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Application of Water Quality Index and Multivariate Statistical Analysis in the Hydrogeochemical Assessment of Shallow Groundwater in Part of Purna Basin, Maharashtra, India

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ABSTRACT

In the present study, descriptive statistics, multivariate statistical technique and geochemical technique was applied to assess the major factors controlling the hydro-geochemistry of the GP-2 watershed, part of Purna basin, Aurangabad, Maharashtra, India. Twenty-one (21) groundwater samples were collected covering entire part of watershed. Groundwater samples were tested for their physico-chemical parameters such as pH, electrical Conductivity (EC), total dissolved solids (TDS), total hardness (TH), calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^{+}), potassium,(K^{+}) chlorides (Cl^{-}), sulphate (SO_4^{-}), carbonate (CO_3^{-}), bicarbonate (HCO_3^{-}), nitrate (NO_3^{-}), and fluoride (F^{-}). The results were evaluated and compared with WHO (2011) and BIS (2012) water quality standards. The piper trilinear diagram shows that groundwater samples are of mixed $CaNaHCO_3$ and $CaHCO_3$ type. According to Gibbs diagram, the predominant samples fall in the rock–water interaction dominance field. Based on the WQI results majority of the samples show their excellent to good category. Hydrogeochemical parameters are further studied using statistical tools such as descriptive, correlation and cluster analyses, and Factor analysis. In summary, it is observed that the hydro-geochemical processes are more dominated in study area and the groundwater chemistry is controlled by geogenic and anthropogenic processes such as cation exchange process at soil water interface, domestic waste, solubility of minerals, and dissolution of lithogenic materials and pollution from application of fertilizers and pesticides to agricultural lands.

KEYWORDS: *Water quality Index, Multivariate statistical analysis, Descriptive statistics, Gibbs and Piper diagram, GP-2 watershed, Purna Basin, Maharashtra, India*

INTRODUCTION

India has wide spectral variations of meteorological, topographical, geomorphological, hydrological, geological, and hydrogeological conditions. The chemistry of groundwater is an important factor determining its use for domestic, irrigation and industrial purposes. Utilization of land varies from place to place due to rapid urbanization and industrialization, without following the strict environmental norms, causing a lot of variation of quality of groundwater within a short distance, which constrains the developmental activities drastically everywhere (Subba Rao 1997, 2006; Krishna Kumar et al, 2015). Groundwater is an important water resource for domestic and agriculture in both rural and urban parts of India. Two-thirds of the earth surface is covered by water. Water is very important to life; without water our life cannot move. Availability of quality freshwater is one of the most critical environmental issues of the twenty first century (UNEP, 2002). Groundwater is the largest source of fresh water. It is a renewable natural resource by the annual replenishment of meteoric precipitation. As the availability of surface water becoming scarce, the consumption of groundwater has become unavoidable. Quality of groundwater is a vital factor for mankind as it is directly linked with human health. The quality of groundwater gets altered during its course of movement through the hydrological cycle and through the various processes such as evaporation, transpiration, uptake by vegetation, oxidation/reduction, cation exchange, dissociation of minerals, precipitation of secondary minerals, mixing of waters, leaching of fertilizers and manure, pollution (Appelo and Postma, 1993; Samson and Elangovan, 2017).

Groundwater quality usually varies widely depending on the location, recharge water quality, lithology, and environmental factors and so on. The assessment of hydro chemical flow systems is based on the available information of groundwater chemistry. Concomitantly, the factors determining the quality of groundwater are the geological setting, source rocks property, recharge water composition, soil formations, lithology and the duration of time that the water body has been trapped underground (Faniran et al. 2004; Giridharan et al. 2008; Islam et al, 2017). Drinking water accessibility from the underground aquifers had increased significantly over the last decade, and adverse effects of contaminated drinking water on human health have also been rising according to the World Health Organization (WHO 2006; Rahman et al., 2018).

The contest for groundwater resources has put on importance in recent years. Groundwater is the major source of drinking water in both urban and rural India. But the development of human societies and industry result in bio-environmental problems; pollution puts the water, air and soil resources at risk (Milovanovic, 2007; Das and Nag, 2015). Groundwater quality depends on the quality of recharged water, atmospheric precipitation, inland surface water and subsurface geochemical processes. The chemical composition of groundwater is very important criteria that determine the quality of water. Water quality is very important and often degraded due to agricultural, industrial and human activities. Even though the natural environmental route provide by means of removing pollutants from groundwater, there are definite limits. It is up to the people to provide safety to protect and keep quality of water (Ikhane et al, 2010). Drinking water with good quality is very important to improve the life of people and to prevent diseases (Adewoya and Oludura, 2007). Sustainable groundwater quality is essentially vital for human consumption, and agricultural purposes in any region, while a recent study revealed ''extensive contamination'' possesses more threat to sustainable groundwater supply than depletion (Macdonald et al. 2016).

The evaluation of groundwater quality is not only necessary to know the suitability but also for planning the management of groundwater in a more sustainable way to meet the existing and future demands for drinking and irrigation uses (Islam et al, 2018). For agricultural purposes, groundwater is explored in rural areas, especially in those where other sources of water like dam and river or the canal is not available. During last decade, this is observed that the groundwater gets polluted drastically because of increased human activities. Hence it is very essential to maintain the quality of groundwater for human consumption, for the aquatic life and for other subsequent uses (Elizabeth and Naik, 2005; Vijender Singh, 2006; Mishra and Bhatt, 2008; Murhekar, 2011). The quality together with the suitability of groundwater for different purposes such as industrial, domestic and agricultural uses depends upon the atmospheric precipitation, quality of recharge water, and interior surface water. There are some factors, which cause a variety of groundwater types; these are an ion-exchange process, groundwater residence time in the aquifers, and salt leaching (Sami 1992). The waste materials possibly are absorbed and transported to the groundwater, making the groundwater to be polluted, therefore the necessity for control and frequent monitoring of groundwater quality in these areas. The oxidation-reduction reactions and rock-water interaction throughout the filtration of water in aquifers produce groundwater with different quality (Back 1966; Kumar et al. 2009; Aghazadeh and Mogaddam 2011; Dawood, et al, 2018).

