

Quality characterization and pollution source identification of surface water using multivariate statistical techniques, Nalagarh Valley, Himachal Pradesh, India

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Abstract Sirsa River flows through the central part of the Nalagarh valley, belongs to the rapid industrial belt of Baddi, Barotiwala and Nalagarh (BBN). The appraisal of surface water quality to ascertain its utility in such ecologically sensitive areas is need of the hour. The present study envisages the application of multivariate analysis, water utility class and conventional graphical representation to reveal the hidden factor responsible for deterioration of water quality and determine the hydrochemical facies and its evolution processes of water types in Nalagarh valley, India. The quality assessment is made by estimating pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness, major ions (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and PO_4^{3-}), dissolved oxygen (DO), biological oxygen demand (BOD) and total coliform (TC) to determine its suitability for drinking and domestic purposes. The parameters like pH, TDS, TH, Ca^{2+} , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- are within the desirable limit as per Bureau of Indian Standards (Indian Standard Drinking Water Specification (Second Edition) IS:10500. Indian Standard Institute, New Delhi, pp 1–18, 2012). Mg^{2+} , Na^+ and K^+ ions for pre monsoon and EC during pre and post monsoon at few sites and approx 40% samples of BOD and TC for both seasons exceeds the permissible limits indicate

organic contamination from human activities. Water quality classification for designated use indicates that maximum surface water samples are not suitable for drinking water source without conventional treatment. The result of piper trilinear and Chadha's diagram classified majority of surface water samples for both seasons fall in the fields of $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ water type indicating temporary hardness. PCA and CA reveal that the surface water chemistry is influenced by natural factors such as weathering of minerals, ion exchange processes and anthropogenic factors. Thus, the present paper illustrates the importance of multivariate techniques for reliable quality characterization of surface water quality to develop effective pollution reduction strategies and maintain a fine balance between the industrialization and ecological integrity.

Keywords Industrial effluent · Surface water · Sirsa River · Hydrochemical facies · Principal component analysis · Cluster analysis

Introduction

Surface water is one of the most precious inland resources, necessary to sustain life, agricultural, industrial and recreational purposes (Razmkhah et al. 2010; Biglin and Konanc 2016). The quality of a river at any point reflects major influences, including the lithology of the basin, atmospheric inputs, climatic conditions and anthropogenic inputs (Bricker and Jones 1995; Reza and Singh 2010; Herojeet et al. 2015b; Jung et al. 2016). On the other hand, rivers play a major role in assimilation or transporting multitude of pollutants present in municipal and industrial wastewater and runoff from agricultural land (Qadir et al.

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2008; Wang et al. 2013; Malik and Hashmi 2017). Municipal and industrial wastewater discharge constitutes a constant polluting source, whereas surface runoff is a seasonal phenomenon, largely influenced by climate within the basin (Singh et al. 2004; Kumar et al. 2015; Bhutiani et al. 2016). Seasonal variations in precipitation, surface runoff, interflow, groundwater flow and pumped in and outflows have a strong effect on river discharge and, subsequently, on the concentration of pollutants in river water (Vega et al. 1998). River water pollution is a major global concern [United Nation Environment Programme (UNEP) 2000; Bhutiani et al. 2016] and threat to aquatic ecosystems as stated in the Ministerial declaration of the 2nd World Water Forum (2000). Though industrialization acted as engines of economic development, it deteriorates the air, water, soil resources and biodiversity (Kannj and Achi 2011; Odumosu 1992; Hossain et al. 2012). Developing country like India experiences water pollution problems due to changing lifestyles, economic enhancement, urban sprawl and landuse pattern (Vipan et al. 2013; Herojeet et al. 2015a). In India, industrial effluents both untreated/partially treated wastewaters often get mixed with domestic sewage contaminated the surface water body affecting homeostasis of riverine ecosystem.

