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Application of multivariate statistical analysis and water quality index for quality characterization of Parbati River, Northwestern Himalaya, India

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Abstract
The present study is an attempt to accomplish the understanding of the factors impacting Parbati river water quality in Kullu district of Himachal Pradesh. The main objective is to assess the overall water quality, to explore its hydrogeochemical characteristics including major ion contents and other chemical parameters using Water Quality Index (WQI), statistical techniques (principal component analysis) and conventional graphical representation such as Piper trilinear diagram, Durov. Eighteen surface water samples were collected from different altitudinal sites to analyze physico-chemical parameters for June 2019 and September 2019. Analytical outcomes of thirty-six surface water samples collected in Pre-monsoon and Post-monsoon seasons are well within the permissible limits as per BIS, 2012 and WHO 2011 for drinking and domestic purposes. Water quality characterization for the assigned use shows that maximum surface water samples fall under excellent to good water quality index and are suitable for drinking without conventional treatment. The Piper trilinear diagram classified 100% of surface water samples for both seasons' falls in the fields of Ca^{2+}-Mg^{2+}-HCO_3^- water type indicating temporary hardness. Abundance of ions in the water samples is in the order: anions $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ and cations $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. PCA identifies that the surface water chemistry is influenced by natural factors as well as minor anthropogenic activities in both the seasons. The correlation matrix has been prepared to analyse and observe the significance of the factors on the assessment of river water quality. Periodic assessment of surface water samples of the Parbati river and adjoining areas should be carried out. This approach will help in finding out any contamination of water occurring due to rapid socio-economic development as well as explosion of tourism industry in the region. Present study will work as baseline database for any future work in the region.

Keywords Water quality · Hydrogeochemical characteristics · Water quality index · Principal component analysis · Piper trilinear diagram · Anthropogenic activities

1 Introduction

Rivers form key role in sustainable socio-economic development of a country and account for 0.006% of the freshwater resources in the world [1, 2]. The Himalayan rivers are under immense stress due to exponential population growth, industrialization, agriculture and urbanization. These anthropogenic effects combined with uncertain effects of climate change raising serious concerns on rivers both in terms of quality and quantity [3–5]. The people of Himalayan region

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are dependent on river water and groundwater for drinking, irrigation and other domestic purposes [6] and some towns are major tourist destinations hosting large population during peak tourist season. The discharge of untreated or partly treated sewage in river and poor waste management practices especially along the bank is deteriorating quality of river which sequentially also affecting the ground water quality in adjoining areas [7] Water portability is significantly dependent on its quality which is determined and controlled by its geochemistry in natural conditions [8, 9] whereas pollution in water is also dependent on seasonal variation in precipitation, surface runoff, interflow, groundwater flow from bacterial contamination and toxic elements due to their origin from anthropogenic activities [10]. Developing countries like India are more prevalent to degradation of river water quality where millions of people reside on the river banks with poor sewerage system. Therefore, it is essential to monitor water quality as it is directly related with human health and approximately 21% of communicable diseases are water related as per World Bank estimation [11, 12].

Climate changes have laid impact as there is a profound glacier retreat which has resulted in fresh water scarcity in Indian Himalayan Region (IHR) [13]. Similarly unprecedented urbanization, increased tourism, changing land use pattern, waste disposal and agricultural runoff are the main casual factors other than natural factors affecting the water quality of rivers in the Himalayan region [6, 14]. Parts of Kullu district in Himachal Pradesh are facing the water shortage due to changing climatic conditions and other anthropogenic activities [15, 16].

Studies on surface and groundwater monitoring with respect to WQI has been done by various researchers [17–19]. Water chemistry is constrained by various hidden factors related to natural and anthropogenic influences that are hard to comprehend and decipher significant data using simple techniques [20, 21]. In this study physicochemical properties of 36 water samples collected in pre-monsoon and post-monsoon from different altitudinal sites were analyzed to compare with standards given by Bureau of Indian Standards (BIS) and World Health Organization (WHO) for drinking and domestic purposes and water quality index is generated using compound data set to evaluate and assess the disparity in overall quality among study sites and seasons.In addition to the WQI and hydro geochemical analysis, the multivariate statistical approaches were used to understand complex information grids of water quality for efficient management and identification of effective solutions to pollution problems [22, 23]. Therefore, the findings of study will provide significant information of surface water quality of river Parbati and will help to adopt quality aspect of water in a judicious and sustainable manner.

2 Study area

The study area lies in Parbati valley in Kullu district of Himachal Pradesh. River Parbati is the main flowing river draining an area of 1938 km^2 in the valley and the basin extends between 31°50′ N and 32°05′ N latitude and 77°05′ E and 77°50′ E longitude (Fig. 1). It originates from Mantalai glacier at an altitude of 5200 m amsl and below Pin Parbati pass on the western slope of the Greater Himalaya and traverse down through complex topography into the River Beas at Bhunter (1096 m). River Parbati is fast flowing, several small tributaries join at almost every angle outlining dendritic pattern. However, the valley is tourist hotspot as it is rich in art and culture, white-capped snowy peaks, dense green forest, dazzling rivers, hot water springs and sacred places. The climate is generally cool and dry whereas annual rainfall is 1405 mm out of which 57% occurs from June to September [24].

2.1 Geology and hydrogeology

The area under investigation comprises of Precambrian meta sedimentary now uncovered in the profoundly eroded "Kullu Rampur window" under the crystalline thrust sheets [25]. The geology of the area has been divided into three units, Manikaran quartzites, green bed member and Bhalan member under Banjar formation which includes various high-grade gneiss and schist, pegmatite, migmatite, granite and quartz veins along with carbonaceous phyllite, quartzite and limestone bands [26]. The exposed rock types around Manikaran and Kasol are white to grayish well jointed quartzites which are known as Manikaran quartzites [27]. The probable sources of high radioactivity in the area are due to intrusive tourmaline, whereas hot water emergence is through highly jointed and fractured quartzites at Manikaran and Kasol [24].The geology of the Parbati basin is represented in Fig. 2.

The Kullu district has two hydro geological units in the form of porous and fissured formations. Porous formation has unconsolidated sediments of terrace, valley fills and fluvial channel whereas fissured formations has