Groundwater is the only major water supplying element and thus has a great importance in this large basaltic area of Maharashtra. Every year, the state faces water scarcity due to its naturally prevalent physiographic conditions and erratic rainfall. It is also important to note that the state has more than 80% dependability on groundwater, especially for drinking water purpose. Therefore, groundwater assumes a greater significance both in terms of quality and quantity and in its development and management (Umrikar, 2017). The geochemical assessment of groundwater can be studied in statistical aspects by the means of Multivariate methods namely Hierarchical cluster analysis and Factor analysis. Multivariate statistics concerns understanding the different aims and background of each of the different forms of multivariate analysis, and how they relate to each other. Factor analysis has now been a major tool in the study of groundwater geochemistry has been demonstrated in several studies (Lawrence and Upchurch, 1983; Briz Kishore and Murali, 1992; Sabbarao et al. 1996; Olobaniyi and Owoyemi, 2006; Aris et al. 2007; Gallardo and Marui, 2007; Ramesh and Riyazuddin, 2008; Narmatha et al, 2011). It is also constructive for identifying the temporal and spatial variations and to categorize the geochemical processes which control the groundwater geochemistry. Cluster analysis is a collection of statistical methods, which identifies group of samples that show similar characteristics. This undertaken study helps to improve the groundwater system and utility of multivariate statistical analysis for hydrogeochemical assessment of shallow groundwater aquifer.

Study area

The GP-2 watershed stream locally called Anjana River is tributary of river Purna and lies in Aurangabad district, Maharashtra, Central India. The study area is about 350.5 km^2 around 20°13'9'' to 20°20'34'' N and 75°10'00'' to75°33'88'' E. Groundwater Surveys and Development Agency, Maharashtra (GoM) State agency (GSDA,2019) nomenclature this watershed as GP-2 watershed, GP stands for Godavari-Purna (Fig. 1). The southwest monsoon of the Indian Ocean dominates the climate and rainfall distribution in the study area. The GP-2 watershed is the small tributary that flow through the study area and meet Purna River.

These channels carry flood waters to the Purna River also called as a Khadakpurna River and they also act as drainage channels for rainfall. It receives rainfall from the SW monsoon. The average annual rainfall in the study area is 660 mm that occurs in the months from June to October. The average temperature in the watershed is in the range of 13-40°C. Geologically basaltic flows of Cretaceous to Eocene age called as Deccan Volcanic Province (DVP), is the unique geological formation in Peninsular India. The DVP, is well known for their marked horizontality, characteristic flat-topped hills and step-like terraces. The study area is dominantly constituted of basaltic rocks. The basalts occur in the form of horizontal flows having variation in the thickness and are seen to extend for a considerable distance. A typical spheroidal weathering pattern is very common all over the DVP. On the gentle hill slopes, they are covered by residual and / or colluvial soils. The alluvium is seen to be developed along the banks of stream. The specific rock types exposed in the area show a variety of basalts viz. Compact Basalt, Vesicular Basalt, Amygdaloidal Basalt or composite of both vesicular–amygdaloidal Basalt.