Water chemistry is controlled by various hidden factors related to natural and anthropogenic influences that is difficult to understand and unable to interpret meaningful information (Zhao et al. 2012; Isah et al. 2013; Ismail et al. 2014; Sum and Gui 2015; Herojeet et al. 2016). Such limitations can be overcome by the application of multivariate statistical approach (Singh et al. 2014; Hamid et al. 2016; Herojeet et al. 2016). The application of different multivariate statistical techniques, such as cluster analysis (CA) and principal component analysis (PCA) helps in the interpretation of complex data matrices for better understanding of water quality and its ecological status and allows the identification of possible factors that influence drainage watershed (Vega et al. 1998; Lee et al. 2001; Adams et al. 2001; Wunderlin et al. 2001; Reghunath et al. 2002; Simeonov et al. 2003, 2004). Multivariate statistical techniques are considered trustworthy and authentic approaches to characterize and evaluate surface water quality for efficient management and effective solution to pollution problems (Helena et al. 2000; Singh et al. 2004, 2005; Papazova and Simeonova 2012, 2013; Okiongbo and Douglas 2015; Hamid et al. 2016, Le et al. 2017). Noori et al. (2012) suggested that PCA and CA techniques are useful tools for identifying the importance of water quality monitoring stations.

Nalagarh valley represents a portion of the southernmost expanse of Solan district, belongs to the rapid industrial belt of Baddi, Barotiwala and Nalagarh (BBN) region. The valley has been rated as fastest industrial

growth in the last decade owing to incentives granted by the Government which act as a catalyst in boosting industrial development in the state, particularly in the BBN area (Herojeet et al. 2013a; Kamaldeep et al. 2011). Large- and small-scale industrial development along with urbanization has taken place randomly along the Sirsa watershed resulted to high industrial as well as domestic load in the Sirsa river. Several industries from the far flunk States too have shifted to Nalagarh valley to reap benefits of these incentives (GoHP 2011). Even many industrial units (~55%) are operating without proper legal licenses (Anonymous 2014). As per a report prepared by the BBN Authority in 2007, around 72% of the industries in Nalagarh are processing without effluent treatment plants (ETP). This has further aggravated the pollution menace in surface water and groundwater in the valley (Kamaldeep et al. 2011). Conversion of agricultural land to non-agricultural land, often illegally, for various industrial activities are a common scenario that has led to various environmental problems including pollution of the water resources (GoI 2012). Therefore, the fundamental understandings of hydro-morphological, chemical and biological characteristics are important aspect for virtual and long-term management of surface water (Muangthong and Shrestha 2015). An effective monitoring program is necessary that includes large and complex physicochemical parameters to draw meaningful information of surface water quality related to spatial and temporal variations (Shrestha and Kazama 2007; Guangjia et al. 2010; Muangthong 2015). However, analysis of large datasets of measured parameters is complex; hence, it requires multi-assessment techniques including classification, modeling and interpretations of numerous data matrix due to rich information contain about the water resources (Iscen et al. 2008; Boyacioglu 2006).

From our knowledge, no such study has carried out to assess the impact of rapid industrial development on Sirsa river. The main aim of the study is to examine the dominant ions influencing the water types and the major factors affecting the water quality parameters using multivariate techniques. The results of this study will help proper management of valuable water resources and maintain a balance between the industrial development and environment purity.

Study area

Nalagarh valley forms a South-Eastern narrow prolongation of a great outermost Himalayan intermountain valley area of about 230 sq. km. It lies between Northern latitudes of 30°52'–31°04' and Eastern longitudes of 76°40'–76°55'. The valley is having common border with Haryana towards