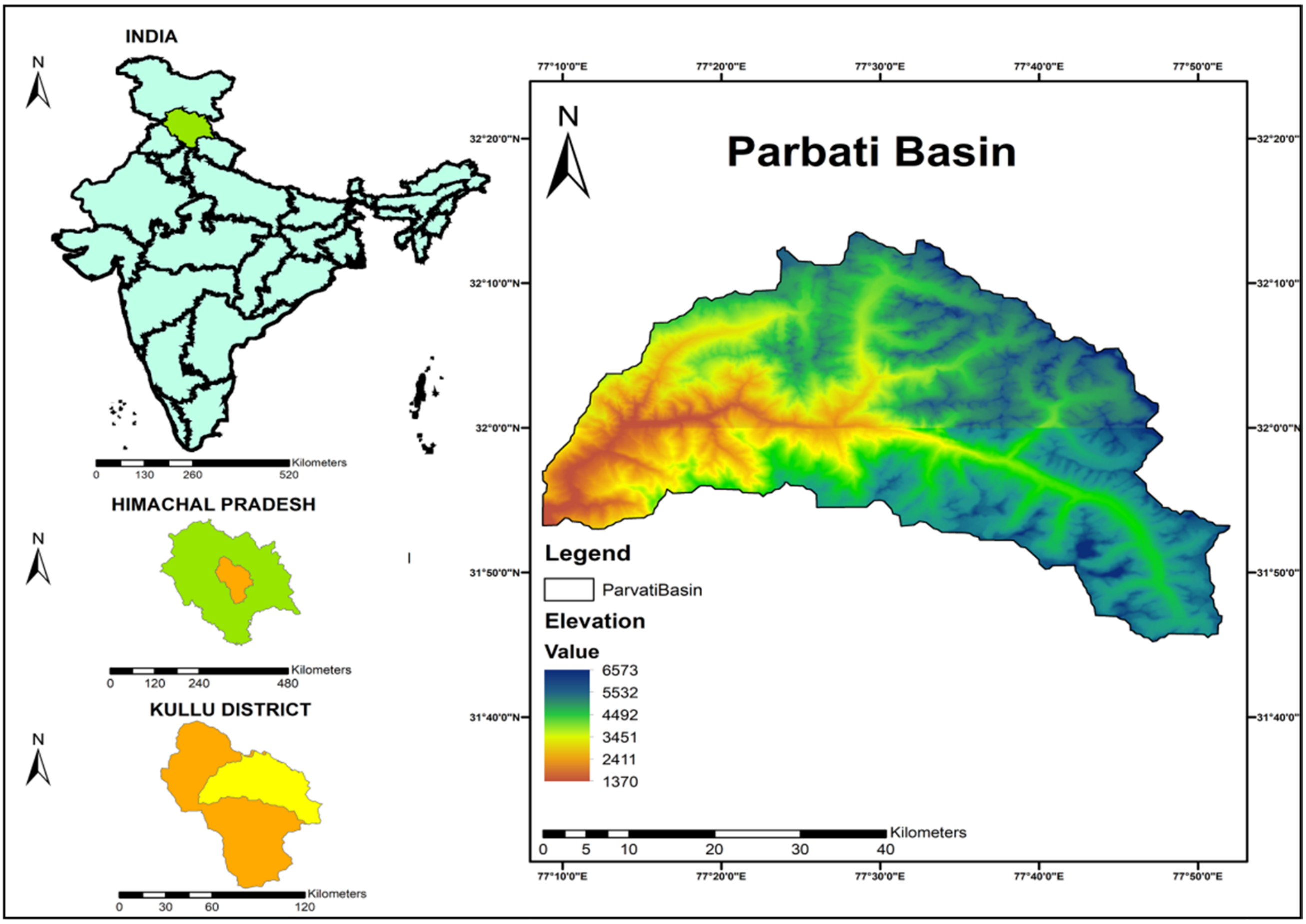


Fig.1 Location of the study area with altitude gradient

semi-consolidated to consolidated sediments of sedimentary, metamorphic and igneous origin descending higher to lower altitude [14]. The Parbati basin has fissured formation as shown in Fig. 2. The porous structures of unconsolidated sediments form the potential aquifers. The occurrence of groundwater in the basin is confined to semi-confined. However, phreatic aquifers form major source of domestic and irrigation water usages in the valley.

2.2 Drainage pattern

The Drainage pattern of the River Parbati exhibits tree-like dendritic pattern which is developed over sedimentary rocks (Fig. 2) [28]. Additionally, other drainage patterns are also present in the basin. Herringbone type of drainage pattern at Marhigarh Nala is one of the patterns where tributaries meet the mainstream at right angle. The trellis drainage pattern representing soft rocks like phyllitic slates and are well developed in the terrace and lower reaches of the valley [29]. In the areas of the uniformly dipping rocks, streams are running parallel to each other forming sub parallel drainage pattern. The sampling location in the study area is represented in Fig. 3.

3 Materials and methods

A well approached Stratified sample technique was adopted to collect the surface water sample along the river stretch of the study area. Total of thirty-six water samples, eighteen samples during pre-monsoon (June 2019) and eighteen samples during post—monsoon (September 2019) were collected from river Pārbati and its tributaries.

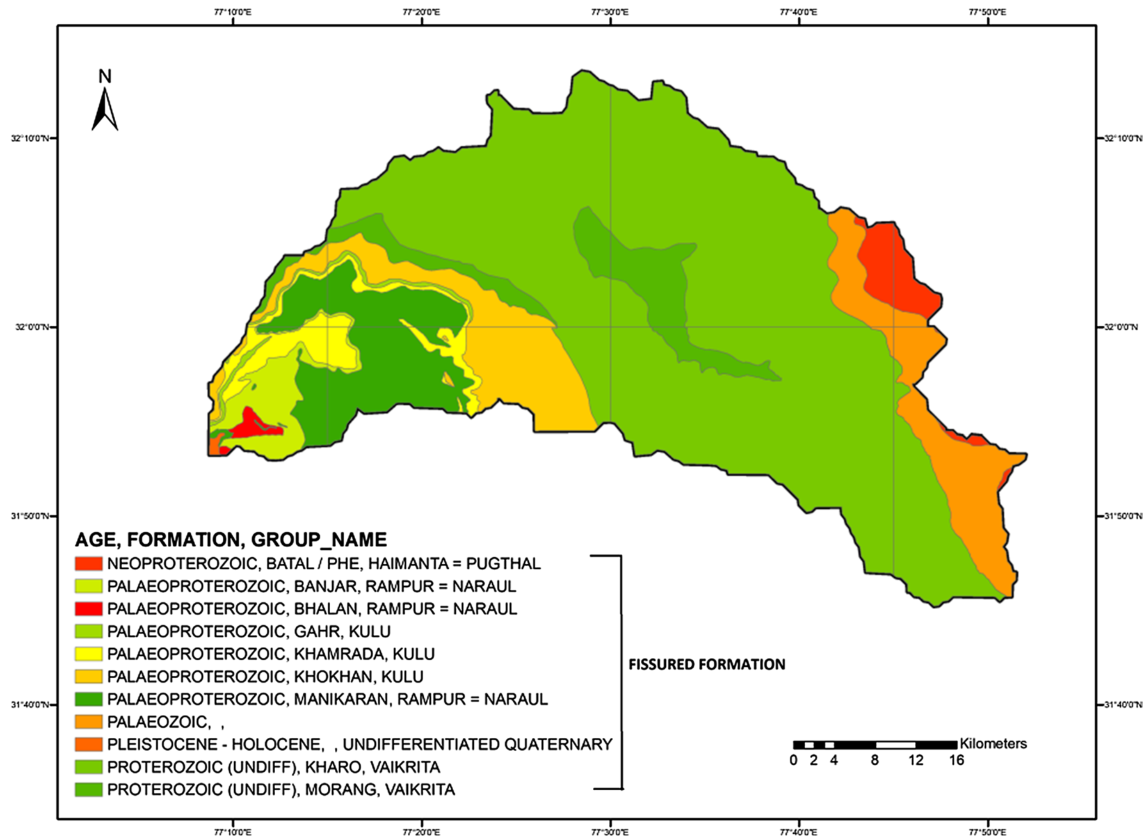


Fig.2 Geological map of Parbati Basin

Samples were collected in1000 ml best quality, sealed shut polyethylene bottles with cover lock. Physical parameters like EC, pH, TDS were measured on the field after sample collection using portable water and soil analysis kit. Major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) were analyzed by following standard procedure given by American Public Health Association [30]. The accuracy of the chemical analysis was checked by Charge Balance Error (CBE) [31].

$$\text{Charge Balance Error (CBE)} = \left(\sum \text{Cations} - \sum \text{Anions}\right) \Big/ \left(\sum \text{Cations} + \sum \text{Anions}\right) \times 100\% \quad (1)$$

Majority of the analyzed samples showed CBE around ± 10%

Calcium, Magnesium, Bicarbonates and Total hardness were determined using EDTA titrimetric method by APHA 2017. Sodium and Potassium using flame photometric method, Nitrate and Sulphate by UV spectrophotometric method respectively. Chloride was estimated through argentometric method and alkalinity with acid titration method. Mean values were calculated for each parameter to understand the seasonal variation as an indication of the precision of each parameter. Maps were prepared using ArcGIS 10.8 software and Piper trillinear, Durov were plotted using Grapher. The statistical software SPSS, Grapher, Aquachem and Microsoft Excel were employed for the calculations and data interpretation.