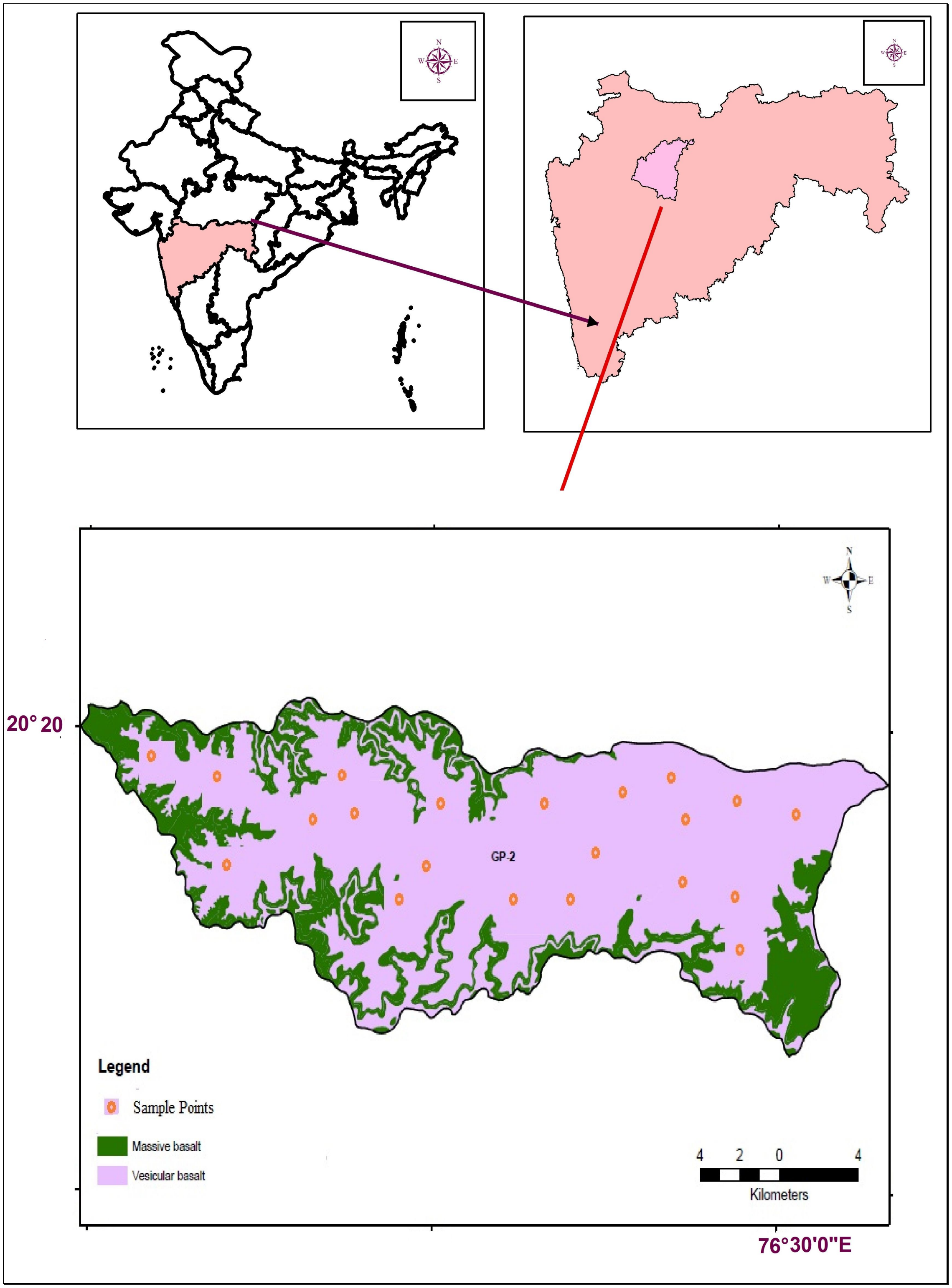

Figure 1: Location and Geological map of study area

MATERIALS AND METHODOLOGY

Sample collection and analytical procedure

In total, 21 groundwater samples were collected from the study area post season. Groundwater samples were collected in 500-mL polystyrene bottles and chemical analyses followed standard guidelines (APHA, 2012). Prior to sample collection, bottles were washed with 1:1 HNO_3 and rinsed three times with distilled water. Samples were collected after pumping the wells for 15–20 min and filtered through 0.45-lm membranes to avoid debris. The pH, electrical conductivity (EC), and total dissolved solids (TDS) were measured immediately after sampling. Total hardness (TH) as $CaCO_3$, Calcium (Ca^{++}), magnesium (Mg^{++}), were analysed titrimerically, using standard EDTA, carbonate (CO_3^-) and bicarbonate (HCO_3^-) were estimated by titrating with H_2SO_4, whereas nitrate (NO_3^-), sulphate (SO_4^-), and fluoride (F^-) were determined by spectrophotometer, and for determination of sodium (Na^+) and potassium (K^+) Flame Photometer were used. Chloride (Cl^-), was estimated by standard $AgNO_3$ titration. For accuracy, a charge balance % error is calculated by the following equation,

$$CBE\ (\%) = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} x\ 100 \qquad (1)$$

The CBE (%) for all samples were within ± 10%, expressing the reliability of analytical data. Microsoft Excel 2007 was employed to execute a mathematical operation on analytical data obtained after analysis.

Water Quality Index System

The water quality index (WQI) was calculated for evaluating influence of natural and anthropogenic activities based on several key parameters of groundwater chemistry. A water quality index, common with many other indices systems, relates a group of water quality parameters to a common scale and combines them into a single number in accordance with a chosen method of computation. The desired use of WQI is to assess water quality trends for management purpose even though it is not meant for an absolute measure of the degree of pollution or the actual water quality. WQI is defined as an index reflecting the composite influence of different water quality parameters which is considered and taken for calculation of water quality index. The standards for drinking purposes as recommended by Bureau of Indian Standards (BIS, 2012) have been used for the calculation of WQI, which involves three steps.

To calculate the WQI, the weight has been assigned for the physio-chemical parameters according to the parameter's relative importance in the overall quality of water for drinking water purposes. In the first step each of the 12 parameters like pH, total dissolved solids (TDS) total hardness (TH), Calcium (Ca^{++}), Magnesium (Mg^{++}), sodium (Na^+), Potassium,(K^+) Chlorides (Cl^-), Sulphate (SO_4^-), bicarbonate (HCO_3^-), Nitrate (NO_3^-), and fluoride (F^-), were assigned weights (w_i) ranging from 2 to 5, and its selection depends on their significance in quality of water for drinking purposes (Ramakrishnalah et al., 2009). In the second step is relative weights (W_i) are calculated through equation (2).

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \qquad (2)$$

Where (W_i) is the relative weight, (w_i) is the weight of each parameter and (n) is the number of parameters Table 1. In the third step, quality rating scale calculation (Qi) for each individual parameter is computed by dividing its concentration for each groundwater sample with drinking water quality standards of and then multiplied by 100 using equation (3).

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

Where Q_i is the quality rating, C_i is the concentration of each chemical parameter in each water sample in milligrams per litre (mg/L) and S_i is the drinking water standard guidelines for each chemical parameter. Eventuality, water quality sub-indexes (SIi) for each chemical parameter was computed by equation (4), and whole the WQI was determined by equation (5).

$$SI_i = W_i \times Q_i \quad (4)$$

$$WQI = \sum S\, I_{i-n} \quad (5)$$

Where,

SI_i is the sub-index of the i^{th} parameter,

Q_i is the rating based on the concentration of i^{th} parameter, and n is the total numbers of parameters. The assigned weight and relative weight of physicochemical parameters for calculation of WQI are presented in Table 1.