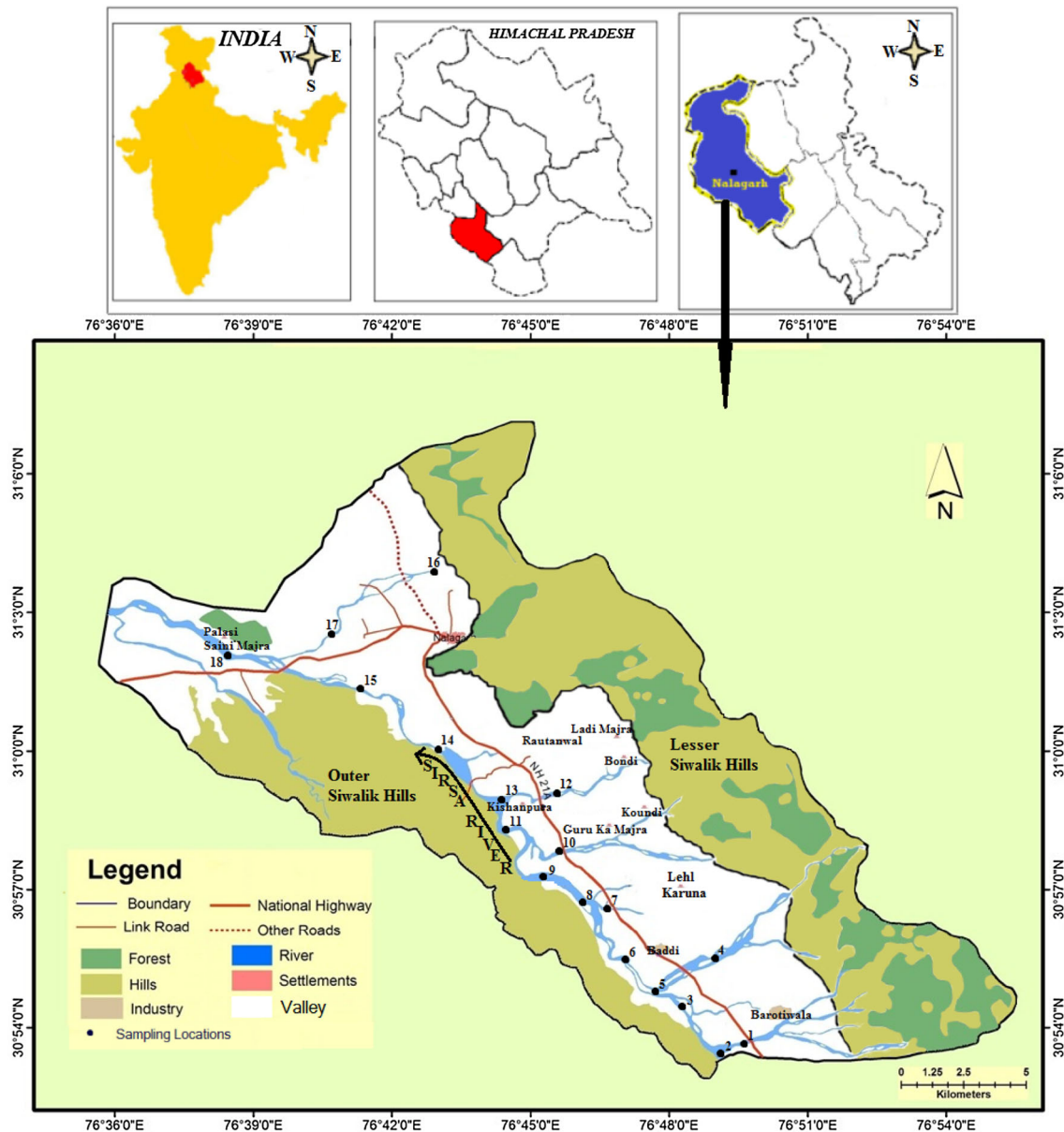


Fig. 1 Map showing sampling points in the study area

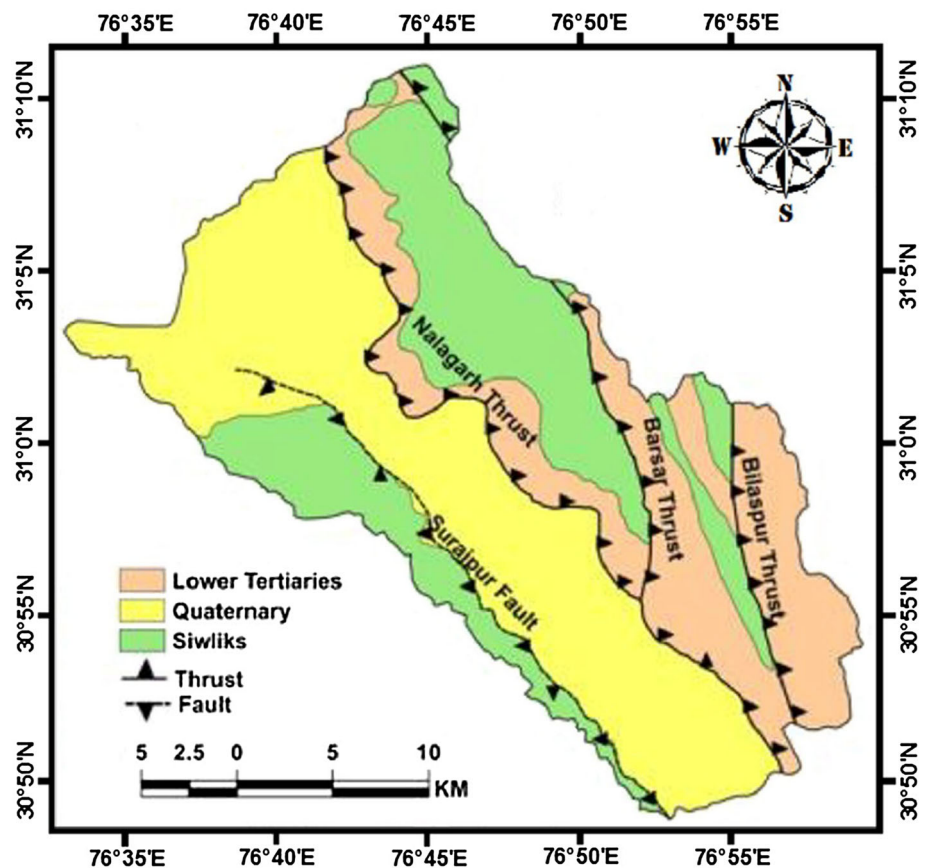
south-east, i.e., Kalka-Pinjor area and with Punjab towards south-west, i.e., Ropar district. Sirsa river is perennial river which flows southwesterly in the area and joins Sutlej 10 kms upstream of Ropar (Fig. 1). There are numerous perennial and ephemeral streams emerging from the northeast (NE) flank passing through industrial belt often loaded with industrial and sewage discharges and transverse flow across the valley to join Sirsa nadi (CGWB 1975). The important streams among them are Chikni nadi, Phula nadi, Ratta nadi, Balad nadi and Surajpur chao. The discharge in the streams fluctuates in accordance with the climatic conditions. During the monsoon, the streams are flooded and carry enormous load of sediment and deposited them in the flood plain of the valley.

Geology

The geology of the area is complex not from the stratigraphical point of view but for its tectonic complexities (Khan 1988). Stratigraphically, the Nalagarh valley and its flanks are bounded by the tertiary formations and structurally they are highly disturbed. The rock types of the area can be broadly grouped into two tectonic zones striking and trending NW–SE direction. So, the direction of their tectonic zones position from North to South is as follows (Fig. 2);

- (a) Belt of lower and middle tertiary occurring along the NE flank of the valley (Para-autochthonous).

Fig. 2 Geological map of the study area (Source: Dash et al. 2013)



- (b) Belt of upper tertiary confined to the valley and along its SW flank (Autochthonous). The contact of these zones is marked by a major fault (Nalagarh thrust).