3.1 Appraisal of Water Quality Index (WQI)

WQI is an effective mathematical tool to evaluate the suitability of water for drinking purpose [32]. It is calculated by adopting the weighted arithmetical index method [33]. In the present study physiochemical parameters namely pH,

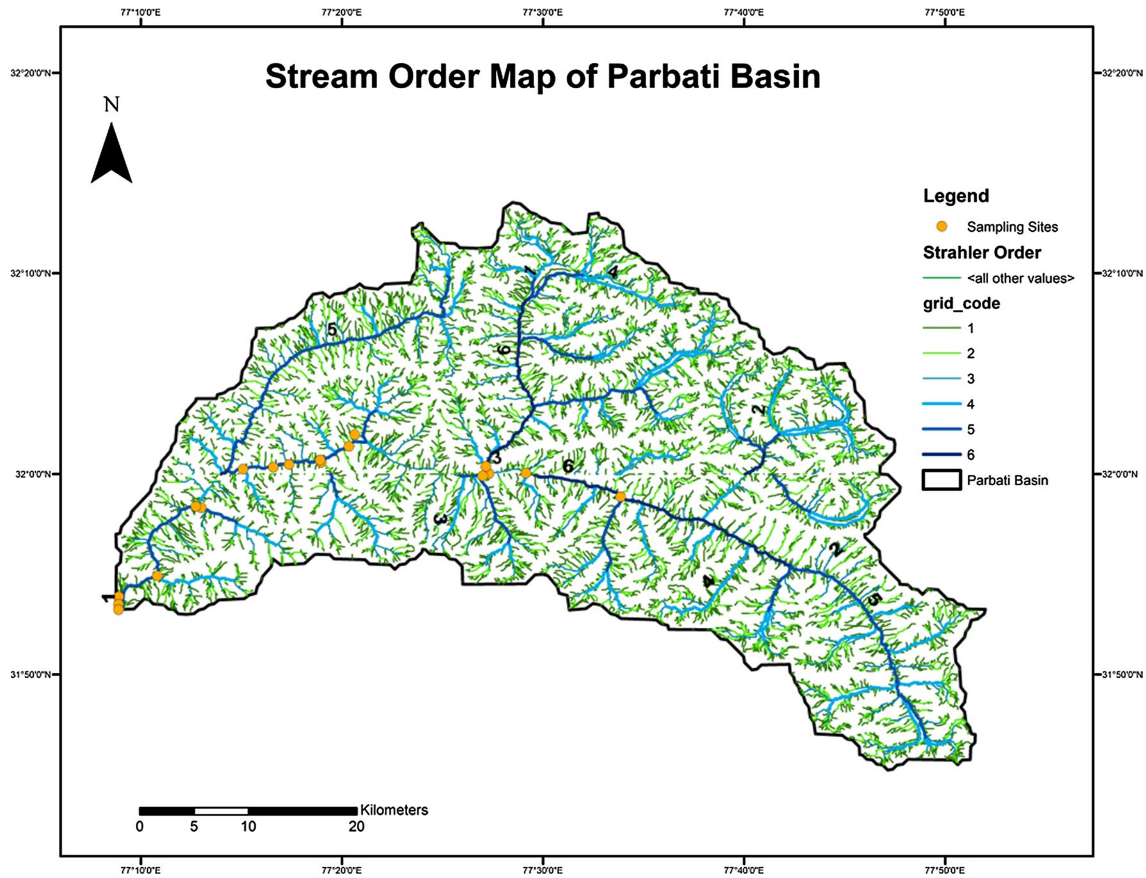


Fig.3 Drainage pattern and sampling sites of the Parbati River Basin

EC, TDS, TH, Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, NO_3^{-} were considered for computing WQI for river Parbati. The weighted arithmetic index method was adopted by many researchers [34, 35] and the equation used is,

$$\text{WQI} = \sum \text{qn}Wn/Wn \tag{2}$$

where W_n = unit weight of nth parameters, q_n = sub-index or quality rating for the ith parameter.

The calculation of WQI involves following steps (Eq. 3–5):

$$W_n = \text{K}/\text{Sn} \tag{3}$$

K, is the proportionality constant obtained from,

$$\text{K} = \left[1/\left(\sum \text{ni} = 01/Si\right)\right][1/ \tag{4}$$

where, Sn and Si are the BIS (Bureau of Indian Standards) standard values of the water quality parameter

$$\text{q}_{\text{ni}} = \text{Va} - \text{Vi}/\text{Vs} - \text{Vi} \times 100 \tag{5}$$

q_{ni} is the quality rating of the ith parameter for a total of n water quality parameters.

Where, Va = value of the water quality parameter obtained from laboratory analysis, Vi = ideal value (for pH = 7 and 0 for other parameters) and Vs = BIS standard value of water quality parameters.

3.2 Evaluation of hydrogeochemical facies of surface water

To comprehend the hydro geochemical attributes of surface water, different plots were utilized specifically, Piper, Durov and Gibbs plot [36–38]. These plots represent the graphical relationship characterizing different geochemical marks in surface water samples. The Grapher 12.0 was used to prepare the Piper diagram and Durov, while Gibbs plot was prepared by Aquachem software.

3.3 Multivariate statistical analysis

Multivariate Statistical techniques have been used to organize and simplify datasets and characterize freshwater, marine water and sediment quality [39–41]. In recent years, water quality assessment has been widely done using multivariate statistical techniques [42, 43].

Correlation analysis is a technique which determines the correlation coefficient between variables. The relationship between two variables can be measured by the strength and significance of the variables. The strength is indicated by the correlation (r), whereas the significance is expressed in probability levels (p values). Larger the correlation coefficient, stronger the relationship, whereas smaller the p level, more significant the relationship.

Statistical extraction of linear relationship from a given set of variables is performed by applying Principal Component Analysis (PCA) technique [22]. PCA allows to gain insight into the data without significant loss of information in the process [44, 45]. Principal components generated during the analysis are arranged in such a manner that they correspond to decreasing contribution of variance, i.e., principal component 1 (PC1) explains the highest amount of variance in the original data [46, 47] classified the factor loadings as "strong", "moderate" and "weak", corresponding to absolute loading values of 0.75, 0.75–0.50 and 0.50–0.30, respectively. However, loading reflects the relative importance of a variable within the component and does not reflect the importance of the component itself [48].

Cluster analysis was performed to arrange large data set of data into groups on the basis of given set of characterstics. Cluster analysis identifies relatively homogeneous groups or cluster of sampling sites based on their similarities/dissimilarities [49]. In this study dendogram was obtained by performing wards method using squared Euclidean distance as a measure of similarity.

The datasets adequacy for PCA was calculated by the Kaiser–Meyer–Olkin Test (KMO) and Bartlett's test [50]. A KMO value of 0.5 is considered the smallest value acceptable and high values near to 1 indicates usefulness of PCA in the study.

4 Results and discussion

Statistical summary of river water samples analyzed for various physio-chemical parameters is given in Table 1 with permissible limits prescribed by BIS and WHO [51, 52]. Mean value for all physio-chemical parameters, except Ca^{2+}, Na^{+}, K^{+} and Cl^{-}, were showing higher values during the pre-monsoon period than post-monsoon.; EC accounted for 100% within desirable limit with mean values 93.44 and 81.05 µS/cm during the period of investigation. TDS values were well within desirable limit in both seasons with mean values 58.8 and 51.06 mg/L. The average values of total hardness are 95.36 mg/L in pre-monsoon and 83.44 mg/L in post-monsoon, respectively. Classification of river water based on total hardness [53] and total dissolved solids [54] are shown in Table 2. Further during the lab analysis higher soluble concentration of Ca^{2+}, Mg^{2+} and HCO_3^{-} ions was found which may contribute to increased hardness of river water samples. Magnesium accounted for 12.62 mg/L in pre-monsoon and 8.85 mg/L for post-monsoon representing samples within desirable limits as the calcium starts precipitating after super saturation has been attained the dissolved concentration of magnesium exceeds that of calcium. Weathering of sandstone and dolomite, in the study area, accounts for higher concentration of Mg^{2+} found during the analysis [55]. Mean value of HCO_3^{-} was more significant during pre-monsoon due to dissolution of carbonate rocks, weathering of feldspar by carbonic acids and oxidation of NO_3^{-} and SO_4^{2-} with organic matter as compared to post-monsoon [56]. The parameters like Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-} and Mg^{2+} were all within the desirable range. During the pre-monsoon season the ionic dominance pattern in the water is governed by cationic species in the order of $Mg^{2+} > Ca^{2+} > Na^{+}$ and K^{+}. However, during the post-monsoon season, such dominance of cations is exceeded by that of anionic species in the order of $HCO_3^{-} > SO_4^{2-} > NO_3^{-} > Cl^{-}$.

