having positive loadings on turbidity (0.85) and NO_3^- (0.51). The coastal regions are fast-growing centres all over the world. But inadequate waste disposal systems triggerssignificant impact on the freshwater aquifers in these pristine land mass. Subsequently in the study area Alappad coast, Kerala, India the presence of NO_3^- and Cl^- is influenced by anthropogenic inputs, salt intrusion and consequence of agricultural activities.

Hill-Piper Trilinear diagrams are useful to represent the hydrochemical facies of groundwater sources [43]. The milli-equivalent percentage of major cations and anions are plotted in the base triangles and the results are projected onto the central diamond plot. The diamond field is divided into six segments to distinguish the hydro-geochemical facies (Fig. 4). In cation triangle, the dominance of Ca^{2+} (>50%) over Na^+ and Mg^{2+}. The anion triangle showed the dominance of HCO_3^- (>50%), where the samples clustered on the left corner of the base triangle. As shown in Fig. 4, the samples (82%) clustered in Ca–HCO_3 facies indicate temporary hardness of water. The alkaline earth (Ca^{2+}+Mg^{2+}) exceeded the alkalis (Na^++K^+) and weak acids (HCO_3^-) exceed over the strong acids (Cl^- + SO_4^{2-}) in 84% of total samples during the study period. The diamond plot is divided into six and the corresponding water types are: (1) Ca–HCO_3, (2) Na–Cl, (3) Mixed Ca–Mg–Cl, (4) Mixed Ca–Na–HCO_3, (5) Ca–Cl and (6) Na–HCO_3 [42]. During pre-monsoon and post-monsoon 7% of samples observed saline (Na–Cl) and permanent hardness (Ca–Cl) type water. It is observed that, the groundwater tends to saline with increasing TDS, which are mainly related to evaporation of shallow groundwater [5].

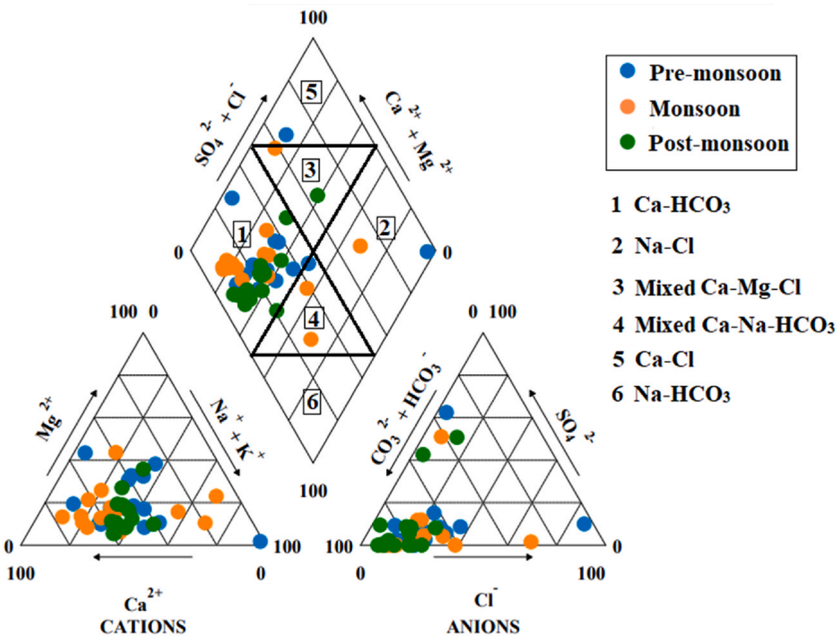

Fig. 4. Hill-Piper Trilinear diagram representing hydrochemical facies of groundwater sources in the study area- Alappad Coast, Kollam, Kerala, India.

The general process involved in the solute concentration of groundwater are silicate weathering, evaporate dissolution and carbonate dissolution [44]. Carbonate weathering contributes the release of Ca^{2+}, Mg^{2+}, HCO_3^- and silicate weathering results the Na^+, K^+, Si, Ca^{2+}, Mg^{2+} and HCO_3^- contribution in water [66]. The relationship between molar ratios of Ca^{2+}/Na^+ *vs* Mg^{2+}/Na^+ and Ca^{2+}/Na^+ *vs* HCO_3^-/Na^+ are shown in Fig. 5a&b. Indicate that, the silicate weathering is the dominant process affecting the groundwater chemistry of the region. Samples, are mostly clustered on areas of silicate weathering and evaporate dissolution for the pre-monsoon, monsoon and post-monsoon season. The Na^+ and K^+ ions are primarily derived from the weathering and dissolution of silicate minerals [44,66]. The bicarbonate content was high in the study area, which implies the dissolution of silicates [5].