Table 1: Relative weight of chemical parameters

Sr. No.	Chemical Parameter	Drinking water Standards	Weight (wi)	Relative weight (Wi)
1	pH	6.5-8.5	4	0.10811
2	TDS	500-2000	4	0.10811
3	TH	200-600	2	0.05405
4	HCO_3^-	200-600	3	0.08108
5	Cl^-	250-1000	3	0.08108
6	SO_4^-	200-400	4	0.10811
7	NO_3^-	45	5	0.13514
8	F^-	1-1.5	4	0.10811
9	Ca^{++}	75-200	2	0.05405
10	Mg^{++}	30-100	2	0.05405
11	Na^+	200	2	0.05405
12	K^+	12	2	0.05405
		Sum	$\sum 37$	1.0000

RESULTS AND DISCUSSION

Hydrogeochemical Properties of Groundwater in the Study Area

Statistical elucidation of physicochemical parameters of groundwater in the study area is given in Table 2. Also, a comparative figure is placed based on Indian Standards and WHO standards (Table 2). It is a statistical analysis which describes a data set with maximum and minimum values, mean value and standard deviation. A central tendency measure representing the arithmetic average of a set of observations is explained as mean. The square root of arithmetic mean of squares of deviations of given observations from arithmetic mean is presented as standard deviation. The standard deviation enables us to determine the location of any value within the data set, with relation to the mean (Levin and Rubin, 1995; Samson and Elangovan, 2017).

Table 2: Descriptive statistics and comparison with different standards of groundwater-quality parameters of the study area

Parameter	Mini-mum	Maxi-mum	Mean	Std. Deviation	Skewness	Kurtosis	Drinking water-quality standards	
							Indian Standard 2012	WHO 2011
pH	6.59	8.47	7.48	0.49	0.61	0.04	6.5-8.5	6.5-8.5
EC	360	1320	928.67	263.99	-0.35	-0.56	-	750
TDS	234	858	603.76	171.58	-0.35	-0.56	500	500
TH	112	496	330.86	105.47	-0.21	-0.61	200	300
Ca^{++}	24	157	80.52	33.99	0.63	-0.07	75	75
Mg^{++}	10	68	31.52	19.05	0.76	-0.65	30	30
Na^{+}	27	101	54.85	20.41	0.65	-0.27	-	200
K^{+}	0.10	1.90	0.51	0.60	1.42	0.72	-	30
HCO_3^{-}	44	404	226.67	85.54	0.01	0.14	-	-
Cl^{-}	50	244	127.62	58.40	0.32	-0.99	250	250
SO_4^{-}	14	64	35.29	15.10	0.50	-0.97	200	200
F^{-}	0.39	1.91	1.22	0.32	-0.37	1.341	1	0.6-1.5
NO_3^{-}	12	79	42.71	13.26	0.34	2.682	45	45

The results revealed that most of the water quality parameters possessed a wide range of standard deviation. Descriptive statistics for pH showed that pH ranges from 6.59 to 8.47 with the mean value of 7.48 and found within the acceptable limit of Indian standard (2012) WHO (2011) standard, this result suggested that the groundwater has neutral to moderately alkaline in nature. The EC values were varied from 360 to 1320 µ/cm with mean of 928.37µ/cm. According to WHO (2011) guidelines, permissible EC value for drinking water is 750µ/cm, and EC values obtained were found to exceed the standard limit with no significant temporal variation. These highly enriched mean EC values might be attributed to the dissolution of aquifer minerals, semi-arid climatic condition of the study area, high nutrient availability, as well as high rate of evaporation (Deshpande and Aher, 2012; Ayers et al. 2016; Islam et al. 2017, Aher, 2017). The TDS value ranged from 234 to 858 with a mean of 603.76 mg/L. The desirable total dissolved solids limit of 500mg/L indicating 13(62%) samples were exceeding desirable limit but within the maximum permissible limit of drinking water standards (BIS, 2012; WHO, 2011). The standard deviation is 171.58 in TDS, it is the maximum value of standard deviation when compared with other parameters except electrical conductivity. The mean value of TDS is 603.76 (mg/L) and it is above the desirable limit (500mg/L) and below the permissible limit (2000mg/L) as recommended by drinking water standards (BIS, 2012; WHO, 2011). The minimum and maximum values of concentrations of water quality parameters will provide necessary information about the extent of variations of concentration among the samples collected from a locality. Since TDS has high variations in its concentrations and has higher value of standard deviation among other samples in the data set, it may have its contribution in classifying groundwater of the study area as mixed water type. The total hardness value varies from 112 to 496 mg/L with a mean values 331 mg/L. The desirable limit of total hardness (TH) for drinking water is specified by BIS as 200 mg/L and a maximum permissible limit of 600 mg/L. It is observed all the samples are within maximum permissible limit of drinking water standards.

Groundwater classifications based on Piper diagram

Groundwater classifications are used to understand the groundwater body that differs in their chemical properties and compositions (Mahlnecht et al. 2004). Depending on lithology, regional flow patterns of water and resident time hydrochemical properties of groundwater vary (Domenico 1972). From the viewpoint of chemical compounds, all waters are divided into three main categories: chloride, sulphate and bicarbonate types (Chebotarev 1955; Islam et al, 2017). The Piper diagram can be used to identify the type of water. It consists of three parts: one diamond shaped diagram in the middle and two trilinear diagrams along the bottom. The relative concentrations of cations (left diagram) and anions (right diagram) in each sample is shown in the trilinear diagram. For the purpose of a piper diagram, the cations are grouped into three major divisions: sodium (Na^+) plus potassium (K^+), calcium (Ca^{++}), and magnesium (Mg^{++}). The anions are likewise grouped into three main categories: bicarbonate (HCO_3^-) plus carbonate (CO_3^-), chloride (Cl^-), and sulphate (SO_4^-). Each sample is represented by a point in each trilinear diagram; the type of water samples will qualify according to the symbolic area in piper diagram. The high variability of major ion chemistry is shown in Fig. 2. The geochemical evolution of groundwater can be understood by plotting the concentrations of major cations and anions on the Piper (1953) trilinear diagram. The plot shows that 71% of the groundwater samples fall in the field of mixed $CaNaHCO_3$ type of water and remaining 29 % falls in the field of $CaHCO_3$ type of water. Higher values for calcium (Ca^{++}), and bicarbonate (HCO_3^-) in the groundwater indicating recharge, mixed, weathering and leached from sewage (Aher et al, 2019).