Table 1 Statistical summary of physicochemical parameters of Parbati River water

Parameters	Prescribed limit IS: 150,500,2012		Pre-monsoon		Mean	Post-monsoon		Mean	Undesirable effect produced beyond the MPL*
	PL*	DL*	Range			Range			
			Min.	Max.		Min.	Max.		
pH	–	6.5–8.5	6.7	8.6	7.66	6.48	7.32	6.84	Taste effects, mucus membrane
EC	2000 µS/cm	750 µS/cm	78	108	93.44	72	96	81.05	High concentration laxative effect on human
TDS	2000 mg/L	500 mg/L	49.14	68.04	58.8	45	60.48	51.06	Gastrointestinal irritation
TH	600 mg/L	300 mg/L	60	124	95.36	64	116	83.44	Calcification at arteries, gastrointestinal irritation
Major cations									
Ca^{2+}	200 mg/L	75 mg/L	15.13	20.18	17.38	1.13	26.91	18.83	May cause kidney and bladder problems
Mg^{2+}	100 mg/L	30 mg/L	2.38	19.97	12.62	4.8	15.94	8.85	Laxative effect
Na^{+}	200 mg/L		1.8	2.9	2.6	2.4	4.2	3.4	High blood pressure
K^{+}	12 mg/L		3.6	4.2	3.8	3.2	4.8	3.85	Bitter taste, laxative effects on human digestive and nervous system
Major anions									
HCO_3^{-}	600 mg/L	200 mg/L	91.5	183	122	91.5	152.5	108.44	Combined with Ca^{2+} and Mg^{2+} forms carbonate hardness
Cl^{-}	1000 mg/L	250 mg/L	2.55	4.11	3.69	3.26	4.6	4.03	Injurious to people with heart and kidney
NO_3^{-}	–	45 mg/L	0.8	1.8	1.27	0.984	2.1	1.52	Methemoglobinemia in infants
SO_4^{2-}	400 mg/L	200 mg/L	1.84	3.4	2.58	2.36	3.6	3.02	Gastrointestinal irritation along with Mg or Na, can have a cathartic effect on users

**PL* permissible limit, *DL* desirable limit, *MPL* maximum permissible limit

Table 2 Classification of Parbati River water based on total hardness and total dissolved solids

TH (as $CaCO_3$ mg/L)	Water Classification	Pre-monsoon samples (%)	Post-monsoon samples (%)	TDS (mg/L)	Water category	Pre-monsoon samples (%)	Post-monsoon samples (%)
< 75	Soft	12%	28%	< 500	Desirable for domestic purposes	100%	100%
75–150	Moderately Hard	82%	72%	500–1000	Permissible for domestic purposes	–	–
150–300	Hard	–	–	1000–3000	Useful for irrigation	–	–
> 300	Very Hard	–	–	> 3000	Not fit for both domestic & agricultural purposes	–	–

4.1 Hydrogeochemical evaluation

Hydrogeochemical facies layouts in the form of graphical representation aiming to provide the analogies, dissimilarities and interpretation of evolutionary trends and different type of water in a particular area. For studying the effects of mixing water within the different lithological frameworks and for understanding various geochemical processes the value of graphical representation techniques is of immense importance. Many researchers such as Piper, Chadha, Collins and Black have contributed to the concept of graphical representation of geochemical analysis of water [36, 57–59].

4.1.1 Piper trilinear diagram

Piper diagrams are widely applied to graphically study the sources of dissolved constituents in water samples [36]. The ionic concentration was plotted in piper diagram to characterize the hydrochemistry of surface water in the study area (Fig. 4a, b). Piper diagram shows that all the samples are in Ca^{2+}- Mg^{2+}-HCO_3^- facies belongs to temporary hardness and alkaline earth elements (Ca^{2+} + Mg^{2+}) exceeding the alkali elements (Na^+ + K^+) where Ca^{2+} and Mg^{2+} are leading cations in the study area shown in Table 3. Further, it was found that the concentration of weak acids (CO_3^{2-} + HCO_3^-), during both the seasons, is higher than the strong acids (SO_4^{2-} and Cl^-). This further indicates the presence of HCO_3^- as principal anion in the surface water. The Cation triangle shows that 16% samples are Ca^{2+} type, 56% in Mg^{2+} and remaining 28% falls in no dominant cation zone for pre monsoon (Fig. 3a), whereas in post monsoon 44% is dominating in Mg^{2+} zone, 33% in no dominating zone and 23% in Ca^{2+} type (Fig. 3b). The anion triangle exhibits that HCO_3^- (100%) is the dominant ion during pre-monsoon and post-monsoon (Table 3). Consequently, concentration of ions such as Na^+, K^+ and Cl^-, SO_4^{2-} is very low and thus insignificant in both the seasons. As all the samples fall within the field of Ca^{2+}-Mg^{2+}-HCO_3^- water type, we can infer that the surface water chemistry is controlled by leaching process of dolomites, limestones and gypsum.

4.1.2 Durov plot

Durov plot is a significant graphical structure that gives better data on the hydrochemical portrayal and possible geochemical processes (mixing, cation exchange, reverse ion exchange dissolution) influencing the water quality of the area. This diagram is a composite plot consisting of two ternary diagrams where the milli equivalents percentages of the cations of interest were plotted against that of anions of interest; sides form a central rectangular, binary plot of total cation vs. total anion concentrations [60]. This diagram is very useful in indicating the samples with similar chemical composition as well as determines a useful relationship among different water samples [61]. The Durov plot of the water

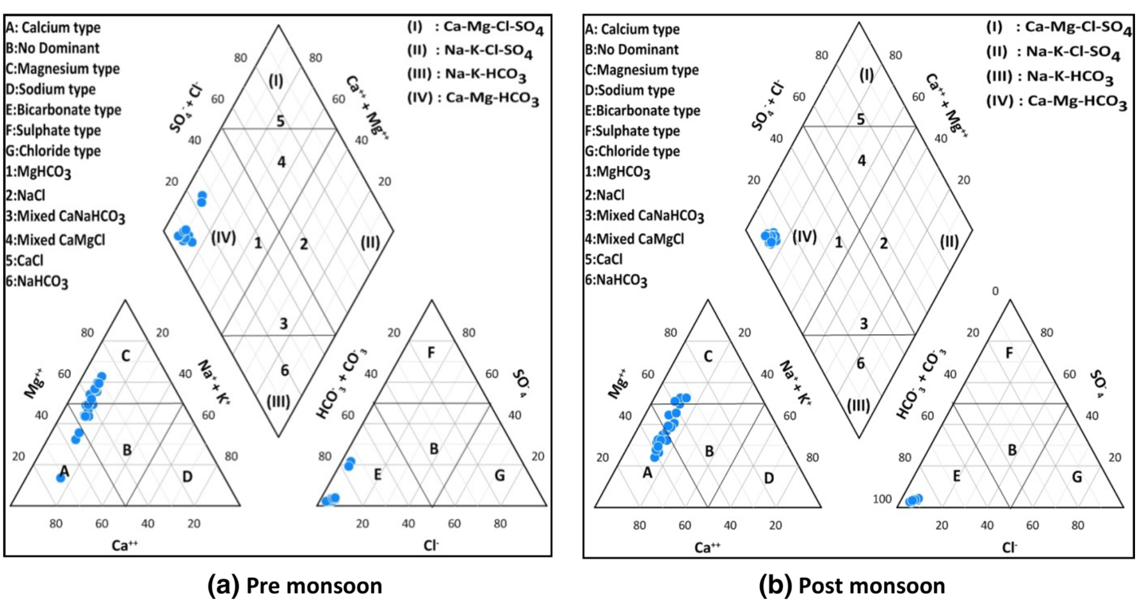


Fig. 4 Piper classification diagram illustrating the chemical composition of Parbati River water. **a** Pre monsoon. **b** Post monsoon