4.6. Suitability of groundwater for irrigation purposes

In addition to test/check if ground water could be useful for irrigation, is assessed in terms of sodium adsorption ratio (SAR) and soluble sodium percentage (Na %). Sodium adsorption ratio is a measure to find the sodium hazard caused by the excess sodium ions in the irrigation water [40]. Ion exchange process leads to the removal of Ca^{2+} and Mg^{2+} ions bound in the aquifer material to the groundwater which is having high Na^+ content [69]. The subsequently bound Na^+ to soil become more saline when combined with Cl^- and CO_3^{2-}, which are harmful to crops by altering the soil texture, permeability and porosity [66,70]. SAR<10 is ideal for irrigation and high SAR values indicate the intensity of the sodium hazard, and water is unsuitable for irrigation. On the basis of sodium adsorption ratio, the classification is as follows SAR<10 (ideal or excellent), SAR = 10-18 (good), SAR = 18–26 (doubtful), and SAR >26 unsuitable. SAR is calculated using equation (16).

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \tag{16}$$

Higher SAR indicate the water is unsuitable for irrigation, which affects the permeability and porosity of soil [66]. SAR values of coastal groundwater varied between 0.4 and 46.7 in pre-monsoon (4.3 ± 11.8), 0.43–8.72 in monsoon (1.5 ± 2.1) and, 0.57–5.19 in post-monsoon (2.1 ± 1.1). Groundwater (DW8) in pre-monsoon was observed unsuitable (SAR = 46.7) for irrigation, because the salt ingress to the aquifers near the coast is more (See Fig. S4, Table S11, Supplementary material).

Irrigation water containing high amount of Na^+ influence the plant growth [41]. It is necessary to assess the sodium percentage in phreatic coastal aquifers of this region for further discussions. Classification of water based on Na% (Equation (17)) is excellent (Na% < 20), good (Na% = 20–40), permissible (Na% = 40–60), doubtful (Na% = 60–80) and unsuitable (Na% > 80) [41,71].

$$\text{Na}\,\% = \frac{\text{Na}^+ + \text{K}^+}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+} \times 100 \tag{17}$$

For agricultural purposes, groundwater in pre-monsoon season is in good category (60%) with seasonal mean 35.4 ± 20.7. Whereas, monsoon (32.2 ± 18.5) and post-monsoon (44.2 ± 15.1) seasons has showed 47 and 27% respectively (See Table S12, Supplementary material). The southern part of the study area showed elevated sodium percentage and not suitable for irrigation. The spatial variation of sodium percentage is shown in Fig. 6d–f. Alappad coast and its nearby regions is one of the prominent fishing

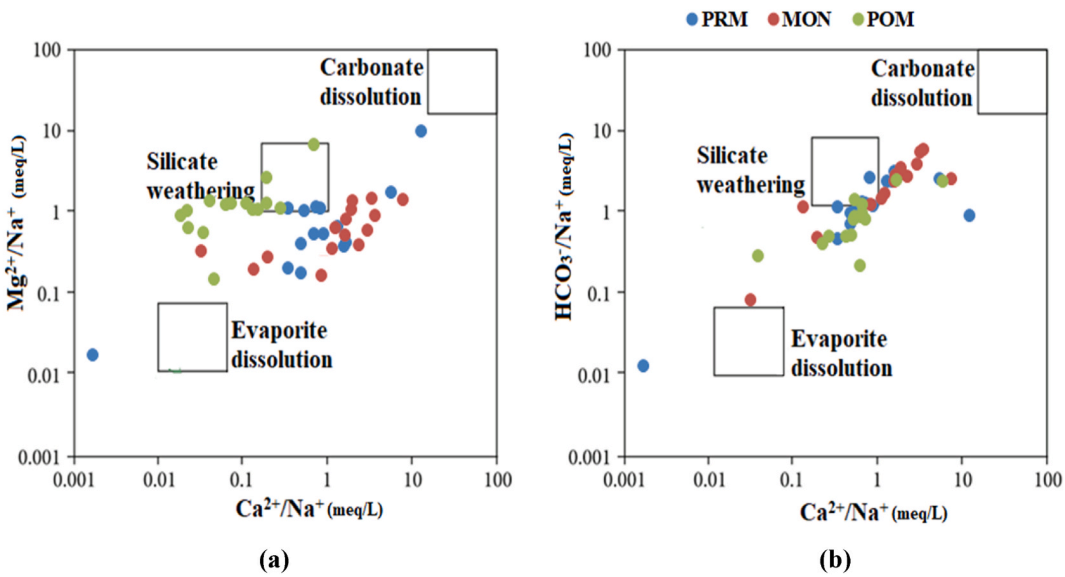

Fig. 5. (a) Mixing diagram of Ca^{2+}/Na^+ vs Mg^{2+}/Na^+, and (b) Mixing diagram of Ca^{2+}/Na^+ vs HCO_3^-/Na^+ in the study area Alappad Coast, Kollam, Kerala, India.