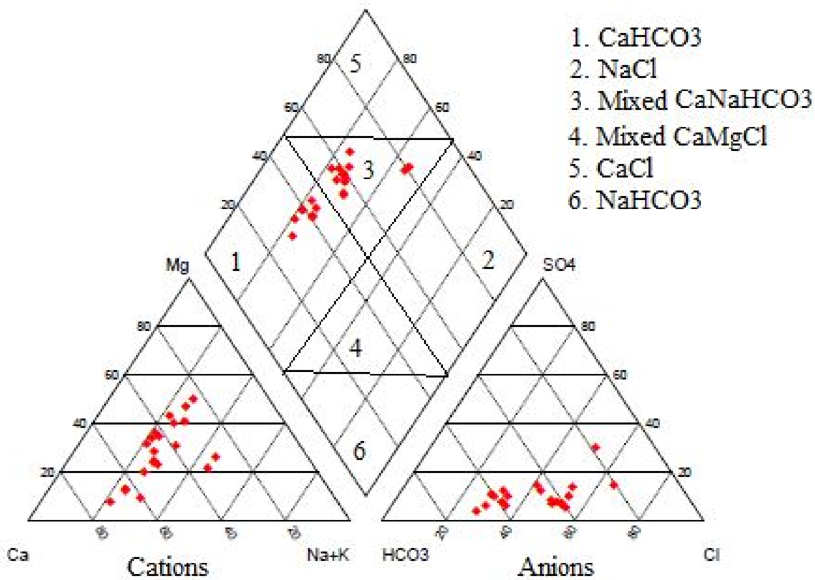

Figure 2: Distribution of groundwater samples on Piper diagram

Mechanism of rock water interaction (Gibb's diagram)

Gibbs (1970) has well established the mechanism controlling the chemical composition of water and ascertained a close relationship that can exist between water chemistry and aquifer lithology. Gibbs plots was constructed by plotting ratios of

(1) Dominant anions: Na^+ / (Na^++Ca^{++}) and TDS,

(2) Dominant cations: Cl^- / (Cl^-+HCO_3^-) and TDS.

The result of study indicates that the mostly all groundwater samples fall in the rock dominant category, indicating an interaction between rock and the percolating water into the subsurface by means of mineral dissolution. The distribution of the sampling points also suggests that the major ion chemistry of the groundwater seems to be controlled by chemical weathering of rock forming minerals and anthropogenic activities.

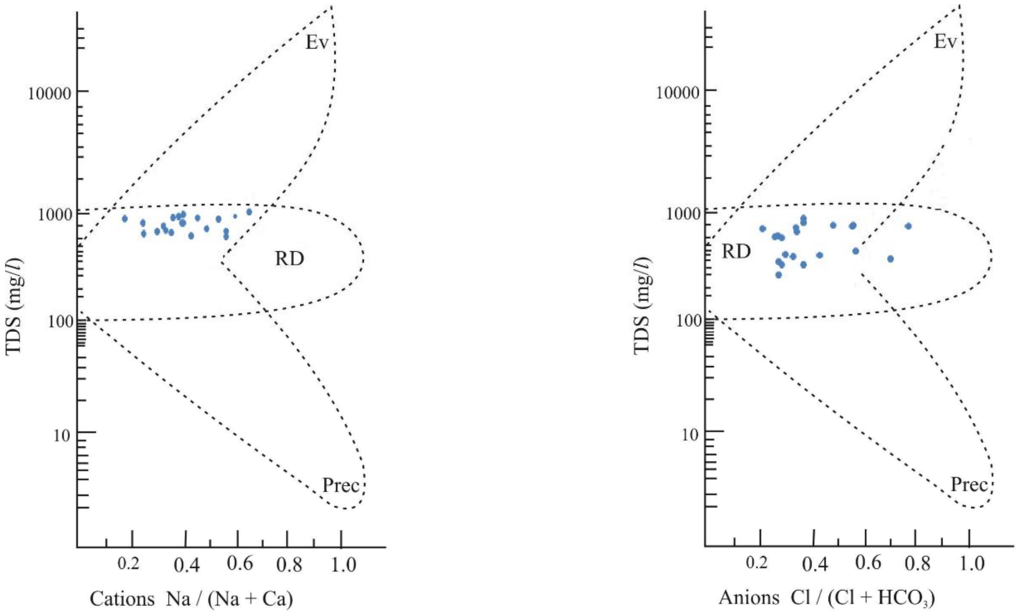

Figure 3: Mechanism controlling the groundwater chemistry (After Gibbs, 1970)

Statistical Analysis

Major Cations and anions Composition of Groundwater

The groundwater of the study area is clearly dominated by Ca^{++}, in cations and HCO_3^- in anions, the dominance of chemical constituents is in the order of Ca^{++}> Na^+>Mg^{++}>K^+ in cations and HCO_3^-> Cl^- >NO_3^- > SO_4^->F^- in anions. The 48 % of Ca^{++} and 33 % of Mg^{++} samples were exceeding desirable limit but are within the maximum permissible limit, The higher contents of Ca^{++} and Mg^{++} is because of overextraction of groundwater, or due to rock weathering, whereas Na^+ and K^+ as well as SO_4^- and Cl^- were found to within the desirable limit of Indian, and WHO standard for drinking water. The contents of F^- and NO^-- in the groundwater were showing that 19% F^- and 29 % NO_3^- were above the acceptable limit for drinking purposes (Table 2). The fluoride infectivity in the groundwater point out the existence of fluoride-bearing minerals (Aher et al, 2015) Nitrate is pragmatic in preponderance of the groundwater samples of the study area. Household ravage and obscured organic stuff have thrown in nitrate to groundwater (Aher, 2014). Furthermore, HCO_3^- concentrations varies from 44 to 404mg / L with an average value of 227 mg / L (Table 2.).