Tectonically, the area is highly disturbed, two major thrust trending NE–SW are Nalagarh and Sirsa thrusts. Nalagarh thrust is formed between Kasauli and middle Siwaliks whereas Sirsa thrust separates upper and middle Siwaliks. The Sirsa River flows along a fault line, called Surajpur Fault (Khan 1970). The major part of the Sirsa river basin is covered by alluvium soil with Holocene and Pre-Holocene deposits. The alluvium soil varies from 10 to 20 cm thickness and is mostly granular. The upper and middle parts of the river basin are predominated by alternate beds of clay and cobbles, pebbles, gravel, sand. The sediments get finer and finer till it become clay in the downstream part of basin. The stratigraphical sequence of the basin is given in Table 1.

Materials and methods

Sampling and laboratory analysis

12 samples were collected along the Sirsa River and 6 samples from the tributaries flowing around the industrial region to appraise the surface water quality during per monsoon (May

2012) and post monsoon (October 2012) seasons (Fig. 1). Water sample were collected on HDP (1000 mL) plastic bottles. At the time of sampling, the bottles were thoroughly rinsed two to three times with the water to be sampled. pH, electrical conductivity and total dissolved solids were measured on the spot of sample collection by portable water and soil analysis kit. For major cations analysis samples were filtered through using Whatman filter paper no. 42 of diameter 125 mm and pore size 2.5 μ m and preserved by acidifying to pH \sim 2 with HNO₃ and kept at a temperature of 4 °C until

Table 1 Geological succession of the study area

Rocks	Lithology	Age
Holocene deposits	Modern alluvium and river sediments	Recent
Pre-holocene deposits	River terrace	Upper pleistocene
Upper siwaliks	Boulder conglomerates, Sand rocks and clays	Lower pleistocene
Middle siwaliks	Sandstones, clays and conglomerates	Pleistocene
Lower siwaliks	Gray sandstones and purple clays	Upper miocene
Kasauli series	Purple, gray sandstones and purple clays and shales	Lower miocene

Table 2 Summarized water quality parameters along with their abbreviations, units and analytical methods used

Parameters	Abbreviations	Units	Analytical methods
pH	pH	pH unit	pH meter
Electrical conductivity	EC	$\mu\text{S}/\text{cm}$	Electronic India, Model-161
Total dissolved solids	TDS	mg/L	Electronic India, Model-161/indirect method (TDS = EC \times 0.65)
Total hardness	TH	mg/L	Titration with EDTA using Eriochrome Black T as indicator
Calcium	Ca^{2+}	mg/L	Titration with EDTA using Murexide as indicator
Magnesium	Mg^{2+}	mg/L	Titration with EDTA as titrant and eriochrome black T as indicator
Sodium	Na^+	mg/L	Flame photometer
Potassium	K^+	mg/L	Flame photometer
Bicarbonate	HCO_3^-	mg/L	Titration method using standard H_2SO_4 with phenolphthalein and methyl orange as an indicator
Chloride	Cl^-	mg/L	Titration with AgNO_3 using potassium dichromate as indicator
Nitrate	NO_3^-	mg/L	Spectrophotometer (using phenol disulfonic acid)
Sulfate	SO_4^{2-}	mg/L	Spectrophotometer (using BaCl_2 as conditioning agent)
Phosphate	PO_4^{2-}	mg/L	Spectrophotometer (using stannous chloride)
Dissolved Oxygen	DO	mg/L	Winkler's Azide method at 20 °C (5 days)
Biological oxygen demand	BOD	mg/L	Winkler's Azide method
Total coliform	TC	MPN/100 mL	Multiple tube fermentation techniques

analysis. Chemical analysis of major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), major anions (SO_4^{2-} , Cl^- , HCO_3^- and NO_3^{2-}), DO, BOD₅ and TC were determined according to the standard methods for the examination of water and wastewater (APHA, AWWA, WEF 2005). The different water quality parameters, their units and methods of analysis are summarized in Table 2. The analytical data quality was ensured through careful standardization, procedural blank measurements and duplicate samples. The ionic charge balance of each sample was within $\pm 5\%$. Maps were prepared using Mapinfo 6.5 and Vertical Mapper 3.0 and Piper trilinear diagram were plotted using RockWorks 15. A Microsoft Excel 2007 is employed for the calculations and data analysis.