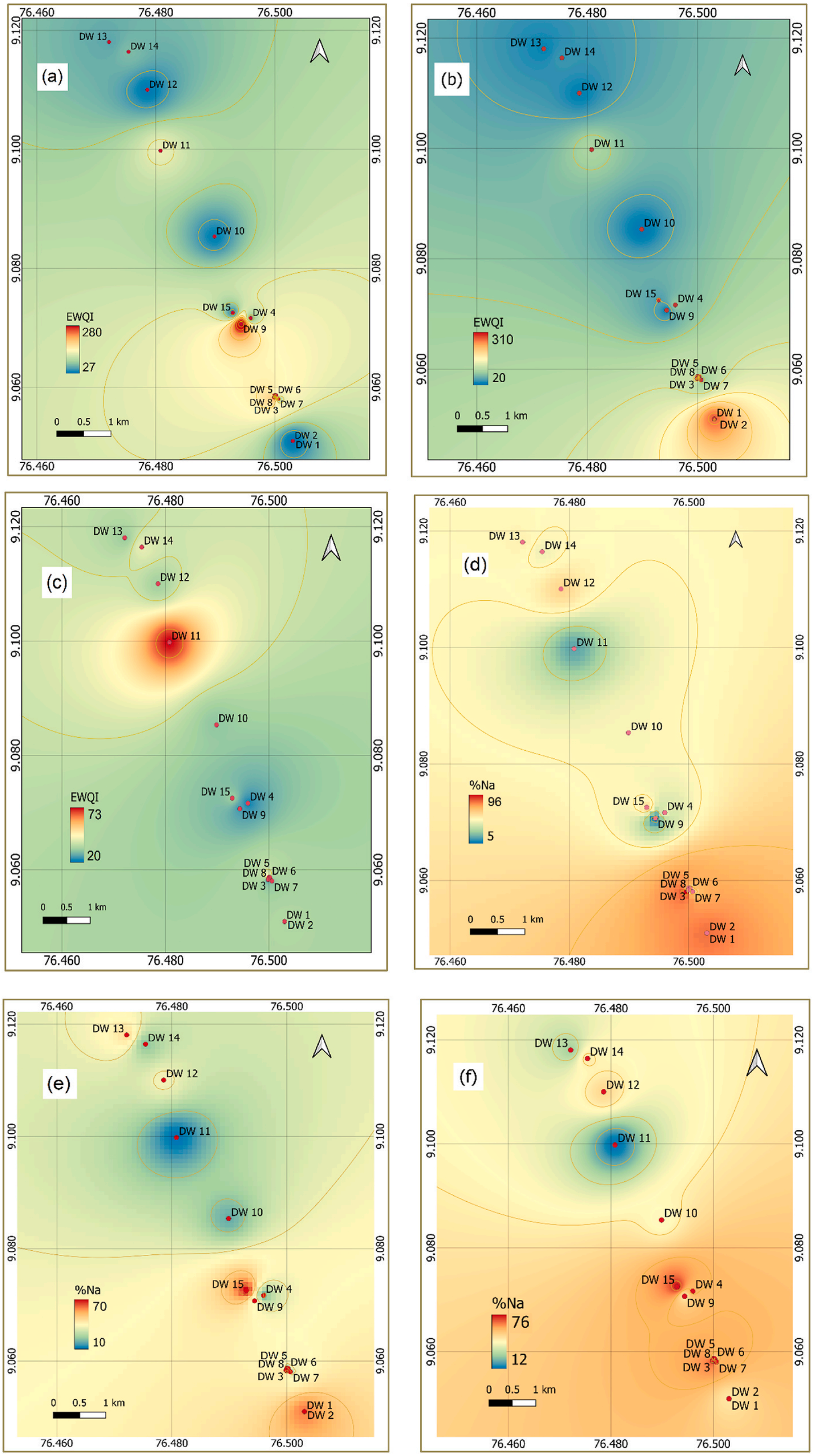

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Fig. 6. Drinking water quality status based on EWQI (a-Pre-monsoon, b-Monsoon, c-Post-monsoon) and irrigation water quality based on Na% (d-Pre-monsoon, e-Monsoon, f-Post-monsoon) in the study area- Alappad Coast, Kollam, Kerala, India.

villages in the Kerala state, bears rich black sand deposits- mined, explored and largely exported by public industries. Sand mining has stronginfluence on groundwater quality by mixing the freshwater with the saline water. High spatial variability of anions and nitrate content indicate the anthropogenic activities [69]. Overall, Na% of some locations (DW8) are 'doubtful' (Na% 60–80) and 'unsuitable' (Na% > 80) for irrigation indicate higher salinity and TDS in the groundwater [41]. Any change in the natural flow or by acid leachate or pH variation of rainwater by atmospheric deposition in the region, will alter the ionic balance of the ground water and hence its suitability for any kind of intended purpose for a stable and healthy society.