Water quality index calculation (WQI)

The chemistry of groundwater is often used as a tool for discriminating the drinking and irrigation water quality (Subba Rao 2006; Vasanthavigar et al. 2010). Water quality index (WQI) is an important parameter for identifying the water quality and its sustainability for drinking purposes (Subba Rao, 1997; Magesh et al. 2013). With increasing water quality index (WQI) value, the unsuitability of water for drinking increases. The calculation of WQI for groundwater samples is shown in Table 4. The computed WQI values for the 21 groundwater samples in study area ranged from 40.64 to 118.23 with mean value 81.52 (Table 4.), among these, 5% of the samples fell under excellent category, 86 % samples fell under good water category and 14 % of the samples showed poor water category, for drinking purposes.

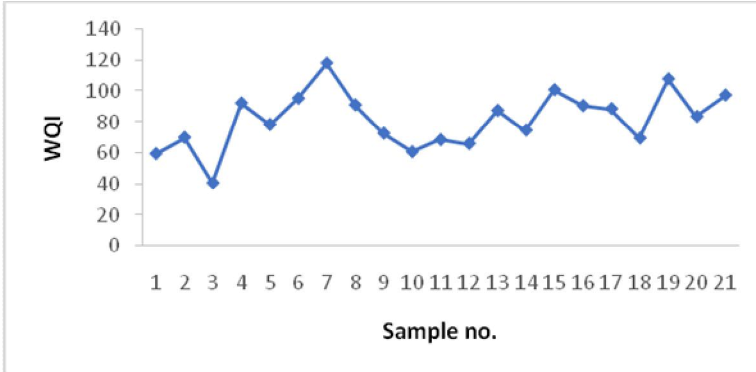

Figure 4: The variation of Water Quality Index (WQI) for each groundwater sampling sites

The category of water samples with percentages were pointed in Fig. 4, whereas the individual strength of WQI for all the sampling sites in study area is presented in Fig. 5.

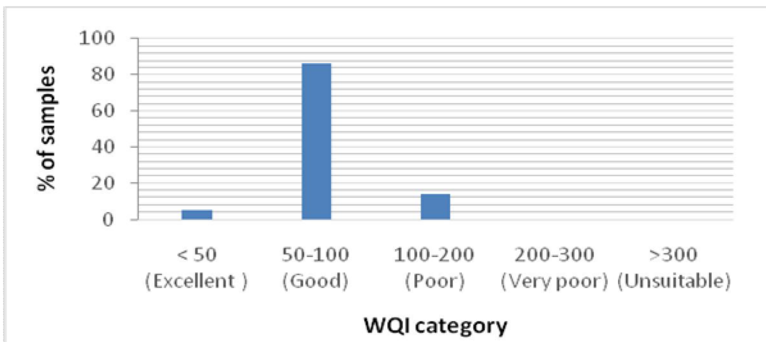

Figure 5: Classification of water by Water Quality Index

Table 3: Water quality classification based on WQI value

Sr. No.	WQI Values	Water Quality	No. of samples	% of samples
1	< 50	Excellent	1	5
2	50-100	Good water	18	86
3	100-200	Poor water	3	14
4	200-300	Very poor water	-	-
5	>300	Unsuitable	-	-
		Total	21	100

This may be due to effective leaching and dissolution process of rock salt and gypsum-bearing rock formations and the rock–water interaction process is the main source for degrading the water quality in the study area. WQI of the samples was calculated by using raw data and the values representing each sampling site were presented in Table 4. The reasons for the high WQI values obtained for this study area strong to moderate positive correlation with of TDS (r=0.91), total hardness (r=0.95), Ca^{++} (r=66), Mg^{++} (r=0.66), Na^{+} (r=0.74), HCO_3^- (r=0.83), Cl^- (r=0.72), and NO_3^- (0.89). Very high correlation coefficients between these values were also reported by WHO (1993), Mitra et al. (2007), Gupta et al. (2004), Deshpande and Aher (2012), and (Aly et al, 2015). Based on the WQI results majority of the samples are falling under excellent to good category indicating their suitability for drinking water purposes (Table 3).

Table 4: Water Quality Index (WQI) for individual sample sites in the study area

Sample No.	Water quality Index	Classification
1	59.5	Good
2	69.9	Good
3	40.6	Excellent
4	92.2	Good
5	78.2	Good
6	95.2	Good
7	118	Poor
8	90.9	Good
9	72.6	Good
10	60.7	Good
11	68.4	Good
12	66	Good
13	87.3	Good
14	74.6	Good
15	101	Poor
16	90.4	Good
17	88.5	Good
18	69.5	Good
19	108	Poor
20	83.5	Good
21	97.3	Good

Correlation matrix

Correlation matrix for groundwater samples in study area shows that the parameter TDS has very high positive correlations with total hardness (r=0.84), calcium, (r=0.53), magnesium (r= 0.55), sodium (r=0.82), bicarbonate (r=0.65), nitrate (r=0.75) and chloride (r=0.75). Groundwater samples of the study area have TDS containing strong correlations with major cations and anions (Table 5). Since TDS has high correlation with major cations and anions of the samples in the data set, it may have its contribution in classifying groundwater of the study area as mixed water type.