Table 3 Parbati River water samples characterization based on Piper diagram

Class	Surface water types corresponding subdivision of facies	Samples in the different category			
		Pre-monsoon		Post-monsoon	
		No. of samples	Percentage	No. of samples	Percentage
Surface water samples characterization based on Piper diagram					
I	Ca^{2+}- Mg^{2+}-Cl^{-}-SO_4^{2-}	–	–	–	–
II	Na^{+}-K^{+}-Cl^{-}-SO_4^{2-}	–	–	–	–
III	Na^{+}-K^{+}-HCO_3^{-}	–	–	–	–
IV	Ca^{2+}- Mg^{2+}-HCO_3^{-}	18	100	18	100
1	HCO3^{-}-CO_3^{2-}- and Ca^{2+}-Mg^{2+} (temporary Hardness); magnesium bicarbonate type (carbonate hardness exceeds 50%)	18	100	18	100
2	Cl- SO42- and Na+-K+(Saline); Sodium chloride type (non carbonate alkali exceeds 50%)	–	–	–	–
3	Mixing zone (Ca2+-Na+-HCO3-);base ion exchange processes	–	–	–	–
4	Mixing zone (Ca2+-Mg2+-Cl-);reverse ion exchange processes	–	–	–	–
5	Cl-SO42- and Ca2+-Mg2+(Permanent hardness); Calcium chloride type (non carbonate hardness exceeds 50%)	–	–	–	–
6	HCO3–CO32– and Na+-K+(alkali carbonate); Sodium bicarbonate type (carbonate alkali exceeds 50%)	–	–	–	–

samples indicates that there are mainly two geochemical processes that could affect the genesis of water in the study area (Fig. 4a, b). According to the classification of [61], 88% samples in Pre-monsoon and 86% in Post-monsoon belong to HCO_3^- and Mg^{2+} dominant cation, this water type indicates probable mixing, uncommon dissolution influences and reverse ion exchange process (Fig. 5a) whereas 12% samples in pre-monsoon and 14% samples in post-monsoon falls where HCO_3^- and Ca^{2+} dominant type of water, indicating the partial ion exchange processes (Fig. 5b). None of the data points lie in the lower-right side of the boomerang, where water composition is dominated by atmospheric precipitation process.

4.1.3 Gibbs plot

Hydrochemical processes such as precipitation, rock water interaction and evaporation are well interpreted through gibbs plot [36]. Gibbs demonstrated that if total dissolved solid is plotted against Na + K/ (Na + Ca + K), it would provide information on the mechanism controlling chemistry of water. Collectively, the chemistry of water is influenced by the following three main factors: (1) evaporation dominance; (2) precipitation dominance and (3) rock dominance. Figure 6 exhibits that all the surface water samples for pre-monsoon and post-monsoon fall in the precipitation dominance zone which indicates that water is mainly controlled by rock dominance however geochemical process such as precipitation -dissolution; oxidation -reduction and ion exchange are the main governing factors of water chemistry.

The studies in other parts of Himalayan regions confirmed rock dominance as main factor for controlling ionic composition in water bodies [6, 62, 63]. In the study area due to long time rock water interaction, percolations and flow through the rocky lithology has resulted in high solute concentration which is significantly controlling the water quality of the area. However, during post monsoon there is minor influence of precipitation dominance and melting of ice in the region. This reflects that water chemistry is mainly controlled by interaction of rock formation with precipitation for both seasons in Parbati river.

4.2 Water Quality Index

The cumulative effect of various physio-chemical parameters governing the overall water quality is holistically represented in Water Quality Index (WQI). The weighted arithmetic index method [33] has been used for the calculation. WQI reveals variation in the water quality status related to suitability for human consumption. A perusal of Table 4 reveals that 22% water samples in pre-monsoon and 50% water samples in post monsoon season respectively fall in excellent class whereas 73% water samples in pre monsoon and 50% water samples in post-monsoon falling in good class. Water quality of the river water samples has WQI = < 50 which represents the excellent to good water quality of analyzed river water samples (Table 5). Most of the sampling locations meets the requirement of good water quality except in Bhunter during pre-monsoon. The Bhunter town is situated on banks of river Beas, due to incessant growth of population, modern infrastructure and small industries the water quality of the town maybe influenced by household and industrial wastewater followed by agricultural run-off. Along the altitudinal gradient, most of the upstream segments have excellent to

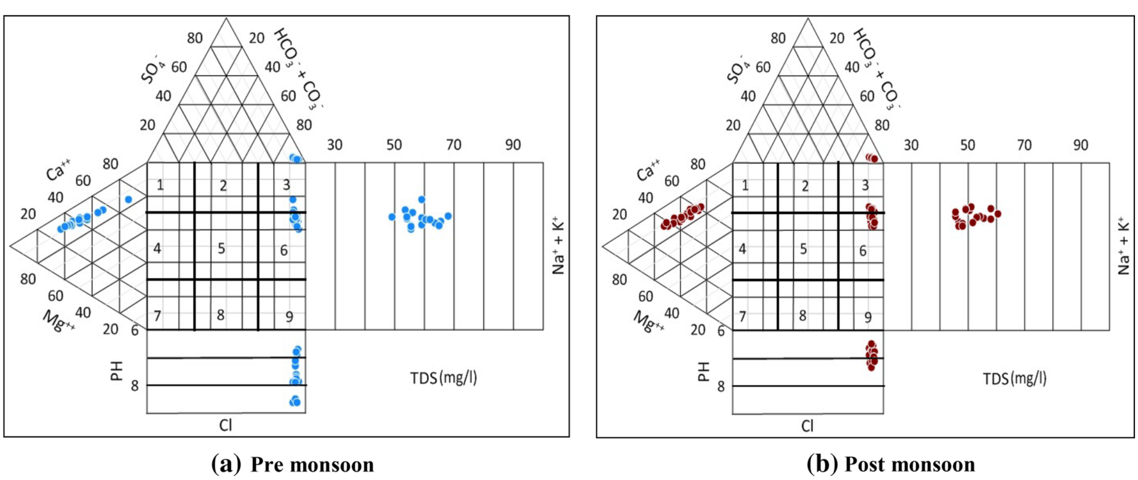


Fig. 5 Durov diagram showing the hydrochemical facies in the Parbati River water. **a** Pre monsoon. **b** Post monsoon

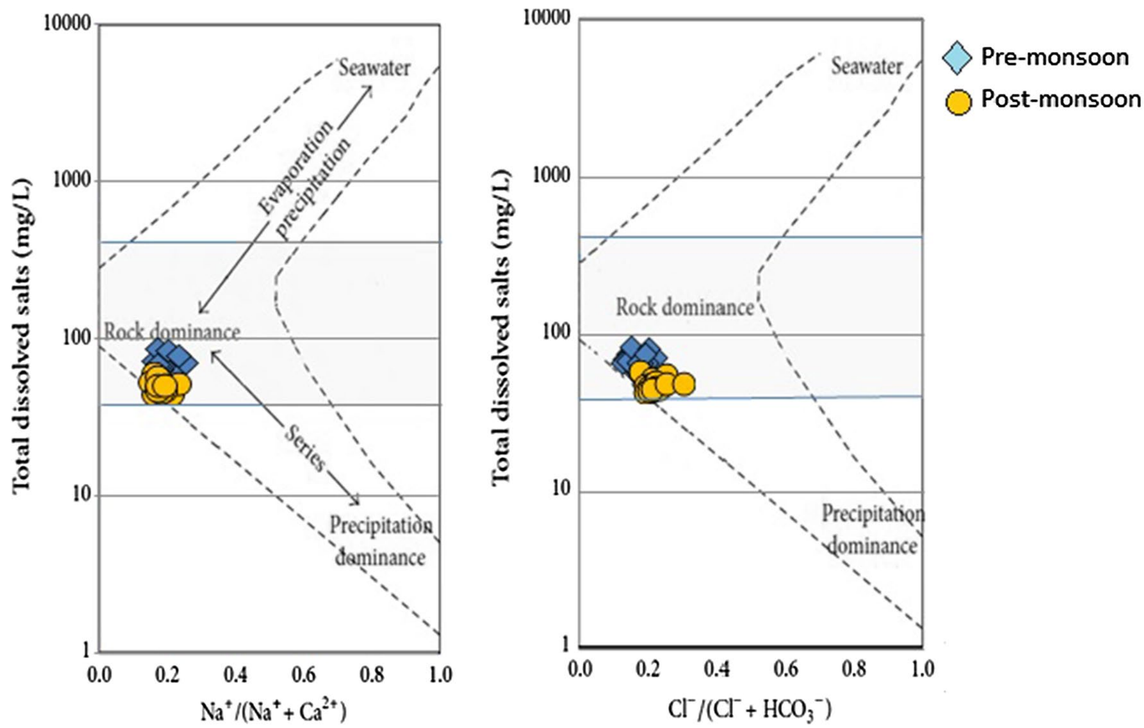


Fig. 6 Mechanism controlling water chemistry in Parbati River (after Gibbs [38])