4.7. Correlation analysis

Pearson's correlation matrix for pre-monsoon season is shown in Table 6, indicates significant correlations ($p < 0.05$ and 0.01) between water quality parameters. The correlation coefficient >0.75 indicate strong correlation [47] (statistically significant at the 0.05 level), moderate (0.75–0.50), weak correlation (0.50–0.36). The linear relationship between ground water quality parameters and computed EWQI in pre-monsoon showed the positive correlation on EC ($r = 0.82$), TDS ($r = 0.83$), Cl^- ($r = 0.82$), Na^+ ($r = 0.82$), K^+ ($r = 0.77$) and SO_4^{2-} ($r = 0.53$). These contributed the elevated score for the EWQI during the season (See Text S1, Supplementary material). The relationship between EC and TDS was high due to the salt ingress from the nearby sea in the study region. This further confirms that, seawater intrusion is a widespread problem of coastal aquifers of the Alappad coastal region of Kerala. The significant positive correlation between total hardness and Ca^{2+} ($r = 0.99$), total hardness and Mg^{2+} ($r = 0.99$) showed, the hardness of the water is permanent and cannot be removed by conventional boiling practices. Positive correlation between the alkali earth metals, Ca^{2+} and Mg^{2+} ($r = 0.59$) signifies that, these ions have the same origin, possibly silicate rock weathering in the ecologically sensitive coastal region [72].

Monsoon season showed strong positive correlation (See Table S13, Supplementary material) between EWQI and turbidity ($r = 0.93$), iron ($r = 0.93$), and K^+ ($r = 0.88$). During monsoon season, the TDS and EC observed more correlation with more number of parameters. This indicates, the monsoonal dilution and leaching of rock and sediments into the groundwater sources (Text S1, Supplementary material). EC showed positive correlations with TDS ($r = 0.99$), alkalinity ($r = 0.59$), hardness ($r = 0.84$), Cl^- ($r = 0.91$), NO_3^- ($r = 0.94$), Na^+ ($r = 0.90$) and Mg^{2+} ($r = 0.94$).

In post-monsoon, the EWQI showed positive correlations with EC ($r = 0.75$), TDS ($r = 0.75$), BOD ($r = 0.72$), hardness ($r = 0.73$), iron ($r = 0.59$), SO_4^{2-} ($r = 0.55$), Ca^{2+} ($r = 0.66$) and Mg^{2+} ($r = 0.74$). Post-monsoon showed 9 positive strong correlations ($r > 0.75$), and 14 moderate positive correlations between water quality parameters (See Text S1 and Table S14, Supplementary material). This implies the hydro geochemistry of the coastal aquifer is mostly controlled by the geogenic anomalies and dissolution of the minerals along with weathering and evaporation [73]. Alkalinity showed positive correlation with hardness ($r = 0.51$) and Mg^{2+} ($r = 0.62$). Hardness observed strong positive correlation with Ca^{2+} ($r = 0.99$) and Mg^{2+} ($r = 0.72$).

4.8. Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is applied on the physico-chemical parameters in pre-monsoon, monsoon and post-monsoon seasons. Before implementingHCA to the data, they were log-transformed and standardized (z-score), to provide equal weight to all variables and approximate normality [74]. Hierarchical agglomerative clustering is the most common approach, provides intuitive similarity relationships between any one sample and the entire data set [75]. The R-mode HCA was performed to cluster the parameters based on their similarity [76]. For each cluster, the mean for all variables was calculated using the Ward's method with Squared Euclidean distance of 25 chosen as proximity measure. The dendrogram produced in the cluster analysis is shown in Fig. 7. Mainly, two groups are able to distinguish in all the three seasons, they are further divided into subgroups. The HCA analysis displays, how the water quality parameters are related to one another in three seasons.