Multivariate statistical analysis

Multivariate statistical techniques have been applied by many researchers to assess and characterize freshwater, marine water and sediment quality (Noori et al. 2010; Muangthong and Shrestha 2015; Hamid et al. 2016; Jung et al. 2016). Principal component analysis (PCA) and cluster analysis (CA) are employed with the objective to group the similar sampling locations based on water quality characteristics and identify the pollution sources influencing the water chemistry. Both PCA and CA are analyzed using statistical software Minitab 16, respectively.

Principal component analysis (PCA)

Principal component analysis (PCA) is one of the best multivariate statistical techniques for extracting linear

relationship among a set of variables (Simeonov et al. 2003). PCA is an analytical technique whereby a complex data set containing variables is transformed to a smaller set of new variables, which maximize the variance of the original data set. PCA provides information on the significant parameters with minimum loss of original information (Singh et al. 2004; Helena et al. 2000). This is achieved by transforming to a new set of variables which are uncorrelated, and which are ordered so that the first few retain most of the variation present in all of the original variables. Therefore, standardization (z scale) was made on each chemical parameter prior to statistical analysis to eliminate biasness by any parameter of different units with high concentration and renders the data dimensionless (Simeonov et al. 2004). The principal components are generated in a sequentially ordered manner with decreasing contributions to the variance, i.e., the first principal component (PC1) explains most of the variations present in the original data, and successive principal components account for decreasing proportions of the variance (Pires et al. 2009; Vieira et al. 2012). Liu et al. (2003) 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.

Cluster analysis (CA)

Cluster analysis (hierarchical clustering), on the other hand, is a useful method of objectively organizing a large data set into groups on the basis of a given set of characteristics. The primary objective of CA is to identify relatively homogenous groups or clusters of objects based on

their similarities/dissimilarities (Wai et al. 2010). The grouping of similar objects occurs first and eventually, as the similarity decreases, all subgroups are merged into a single cluster. This can ultimately assist in the recognition of potentially meaningful patterns (Swanson et al. 2001). Cluster analysis (CA) is performed on the standardized data set (z -transformation) by means of the Ward's method using squared Euclidean distance as a measure of similarity to obtain dendrogram (Otto 1998). The seasonal variability of water quality sampling locations is determined from CA, using the linkage distance, reported as $(D_{\text{link}}/D_{\text{max}}) \times 100$, which represents the quotient between the linkage distances for a particular case divided by the maximal linkage distance. The quotient is then multiplied by 100 as a way to standardize the linkage distance represented on the y -axis (Wunderlin et al. 2001; Simeonov et al. 2003; Singh et al. 2004, 2005).

Results and discussion

Physicochemical and biological compositions of surface water samples are presented in Tables 3 and 4. Table 5 provides the statistical description of water quality parameters that include range, mean and standard deviation and also calculates the percentage of water samples that exceed the prescribed desirable and permissible limits of the Bureau of Indian Standards (BIS 2012) and World Health Organization (WHO 2011) for drinking water. Maximum, minimum and median of the surface water samples for pre monsoon and post monsoon is depicted by box plot (Fig. 3). pH value varied between 7.07 and 7.83 with a mean \pm standard deviation (SD) of 7.53 ± 0.23 in pre monsoon season and 7.12–7.62 with a mean \pm SD of 7.38 ± 0.16 during post monsoon. The entire water samples are within the prescribed limits of BIS (2012). EC values ranged between 428 and 1570 $\mu\text{S}/\text{cm}$ and 429–1512 $\mu\text{S}/\text{cm}$ with a mean \pm SD of 1079.89 ± 387.56 and 769.78 ± 276.26 during pre and post monsoon. 16.67 and 5.56% samples are above the permissible limit of 1500 $\mu\text{S}/\text{cm}$ (WHO 2011) indicating temporal variation during the period of investigation. CGWB and CPCB (1999) classified EC values of water for irrigation purpose as given in Table 6. It is observed that 7 and 11 samples during pre monsoon whereas for post monsoon 10 and 8 samples fall in moderate saline to high saline class. Moreover, lower values of EC are recorded in post monsoon due to increasing volume of surface water as rain water causes dilution of effluent. High concentration of TDS in surface water at SW7 (1037 mg/L, pre monsoon) and SW9 (1014 mg/L, post monsoon) is the indicator of excessive anthropogenic activities besides the sampling area (Yisa and Jimoh 2010). The water can be classified