Table 5: Correlation matrix for study area of groundwater parameters

	pH	EC	TDS	TH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^-	F^-	NO_3^-	WQI
pH	1													
EC	0.49	1												
TDS	0.49	1	1											
TH	0.31	0.84	**0.84**	1										
Ca^{++}	0.23	0.54	**0.53**	**0.68**	1									
Mg^{++}	0.17	0.55	**0.55**	**0.61**	-0.2	1								
Na^{+}	0.47	0.82	**0.82**	**0.65**	0.42	**0.43**	1							
K^{+}	-0.1	0.11	0.11	0.07	-0.2	0.36	-0.1	1						
HCO_3^-	0.1	0.65	**0.65**	**0.84**	**0.49**	0.6	0.34	0.37	1					
Cl^-	0.39	0.75	**0.75**	**0.73**	**0.54**	0.4	**0.86**	-0.2	0.297	1				
SO_4^-	0.43	0.315	0.315	0.12	0.33	-0.18	**0.52**	0-.5	-0.18	0.41	1			
F^-	-0.4	-0.18	-0.18	-0.2	-0.2	-0.09	-0.1	**0.47**	-0.09	-0.2	-0.4	1		
NO_3^-	0.22	0.75	**0.75**	0.8	**0.44**	**0.59**	**0.57**	0.27	**0.76**	0.49	-0.1	0.02	1	
WQI	0.32	**0.91**	**0.91**	**0.95**	0.57	**0.66**	**0.74**	0.21	**0.83**	**0.72**	**0.72**	-0.5	**0.**	1

(Bold value indicate that correlation is significant at the 0.05 level)

Cluster Analysis

The dendrogram analysis was performed using Ward method (1963) and the results of parameters are shown three groups. In general, this method is very efficient. In a standardized m-space, Euclidean distance d_{ij} is expressed in terms of the Equation given below.

$$d_{ij} = \sqrt{\frac{\sum_{k=1}^{m}(X_{ik} - X_{jk})^2}{m}}$$

Where, X_{ik} denotes the kth variable measured on object i and X_{jk} is the kth variable measured on object j. A hierarchical tree diagram, called a dendrogram can be produced to show the linkage points (Davis, 1986; Samson and Elangovan, 2017).

The clusters are linked at increasing levels of dissimilarity. In this plot, the horizontal axis denotes the linkage distance. The dendrogram is used here to present interpretation of cluster analysis conducted on water quality chemical parameters of groundwater samples.

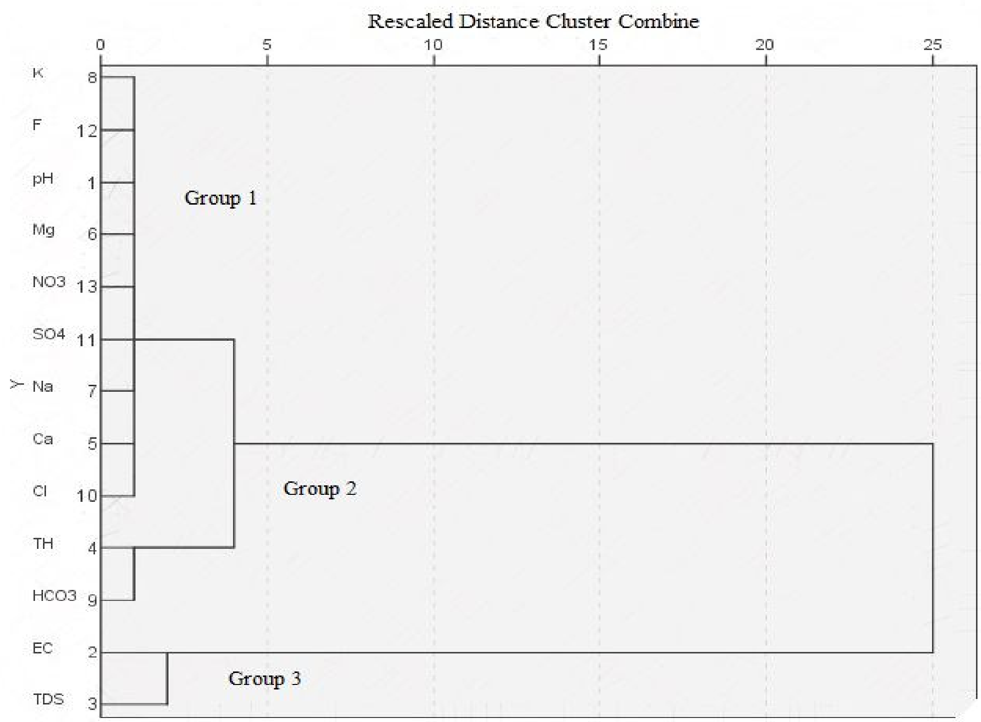

Figure 6: Dendrogram showing CA of groundwater samples

The dendrogram analysis shows that most of the samples were classified in group I and II with good correlation between SO_4^-, Na^+, Ca^{++}, Cl^-, hardness and HCO_3^- with EC and TDS. The group III with one sub-group constructed with EC and TDS. The possible combinations are due to the mineral produced from the rock weathering and agricultural activities. The concentration of nitrate is probably due to the anthropogenic process.

Principal component analysis (PCA)