The first group in pre-monsoon, monsoon and post-monsoon contains total alkalinity, total hardness, HCO_3^-, TDS, Na^+, Ca^{2+}, Mg^{2+} and Cl^- represents the process of calcite dissolution in addition to silicate weathering. Similar observations were reported from the groundwater sources of Bangalore south Taluk in Karnataka State, India [76]. The first group characterises the alkalinity of samples. The majority of the parameters in first group are salinity-related and close together, which are dominant in coastal aquifers. The geology of the study area comprised of coastal alluvium. Seawater intrusions may influence the dominance of salinity-related parameters [65]. The second group consists of NO_3^-, iron, PO_4^{3-}, DO, BOD, turbidity, pH, K^+, Mg^{2+} and SO_4^{2-} indicate anthropogenic activities- use of fertiliser for agriculture and sewage effluents [77]. Similar trend in clustering pattern was observed in monsoon and post-monsoon seasons. The concentration of cations and anions in each seasons is presented in stiff diagrams, showing similar pattern. The dominance of HCO_3^- anion and Na^+ cation is observed during the pre-monsoon and monsoon period, whereas Ca^{2+} is the dominant cation in post-monsoon period indicating reverse ion exchange process.

The dendrogram produced in R-mode HCA is the grouping based on parameters. The Q-mode HCA is used for the clustering of sampling sites [76] based on their similarities and dissimilarities in EWQI and PIG values. In the present study area, the sampling locations has similar geological features, elevation (<5 *m* amsl-above mean sea level), slope and natural background. The clustering of samples indicate the spatial variation based on the similarity or dissimilarity in EWQI and PIG between groups (Fig. 8a–c). In pre-monsoon (Fig. 8a), the first cluster comprises (67%) of ten samples (DW1, DW2, DW3, DW4, DW7, DW10, DW12, DW13, DW14,

Table 6

Pearson's correlation coefficient of EWQI with other water quality parameters in pre-monsoon season, in the study area- Alappad Coast, Kollam, Kerala, India.

	EWQI	pH	EC	Turbidity	TDS	DO	BOD	TA	TH	Cl^-	Iron	SO_4^{2-}	NO_3^-	Na^+	K^+	Ca^{2+}
pH	0.32															
EC	**0.82**[a]	0.21														
Turbidity	−0.30	0.14	−0.19													
TDS	**0.83**[a]	0.20	**0.99**[b]	−0.19												
DO	0.37	**0.60**[a]	0.25	−0.29	0.23											
BOD	−0.15	0.31	−0.02	0.37	−0.02	0.07										
TA	−0.18	0.01	−0.16	0.27	−0.14	−0.56	0.45									
TH	0.44	0.31	−0.13	−0.23	−0.12	0.21	−0.26	0.07								
Cl^-	**0.82**[a]	0.20	**0.99**[b]	−0.17	**0.98**[b]	0.29	−0.05	−0.26	−0.15							
Iron	−0.14	−0.45	−0.27	0.11	−0.27	−0.14	0.11	−0.19	−0.06	−0.22						
SO_4^{2-}	**0.53**[a]	0.14	**0.62**[a]	−0.35	**0.64**[a]	0.29	−0.08	−0.10	0.00	**0.54**[a]	−0.34					
NO_3^-	−0.17	−0.11	−0.09	**0.51**[a]	−0.08	−0.70	0.23	**0.63**[a]	−0.11	−0.13	0.15	−0.22				
Na^+	**0.82**[a]	0.20	**0.99**[b]	−0.18	**0.99**[b]	0.27	−0.05	−0.23	−0.14	**0.99**[b]	−0.24	**0.53**[a]	−0.12			
K^+	**0.77**[a]	0.14	**0.91**[b]	−0.08	**0.92**[b]	0.09	0.17	0.04	−0.09	**0.88**[b]	−0.15	**0.51**[a]	−0.04	**0.89**[b]		
Ca^{2+}	0.40	0.32	−0.15	−0.19	−0.14	0.20	−0.24	0.11	**0.99**[b]	−0.18	−0.09	0.06	−0.08	−0.17	−0.12	
Mg^{2+}	0.47	0.29	−0.10	−0.26	−0.09	0.23	−0.27	0.03	**0.99**[b]	−0.10	−0.03	−0.07	−0.15	−0.09	−0.05	**0.96**[b]

[a] Correlation is significant at the 0.05 level (2- tailed), TH-total hardness, TA-total alkalinity.

[b] Correlation is significant at the 0.01 level (2-tailed).