Table 4 WQI categorization

Sr.No.	WQI	Status	Pre-monsoon		Post-monsoon	
			Samples (in numbers)	Percentage (%)	Samples (in numbers)	Percentage (%)
1	0–25	Excellent	4	22	9	50
2	26–50	Good	13	73	9	50
3	51–75	Poor	1	5	–	–
4	76–100	Very poor	–	–	–	–
5	> 100	Unfit	–	–	–	–

good water quality for both the seasons where as in downstream segments the influence of population and urbanization on water quality is deteriorating towards the lower altitudinal regions. The locations like Rudranag, Guwacha, Toshnalla and Grahan nalla have lesser change in their WQI values whereas Jiyah, Hathithan and Bhunter showed a maximum change in WQI values from pre-monsoon to post-monsoon indicating that runoff played important role in dilution of river pollutant in these areas.

4.3 Correlation matrix

The Pearson's correlation matrix develops relationship among components that how well the variance of each component can be explained through correlation with each of other [64]. A common origin and similar distribution must be defined to correlated variables in order to interpret the coefficient correlation. The value near to -1 or 1 in correlation coefficient depicts the strongest negative or strongest positive relationship between two variables whereas values closest to 0 denotes no linear relationship between variables.

The Pearson's correlation coefficient (r) was prepared to assess correlation among pH, EC, TDS, Hardness and various chemical constituents variables for surface water in pre-monsoon (June 2019) and post-monsoon (September 2019). Several parameters are found to be strong positive ($r_{>}$ 0.8) and positive correlated ($r_{>}$ 0.5–0.79). During pre-monsoon a

Table 5 WQI Calculation for individual water sampling locations

S.No.	Pre-Monsoon			Post-Monsoon	
	Locations	WQI Value	WQI Class	WQI Value	WQI Class
1	Nhyarathach	32.19	Good	22.48	Excellent
2	Rudranag	21.44	Excellent	19.48	Excellent
3	Parvati river Guwacha	20.30	Excellent	21.36	Excellent
4	Tosh nala	24.73	Excellent	22.84	Excellent
5	Barshaini Tail pt	26.62	Good	22.95	Excellent
6	Manikaran bridge	33.76	Good	26.45	Good
7	Manikaran NHPC	35.86	Good	23.65	Excellent
8	Grahan nalla	24.51	Excellent	22.29	Excellent
9	Kasol	39.66	Good	26.31	Good
10	Katagla	37.55	Good	28.43	Good
11	Sumaropa	34.21	Good	26.45	Good
12	Malana Jari	36.64	Good	24.72	Excellent
13	Shat nalla	37.00	Good	24.65	Excellent
14	Shat Parvati confluence	36.09	Good	28.45	Good
15	Charod	35.71	Good	32.34	Good
16	Jiyah	49.08	Good	36.40	Good
17	Hathithan	48.53	Good	32.45	Good
18	Bhunter(Confluence)	53.42	Poor	38.45	Good
19	Overall Quality	34.85	Good	26.67	Good

strong positive correlation value exist between EC-TDS and TH- Mg^{2+}- HCO_3^- whereas positive correlation observed in TH- Ca^{2+}, Mg^{2+}- HCO_3^-, Cl^--HCO_3^- and Na^{2+}–HCO_3^- indicating that these chemical parameters are from similar sources and can be attributed to geogenic process, while water traveling over sedimentary and metamorphic rocks which dissolve calcium, magnesium, chlorides and carbonates in it [65] (Table 6a). The positive correlation indicated influence of one parameter over other. However, during post-monsoon showed strong positive correlation among EC-TDS, TH- Mg^{2+}-Ca^{2+}-HCO_3^- indicating to the dissolution of limestone with the incoming water sources whereas positive correlation between TH- K^+-SO_4^{2-} have distinctive resources (Table 6b).

4.4 Principal Component Analysis (PCA)

Table 7 represents the results of Kaiser-Meyer-Olkin (KMO) and Barlett's Test. The KMO test results were interpreted according to guiding rules [66], the value of 0.743 for Pre-Monsoon (PRM) and 0.718 value for Post-Monsoon (POM) indicates data adequacy for PCA. Another preliminary assumption test (Kolmogorov–Smirnov, KS, and Shapiro–Wilk, SW) was conducted to check the normality of dataset [67] using IBM SPSS Statistics 26. The significant value for KS and SW test must be greater than 0.05 ($p > 0.05$). Results of computed p-value based on KS and SW is presented in Table 8. All the dependent variables had p-value greater than 0.005, it was therefore concluded that the data used is statistically normally distributed.

To distinguish the latent factors influencing the hydrochemistry, PCA was applied on analyzed parameters of surface water samples. Principal components (PCs) taken for interpretation having eigen values > 0.75 and additionally second level of interpretation are considered statistically significant [23, 68]. Table 9 shows the component loading factors, cumulative percentage and percentages of variance and communality explained by each principal component. Standardized datasets were employed for performing PCA and in varimax rotated component matrix only four PCs, whose eigen value is greater than 1, explained 81.17 and 77.64% of the total variance for pre-monsoon and post-monsoon period, respectively. A scree plot representing all the PCs which were extracted during PCA is shown in Fig. 7 (a & b).

During the pre-monsoon period, PC1 explains approximately 1/3rd i.e., 30.35% of the total variance and has strong positive correlation value with Total Hardness, Mg^{2+} and HCO_3^- and a moderately strong positive correlation with Na^+ and Cl^- which reflects the role of lithogenic factors in influencing the water chemistry [69]. High-positive loading of Mg^{2+} and HCO_3^- with TH shows temporary hardness in the water. Strong correlation of HCO_3^- ions with alkali and alkaline earth metals indicated the natural weathering sources [69, 70]. PC2 (25.30% of total variance) has moderate positive

Table 6 a: Matrix of correlation for water variables during pre-monsoon. b: Matrix of correlation for water variables during post-monsoon