Factor analysis is a popular multivariate technique, which identifies the most important components contributing to the data structure and the interrelationships among variables (Lall and Sharma, 1996; Sonkamble et al, 2012). It was used to quantify the contributions of natural chemical weathering and other impacts to the chemical composition of groundwater. It was done as follows: First, the correlation matrix, i.e., the array of correlation coefficients for all pairs of variables, was calculated. Then, the matrix was diagonalized and its principal components (eigenvectors) were obtained. The so-called factor 1 is related to the largest eigenvalue and is able to explain the greatest amount of variance in the data set. The second factor (orthogonal and uncorrelated with the first one) explains most of the remaining variance, and so forth. Principal component analysis usually known as 'factor analysis' in geological work, although it is more correctly designated as Principal component factor analysis with rotation of the axes to some kind of simple structure (Reyment and Joreskog, 1993). Principal component analysis (PCA) is a widely used statistical tool that can reduce a large number of variables to a simple set of latent factors to explore interrelationships among observed variables (Iscen et al., 2008; Islam et al. 2017; Islam et al, 2018; Gupta et al, 2019). Factor analysis of the hydrochemical data was performed on SPSS version 22. At the first step, correlation matrices were created using R mode. In the second step, principal components (PCs) were extracted by eigenvalue. Following Kaiser (1960), all factors having eigenvalue higher than 1 were included in calculations. To ensure better interpretation, extracted components were rotated. Rotation does not affect goodness of fit of factor solution (Jiang et al. 2009). Factor 1 has the highest eigenvalue and explains the largest variation in the dataset. Factor 2 has the second highest eigenvalue, and so on. According to the approach of Liu et al. (2003), the terms ''strong,'' ''moderate,'' and ''weak'' were applied to factor loadings and referred to absolute loading values of >0.75, 0.75–0.50, and 0.50–0.30, respectively. This scale was used to measure the goodness of explaining each component's variance relationship.

Table 6: Summarized results of the factor analysis of hadrochemical data.

Variables	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.502	-0.421	**0.441**	-0.159
TDS	**0.961**	0.030	0.067	0.089
TH	**0.937**	0.151	-0.183	-0.161
Ca	**0.620**	-0.270	-0.700	-0.105
Mg	0.591	0.492	**0.512**	-0.107
Na	**0.841**	-0.237	0.146	**0.396**
K	0.024	**0.829**	0.155	0.092
HCO_3	**0.716**	0.499	-0.222	-0.339
Cl	**0.817**	-0.272	-0.012	0.298
SO_4	0.317	-0.793	0.081	0.182
F	-0.258	**0.541**	-0.206	**0.734**
NO_3	**0.801**	0.404	-0.104	-0.021
Initial Eigenvalues	6.400	2.660	1.140	1.030
% of Variance	49.280	20.520	8.790	7.920
Cumulative % of variance	49.280	69.800	78.600	86.520

Table 6 presents the loading of each variable under each one of the four factors. In factor analysis the first factor usually represents the most important process or mix processes controlling the hydrochemistry. It has the highest eigenvalue and accounts for the high variance among the factors. In the entire study area four factors were identified which were controlling the groundwater chemistry. It suggests that the quality of groundwater is mainly controlled by high loading parameters. The Eigen values of four factors were shown cumulative 86.520 % of variance. Factor 1 shows a high positive loading of TDS (0.961), Total Hardness (0.937), Sodium (0.841) chloride (0.817) and nitrate (0.801) whereas moderate loadings on pH and Mg^{++}, HCO_3^- low loadings on K^+ and SO_4^- having accounts 37.94% variance in the data set. The variables of the factor 1 were TDS, Na^+ and Cl^-, which indicates parent rock weathering, apart from these weathering, the high value of and Cl^- may be derived from surface water leaching to groundwater. The moderate loading of pH (0.502) represents solubility of minerals, the high loading of NO_3^- is related to the long-history of anthropogenic process. Factor 2 shows a positive loading of fluoride (0.541), potassium (0.829) has variance of 20.520% and accounts for 69.80% cumulative variance indicating that potassium and fluoride attributed from weathering processes, the high value of K^+ suggests pollution from application of potash fertilizers to agricultural lands. Factor 3 shows a highly positive loading of magnesium (0.512), whereas negative loading of calcium (-0.700) with variance of having 8.790% Factor 4 shows a positive loading of fluoride (0.731) having variance of 7.920% in the data set indicates that the rock weathering is also dominant in groundwater.

CONCLUSION

In the present study, descriptive statistics, multivariate statistical technique and geochemical technique was applied to assess the major factors controlling in groundwater quality and its sustainability in the study area. Hydrogeochemical parameters are examined from proximity basalt and the following conclusions are drawn from this study that Groundwaters rich in alkaline earth. The statistical results demonstrated that the abundance of major cations was in the order of Ca^{++}> Na^{+}>Mg^{++}>K^{+} while the dominant major anions trend was in the following order: HCO_3^-> Cl^->NO_3^- > SO_4^- > F^-. The piper plot shows that 71% of the groundwater samples fall in the field of mixed $CaNaHCO_3$ type of water and remaining 29% falls in the field of $CaHCO_3$ type of water. Higher values for Ca^{++} and HCO_3^- in the groundwater samples are due to due to the dissolution of the mineral formed due to the rock weathering. Hadrochemical processes show that the predominance of carbonate, dolomite, calcite and silicate weathering in the basalt. Factor analysis shows that there are multiple processes acting on groundwaters. The multivariate analysis showed the existence of up to four significant factors which account for 786.52% of the total variance of hydrochemistry data. The first factor which accounts for about 49.280%, second factor accounts for 20.520%, third factor accounts for 8.790% and four factor accounts for 7.920% of the total variance. The dendrogram analysis shows that most of the samples were classified in group I and II with good correlation between SO_4^-, Na^+, Ca^{++}, Cl^-, hardness and HCO_3^- with EC and TDS. The group III with one sub-group constructed with EC and TDS. The Gibbs diagrams showed that groundwater chemistry is mostly rock-dominance zone in the study area. The geogenic processes such as rock weathering and ionic exchange followed by anthropogenic factors such as domestic waste, agricultural fertilizers and agrochemical were responsible for governing the groundwater chemistry. Based on the WQI results majority of the samples are falling under excellent to good category indicating their suitability for drinking water purposes. In summary, hydro-geochemical processes were more dominated in the study area and groundwater chemistry was controlled by geogenic and anthropogenic process such as cation-exchange processes at soil water interface, domestic waste, solubility of minerals, and dissolution of lithogenic materials and pollution from application of fertilizers and pesticides to agricultural lands.

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