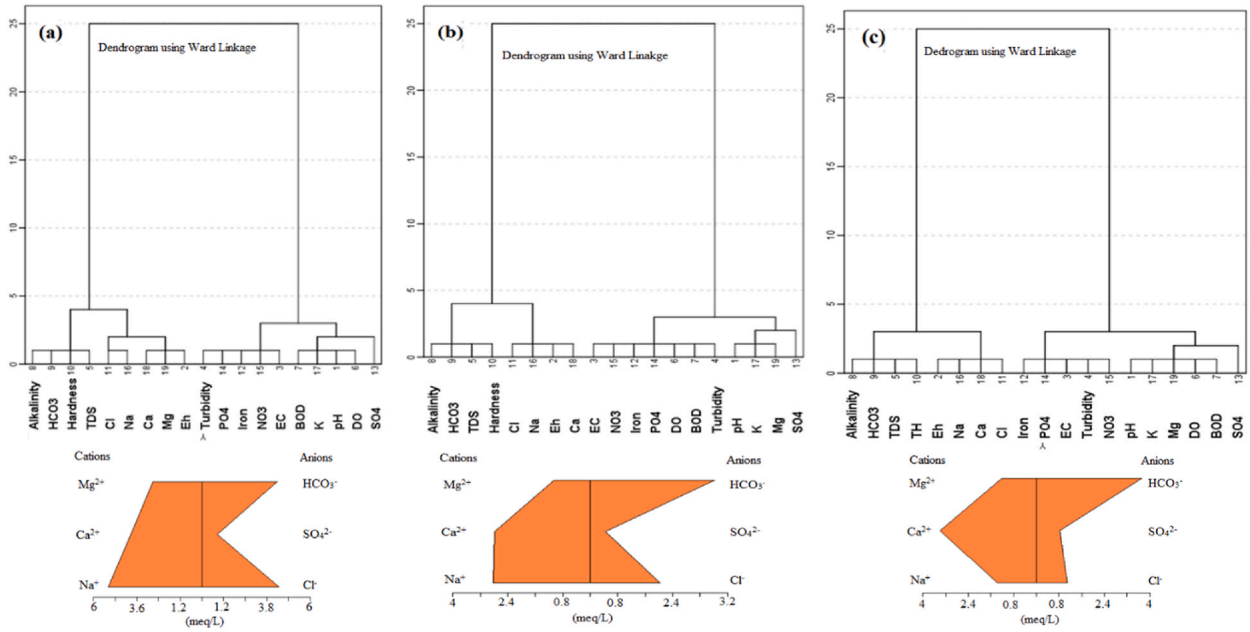

Fig. 7. Dendrogram of the clusters showing groundwater grouping from HCA and Stiff diagram based on mean values in (a) pre-monsoon, (b) monsoon and (c) post-monsoon season representing differences in major ion group.

and DW15). The cluster 1 is subdivided into two sub-clusters. The quality of water in each cluster is decreasing from top to bottom. During pre-monsoon, Cluster 1 has the EWQI varied between 22 and 53 and PIG values between 0.2 and 0.6 indicating suitable water for drinking. Cluster 2 has (20%), EWQI values between 61.8 and 83.6 representing good quality, whereas the PIG falls within the permissible limit. Cluster 3 consists of DW8 and DW9, falls in extremely poor (EWQI = 280.8) and poor quality water (EWQI = 192.7) respectively. EWQI values of each station is presented in Tables S5–S7, Supplementary material.

Cluster 1 in monsoon (67%) and post-monsoon (60%) seasons represents good quality water and suitable for drinking. Cluster 2 indicate, the moderate quality of water. Three samples were in this group during the study period (DW4, DW5 and DW11 in monsoon and DW1, DW3 and DW6 in post-monsoon). These are less influenced by the anthropogenic factors. Cluster 3 indicates the assemblage of poor quality water (DW2 and DW8). During monsoon season (Fig. 8b), the polluted water sources obtained (13%) in cluster 3 are DW2 (EWQI = 309.7) and DW8 (EWQI = 171.8) which are unsuitable for drinking purpose due to more anthropogenic activities and domestic waste input. In the case of post-monsoon, cluster 1 comprises nine stations and the EWQI ranged 28.9–42.7, indicate excellent to good water sources. Cluster 2 in post-monsoon season showed (Fig. 8c) the groundwater sources (DW1, DW3 and DW6) with the lowest values for EWQI and PIG representing 'excellent' category (20%). The cluster 3 in post-monsoon season represents three samples (DW2, DW5 and DW11) in good category (20%). The seasonal and spatial variation of drinking water quality status is depicted in Fig. 6a–c.

4.9. Limitations of the study

In this study, heavy metal concentration and isotopic analysis of groundwater sources in premonsoon, monsoon and post-monsoon is not considered for the present research, will be taken up as the next phase of research. It is helpful, to determine the origin of pollutants and spatio-temporal evolution of water sources [78,79], will be the one of the objectives of the future research. The research will continue in this sampling sites, for a better understanding of groundwater hydrochemical systems, interactions and changes, for over a period of time, such that, outcome could be utilised for any kind of socio-economic engineering, industrial activities, mineral sand mining, and infrastructure development proposed- including fisheries where water quality is a critical factor particularly for a region whih has huge fishermen population.