	pH	EC	TDS	TH	Mg^{2+}	Ca^{2+}	K+	Na^{+}	Cl^{-}	HCO3⁻	SO_4^{2-}	NO3⁻
(a)												
pH	1.00											
EC	− 0.58	1.00										
TDS	− 0.58	**1.00**	1.00									
TH	0.03	0.20	0.20	1.00								
Mg^{2+}	0.07	0.19	0.19	**0.98**	1.00							
Ca^{2+}	0.03	0.04	0.04	**0.54**	− 0.14	1.00						
K+	0.18	0.19	0.19	− 0.18	− 0.23	0.31	1.00					
Na^{+}	0.25	− 0.22	− 0.22	0.34	0.32	0.01	0.14	1.00				
Cl^{-}	0.25	0.12	0.12	0.34	0.32	0.01	0.14	1.00	1.00			
HCO3⁻	− 0.07	− 0.05	− 0.05	**0.79**	**0.77**	− 0.07	0.08	**0.61**	**0.61**	1.00		
SO_4^{2-}	0.28	0.15	0.15	0.20	− 0.13	− 0.15	− 0.47	− 0.26	− 0.26	− 0.15	1.00	
NO3⁻	0.09	− 0.13	− 0.13	− 0.14	− 0.14	0.06	0.03	− 0.27	− 0.27	− 0.19	− 0.14	1.00
(b)												
pH	1.00											
EC	0.11	1.00										
TDS	0.11	**1.00**	1.00									
TH	0.14	0.38	0.38	1.00								
Mg^{2+}	0.05	0.08	0.08	**0.94**	1.00							
Ca^{2+}	0.08	**0.61**	**0.61**	**0.82**	− 0.15	1.00						
K+	0.24	0.20	0.20	**0.62**	0.49	0.33	1.00					
Na^{+}	0.37	0.24	0.24	0.20	0.20	0.03	− 0.11	1.00				
Cl^{-}	0.01	0.58	0.58	0.32	0.15	0.36	0.17	0.32	1.00			
HCO_3^{-}	0.06	0.15	0.15	**0.84**	**0.73**	0.18	**0.51**	− 0.17	0.17	1.00		
SO_4^{2-}	0.39	0.29	0.29	***0.60***	0.36	0.32	0.15	0.02	0.42	0.28	1.00	
NO_3^{-}	− 0.32	0.39	0.39	0.16	0.12	0.10	0.24	− 0.10	0.02	0.13	− 0.03	1.00

Table 7 Kaiser–Meyer–Olkin and Barlett's test

KMO and Barlett's test		PRM	POM
KMO sampling adequacy		0.743	0.718
Barlett's Test of Spherecity	Approx. Chi-Square	913.12	848.67
	df	66	66
	Sig	0	0

correlation with Na^{+} and Cl^{-} and strong negative correlation with EC and TDS. Different hydrogeochemical processes that contribute to enrich more mineralized water is due to the combinations of Na^{+}, Cl^{-}, HCO_3^{-}, SO_4^{-} ions. PC3 was strongly positive weighted on Ca^{2+} and K^{+} and moderate positive score on Na^{+} accounts for 16.37%. PC4 explains 9.15% of the total variance observed and has strong positive correlation with NO_3^{-} which points towards the role of agricultural runoff (NPK) along with the seepage of wastewater into the surface water bodies.

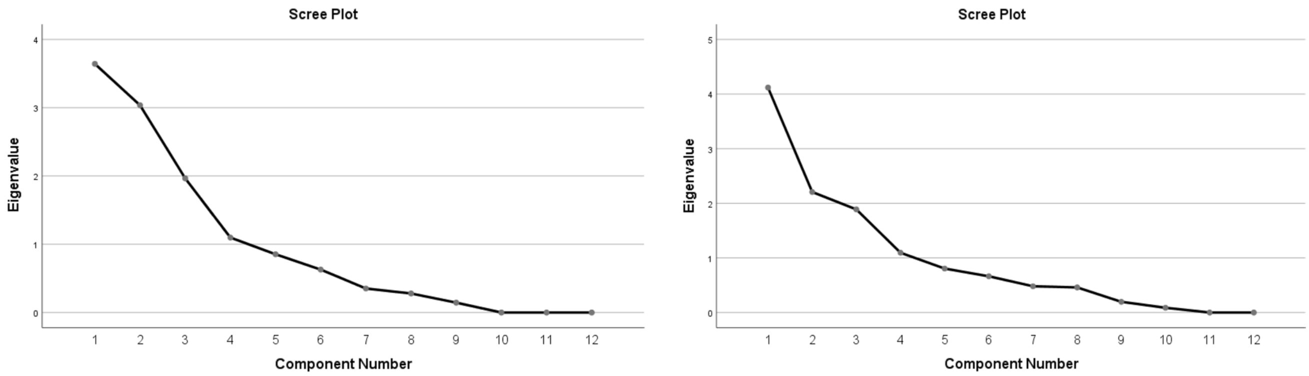
For post-monsoon period, again PC1 explains 1/3rd i.e., 34.32% of the total variance and has a strong positive loading with EC, TDS and TH and a moderately positive correlation with Ca^{2+}, K^{+}, HCO_3^{-} and Cl^{-}. The high positive correlation of Mg^{2+} with total hardness shows temporary hardness [71] indicated that with the high concentration of Mg^{2+} ions the degree of water hardness increases. A high positive loading of Ca^{2+} and HCO_3^{-} is attributed to various natural processes such as- weathering of rock minerals (limestone and calcium carbonate bearing rocks) and to various ion-exchange processes taking place in the groundwater system [69]. PC2 exhibits 18.39% of the total variance and the values of Mg^{2+} show high loading and the concentration of HCO_3^{-} has moderate positive loading on the PC2 (Table 7). PC3 shows the 15.73% of the total variance with moderate positive loading on Na^{+}, moderate negative score on NO_3^{-}. The significant

Table 8 Results of the normality tests

Parameters	Seasons	Kolmogorov–Smirnov Statistic	Shapiro–Wilk Statistic
pH	Pre-monsoon	0.241	0.784
	Post-monsoon	0.189	0.684
EC	Pre-monsoon	0.221	0.842
	Post-monsoon	0.162	0.724
TDS	Pre-monsoon	0.228	0.864
	Post-monsoon	0.178	0.836
TH	Pre-monsoon	0.321	0.848
	Post-monsoon	0.247	0.764
Mg^{2+}	Pre-monsoon	0.411	0.807
	Post-monsoon	0.198	0.758
Ca^{2+}	Pre-monsoon	0.172	0.784
	Post-monsoon	0.203	0.842
K^{+}	Pre-monsoon	0.264	0.812
	Post-monsoon	0.118	0.784
Na^{2+}	Pre-monsoon	0.246	0.846
	Post-monsoon	0.212	0.889
Cl^{-}	Pre-monsoon	0.354	0.742
	Post-monsoon	0.254	0.668
HCO_3^{-}	Pre-monsoon	0.347	0.824
	Post-monsoon	0.244	0.864
SO_4^{2-}	Pre-monsoon	0.504	0.802
	Post-monsoon	0.482	0.794
NO_3^{-}	Pre-monsoon	0.248	0.862
	Post-monsoon	0.164	0.801

Table 9 Varimax rotated matrix of analyzed water samples of Parbati River

Variables	Component (pre-monsoon)						Component (post-monsoon)			
	PC1	PC2	PC3	PC4	Communality	PC1	PC2	PC3	PC4	Communality
pH	− 0.302	0.735	0.147	− 0.044	0.656	− 0.078	0.275	0.811	− 0.127	0.756
EC	0.236	− **0.899**	0.072	− 0.192	0.907	**0.757**	− 0.587	0.004	0.089	0.925
TDS	0.236	− **0.899**	0.072	− 0.192	0.907	**0.757**	− 0.587	0.004	0.089	0.925
TH	**0.881**	− 0.084	− 0.327	0.212	0.931	**0.851**	0.451	0.017	0.083	0.935
Mg^{2+}	**0.869**	− 0.069	− 0.427	0.173	0.972	**0.584**	**0.703**	− 0.012	0.334	0.947
Ca^{2+}	− 0.161	− 0.051	**0.559**	0.126	0.357	**0.604**	− 0.431	0.054	− 0.468	0.773
K^{+}	0.018	− 0.257	**0.767**	0.079	0.661	**0.607**	0.312	− 0.462	− 0.067	0.682
Na^{+}	**0.689**	**0.565**	0.438	− 0.138	0.934	0.207	− 0.114	**0.632**	**0.654**	0.883
Cl^{-}	**0.669**	**0.525**	0.438	− 0.138	0.934	**0.583**	− 0.232	0.345	− 0.006	0.513
HCO_3^{-}	**0.872**	0.253	− 0.064	0.143	0.845	**0.594**	**0.554**	− 0.183	− 0.169	0.721
SO_4^{2-}	− 0.368	0.425	− **0.596**	− 0.272	0.744	**0.564**	0.178	0.446	− 0.407	0.712
NO_3^{-}	− 0.312	− 0.037	0.017	**0.892**	0.894	0.346	− 0.237	− **0.512**	0.315	0.537
Eigen value	3.642	3.036	1.966	1.098		4.119	2.207	1.888	1.095	
Cumulative % of variance	30.351	55.651	72.03	81.181		34.32	52.71	68.44	77.56	
% of variance	30.351	25.301	16.379	9.151		34.32	18.391	15.732	9.123	



(a) Pre monsoon **(b)** Post monsoon

Fig.7 Scree plot extraction principal component in Pre monsoon and Post monsoon. **a** Pre monsoon. **b** Post monsoon

inverse relationship between Na^{+} and NO_3^{-} indicates the diverse source of chemical origin [72]. PC4 explains 9.1% of the total variance observed and has strong positive correlation value with Na^{+} and moderately strong negative correlation with Ca^{2+}.