5. Conclusion

Groundwater is an important resource for drinking, domestic, and agricultural purposes in coastal regions of Kerala, India. In this study, entropy weighted water quality index (EWQI) in groundwater sources of Alappad coastal village revealed groundwater in post-monsoon season was most suitable for drinking purpose. Seasonal variation of EWQI of Alappad coastal groundwater observed 71.4 ± 71.3 (Good quality) in pre-monsoon, 66.1 ± 77.7 (Good quality) in monsoon and 38.2 ± 14.5 (Excellent quality) in post-monsoon season. The seasonal mean of electrical conductivity (EC) and TDS values, of groundwater is in the decreasing order: pre-monsoon (EC = 1559.3 ± 2510.6 μS/cm, TDS = 429.5 ± 629.7 mg/L) > monsoon (EC = 1044.0 ± 771.4 μS/cm, TDS = 257.6 ± 189.8 mg/

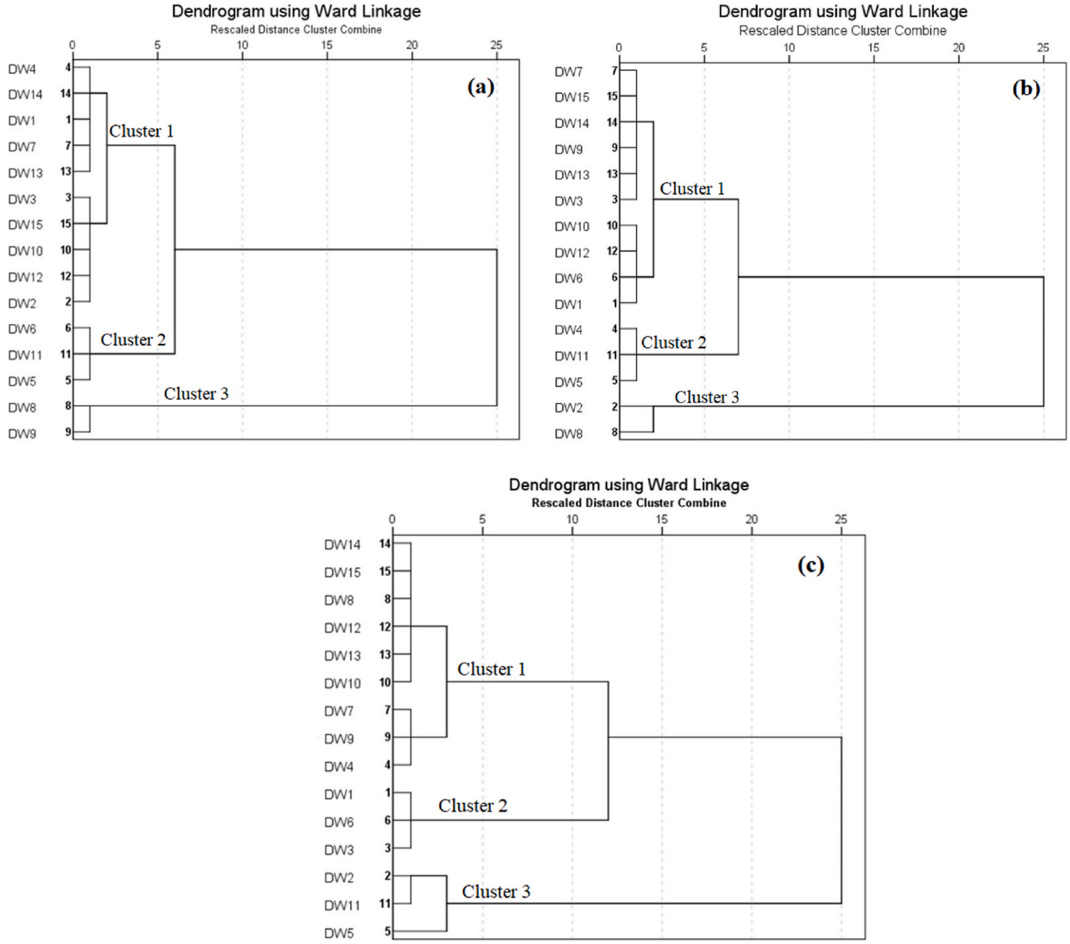

Fig. 8. Hierarchical dendrogram classifying spatio-temporal variation (a-Pre-monsoon, b-Monsoon, and c-Post-monsoon) of groundwater sources based on EWQI and PIG in the Alappad coastal area, Kerala, India.

L) > post-monsoon (EC = 1023.3 ± 413.5 μS/cm, TDS = 250.9 ± 105.1 mg/L). The total hardness of 13% of samples in all the seasons was soft-water class. Very hard water class represented by 27% of samples in pre-monsoon, 20% in monsoon and 7% in post-monsoon season. Iron concentration was above the permissible limit of 0.3 mg/L in pre-monsoon (0.3 ± 0.4 mg/L) and monsoon (0.9 ± 1.3 mg/L) seasons. During post-monsoon season, total iron observed (0.02 ± 0.07 mg/L) below detectable level in most of the stations. Some stations are having variability-stations DW8 (EWQI = 280.8) and DW9 (EWQI = 192.7) showed higher EWQI values in pre-monsoon and DW2 (EWQI = 309.7) and DW8 (EWQI = 171.8) in monsoon seasons respectively indicate poor quality for drinking purpose. The water type on station 'DW8' showed Mg–Ca–Na–Cl–HCO_3 due to Na^+ and Cl^- from the sea.

Multivariate statistical analyses- principal component analysis (PCA), hierarchical cluster analysis (HCA), and correlation were employed to all the three seasons. The PCA demonstrates that anthropogenic (surface runoff, agriculture fertilizers) and natural/geogenic sources (rock–water interaction, weathering and leaching and saline intrusion) are responsible for variation of physico-chemical parameters in groundwater aquifer. During pre-monsoon, Cluster 1 has the EWQI varied from 22 to 53 and PIG values between 0.2 and 0.6 indicating suitable water for drinking (67%). Cluster 1 in monsoon (67%) and post-monsoon (60%) seasons represents good quality water and suitable for human consumption. Cluster 2 and Cluster 3 represents inferior water quality, in premonsoon (13%), EWQI in cluster 3 varied between 32.2 and 192.7, and monsoon (13%) EWQI between 171.8 and 309.7 represents the polluted groundwater sources. Cluster 3 in post-monsoon (20%), EWQI varied from 51.4 to 72.6 indicating good water quality.

Gibbs diagram for cation and anion showed the water-rock interaction, weathering and dissolution along with evaporation affects the solute content in shallow aquifers. Na^+ is dominant during the pre-monsoon period (98.9 ± 200.7 mg/L) and Ca^{2+} and Mg^{2+} observed 89.3 ± 117.9 mg/L and 31.9 ± 61.4 mg/L respectively indicating ion exchange ($Na^+ > Ca^{2+} > Mg^{2+} > K^+$). Whereas, Ca^{2+} dominance is observed in pre-monsoon (55.4 ± 36.4 mg/L) and post-monsoon season (64.3 ± 39.8 mg/L) indicate, reverse ion exchange process ($Ca^{2+} > Na^+ > Mg^{2+} > K^+$). The abundance of anions are $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > PO_4^{3-}$. Hill-Piper Trilinear diagram revealed Ca–HCO_3 is the dominant water type. During pre-monsoon, significant positive correlation between EWQI and conductivity (r = 0.82), TDS (r = 0.83), chloride (r = 0.82), Na^+ (r = 0.82), and K^+ (r = 0.77) indicates that, these factors contribute to the overall WQI of the region.

The sodium adsorption ratio (SAR) values showed a seasonal variation (4.3 ± 11.8) in pre-monsoon, (1.5 ± 2.1) in monsoon and, (2.1 ± 1.1) in post-monsoon seasons, indicate suitability for irrigation. Percentage sodium (Na%) revealed (35.4 ± 20.7) in pre-monsoon, (32.2 ± 18.5) in monsoon and (44.2 ± 15.1) in post-monsoon are suitable for irrigation. Groundwater in station DW8 observed unsuitable for irrigation in all the three seasons (Na% = 96.9 in PRM, Na% = 98.3 in monsoon and Na% = 76.4 in post-monsoon) due to the elevated salinity. The data generated for the current study can be used as a reference for understanding the pollution condition on the coastal aquifer system and for future sustainable planning and development of the coastal area. In this study, water quality indices, and multivariate statistical modelling were used to understand the water quality condition and relationship between various water quality parameters. These baseline data can help to identify the future changes in groundwater quality in this coastal village Alappad, Kollam, Kerala, India and similar locations anywhere for water quality evaluations. The proper management of the limited freshwater resource will be essential to ensure harmonious living and food security for the coastal communities and growing population in the state. The policy makers can adopt the method to evaluate the groundwater to identify quality issues, and variability. Accordingly can choose proper quality treatment methods for water to meet upcoming industrial operations including tourism, fisheries, fish processing, ice making and mineral processing. The results of this study can be utilised for comparing the quality criteria for similar coastal regions in respect of groundwater monitoring and assessment strategies for future economic programs.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Balamurali Krishna: Conceptualization, Formal analysis, Investigation, Writing – original draft, Data curation, Software. **V. Sivanandan Achari:** Conceptualization, Data curation, Investigation, Resources, Supervision, Visualization, Methodology, Writing - original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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