4.5 Cluster analysis

Cluster analysis is applied to obtain common cluster of monitoring locations having relatively similar characterstics. Dendrogram representing the clusters rendered during the analysis are shown in Fig. 8. Three clusters were obtained from pre-monsoon and post-monsoon from the criteria of significant Square Euclidean distance measure of standardized data by applying a complete linkage method. In pre-monsoon cluster 1 consist of monitoring locations Nhyarathach, Kasol and Bhunter (1, 9, and 18). Cluster 2 consist of monitoring location Rudranag, Guwacha, Barshaini, Manikaran bridge, Manikaran NHPC, Grahan nalla, Katagla, Malana-Jari, Charod and Hathithan (2, 3, 5, 6, 7, 8, 10, 12, 15 and 17). Cluster 3 consist of Toshnalla, Sumaropa, Shat nalla, Shat –Parvati confluence and Jiyah(4, 11, 13, 14 and 16). In Post-monsoon cluster 1 consist of Nhyarathach, Rudranag, Guwacha, Tosh nalla, Barshaini, Katagla, Sumaropa, Malana-Jari, Charod and Jiyah(1, 2, 3, 4, 5, 10, 11, 12, 15 and 16). Cluster 2 consists of Malana-Jari and Kasol (9 and 12) and cluster 3 consist Manikaran bridge, Manikaran NHPC, Shat nalla, Bhunter confluence, Grahan nalla and Hathithan (6, 7, 8, 13, 17 and 18).

For both the pre-monsoon as well as post-monsoon seasons three significant clusters were found. All clusters formed have high similarity levels indicating the overall variability of parameters of different sampling points is low within the cluster. However, no specific intra-clusters trend was found to be significant during the analysis.

In the Table 10, average value of each variable is given for all the clusters for both pre-monsoon and post-monsoon seasons. During the pre-monsoon season cluster 1 exhibits the highest level for TH, Mg^{2+}, and HCO_3^{-}. Cluster 2 has

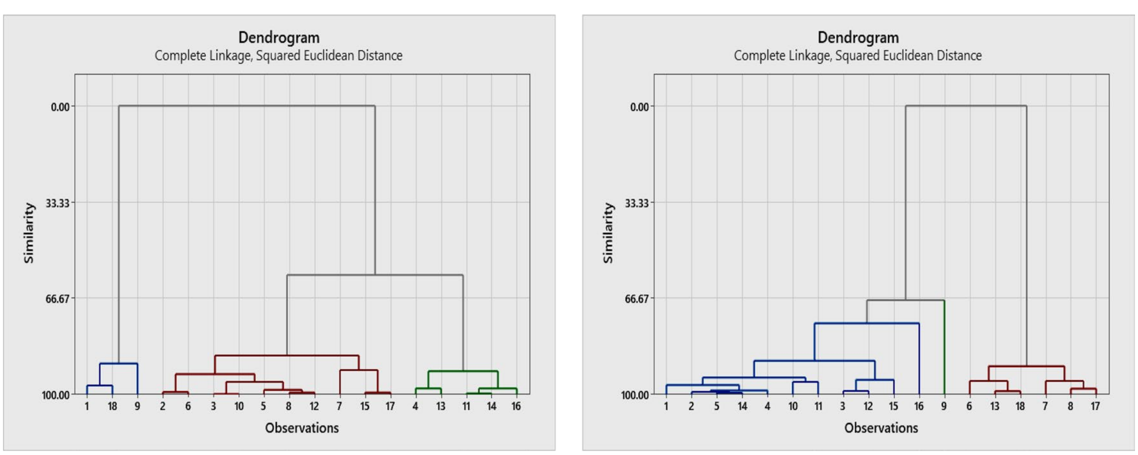


Fig.8 Hierarchical dendrogram showing agglomerate cluster grouping

Table 10 Cluster Centroids for each parameter of analyzed water samples of Parbati River

Pre-monsoon					Post-monsoon			
Variable	Cluster 1	Cluster 2	Cluster 3	Grand Centroid	Cluster 1	Cluster 2	Cluster 3	Grand Centroid
pH	7.717	7.534	7.8800	7.661	6.765	6.998	6.750	6.842
EC	93.333	94.200	92.0000	93.444	162.951	165.369	191.138	165.323
TDS	58.800	59.346	57.9600	58.870	105.918	107.490	124.240	107.460
TH	121.333	98.398	73.7097	95.362	111.348	177.023	133.170	134.452
Mg^{2+}	18.938	13.398	7.2972	12.627	17.858	20.027	20.824	18.745
Ca^{2+}	17.382	17.326	17.4938	17.382	26.773	24.310	22.320	25.705
K^+	3.633	3.870	3.7600	3.800	3.873	3.767	4.200	3.856
Na^+	2.800	2.660	2.3600	2.600	3.200	3.667	4.000	3.400
Cl^-	3.976	3.777	3.3512	3.692	1.123	0.781	0.710	0.986
HCO_3^-	162.667	125.050	91.5000	122.000	182.995	181.333	168.000	181.608
SO_4^{2-}	2.743	2.375	2.9212	2.588	2.506	2.628	2.680	2.557
NO_3^-	1.233	1.262	1.3480	1.281	1.555	1.450	1.640	1.525

lowest level of pH as well as SO_4^- and highest level of TDS. Cluster 3 has highest value for pH, SO_4^- and NO_3^- and least value for EC, TDS, TH, Mg^{2+} and HCO_3^-.

In the post-monsoon season, Cluster 1 exhibit lowest levels of EC, TDS, TH, Mg^{2+}, Na^+ and $SO_4^{-.}$ On the other hand, cluster 2 has highest levels of pH and TH, however, the overall pH of water samples during the post-season is lower than the pre-monsoon season. Cluster 3 has highest value for EC, TDS, Mg, K, Na and $NO_3^{-.}$

5 Conclusion

Usefulness of multivariate statistical methods along with WQI and graphical representation techniques is well illustrated in the present study. In the present study such tools are employed for understanding the physio-chemical characterization of river water system of Parbati river basin. The physicochemical parameters of all the analyzed water samples are well within the desirable limits prescribed by BIS (2012) and WHO (2011). Therefore, the water quality is suitable for domestic purposes, except for the few locations where pH was beyond the permissible range in pre-monsoon season. Piper and Durov plot classified 100% of samples were of Ca^{2+}- Mg^{2+}-HCO_3^- water types indicating temporary hardness in both the seasons. Dominance of alkaline earth metals over that of alkalis and of weak acidic anions over that of strong acidic anions is well represented in the Piper cross plots. Moreover, Piper cross plots also highlighted the natural geochemical processes such as- weathering and dissolution of minerals. The results of Gibbs diagram indicated that the chemical composition of surface water in the Parbati river basin is strongly influenced by rock dominance, weathering of silicates in pre monsoon whereas dominance of rock is followed by precipitation in post monsoon season. The WQI shows maximum water samples were falling in good class followed by excellent in both the seasons. PCA and CA identifies the major factors influencing the surface water chemistry such as- rock-water interaction, ion exchange and leaching of parent materials as well as dominant anthropogenic factors like agri-runoff and domestic waste water runoff.

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Data availability The datasets generated during and/or analyzed during the current study is available from the corresponding author on reasonable request.

Declaration

Competing interests All the authors declare that there is no competing economic interests or personal connections that could have appeared to impact the work reported in this manuscript.

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