based on TDS for irrigation use as Fresh (TDS <1000); Brakish (TDS 1000–10,000); Saline (TDS 10,000–1,000,000) and Brine (TDS >1,000,000) (Todd 1980). Accordingly, majority of the surface water samples fall under fresh for both seasons indicating suitable irrigation purpose. The value of Total Hardness varies from 130 to 476 and 160 to 308 mg/L with mean \pm SD of 230.17 ± 83.08 and 245.39 ± 42.71 for both seasons. Temporal variation is observed in which median value is higher in post monsoon which may be attributed due to the dissolution of calcium and magnesium bearing minerals along with industrial effluent (Herojeet et al. 2013b). As per Durfor and Becker (1964) classification, all the samples come under hard (66.67; 88.89%) to very hard (33.33; 11.11%) category during pre and post monsoon (Table 7). Sidhu et al. (2013) have concluded that long-term consumption of extremely hard water is associated with an increase incidence of urolithiasis, anencephaly, some types of cancer and cardiovascular disorders. None of the samples showed TDS and TH values exceeding their permissible limit of 2000 and 600 mg/L (BIS 2012).

Cations chemistry (Ca^{2+} , Mg^{2+} , Na^+ , K^+)

Among the cations, magnesium is the dominant ions suggesting 61.11 and 72.22% samples are Mg^{2+} -rich water type and remaining 27.78% indicates no dominant cations (Fig. 4a, b; Table 9) for both seasons. The alkaline earth metals, the concentrations of Ca^{2+} ranged from 13.46 to 102.61 and 28.6 to 103.45 mg/L and Mg^{2+} values varied from 27.00 to 109.37 and 23.85 to 63.78 mg/L for pre and post monsoon, respectively. Among the alkalis metals, Na^+ values varies between 6.6–245.7 and 11.8–130.0 mg/L and K^+ concentrations from 1.3 to 13.8 and 1.4 to 9.0 mg/L for both seasons. During pre monsoon, 5.56 samples are above the permissible limit of Mg^{2+} (100 mg/L), Na^+ (200 mg/L) and K^+ (12 mg/L), respectively, and none of the sample exceeds permissible limit for post monsoon (BIS 2012). Based on the average concentrations (mg/L) of all the cations, the ionic dominance in the order of Na^+ (48.55%) > Mg^{2+} (26.38%) > Ca^{2+} (21.87) > K^+ (3.21) and Ca^{2+} (37.73%) > Na^+ (33.77%) > Mg^{2+} (25.65%) > K^+ (2.85%), respectively, for both seasons.

Anion chemistry (HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-})

The concentrations of HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} ranges from 76.0 to 158.0, 3.98 to 40.75, 9.82 to 23.0, 0.38 to 17.89, 0.01 to 0.71 mg/L for pre monsoon and varies between 92.0 and 164.0, 3.98 and 25.84, 10.52 and 23.0, 0.3 and 18.0, 0.01 and 0.09 mg/L, respectively, during post monsoon season. The anions dominance in the order of

Table 3 Analyzed results of surface water for pre monsoon

S. no.	Locations	pH	EC, $\mu\text{S}/\text{cm}$	TDS, mg/L	TH, mg/L	Ca^{2+} , mg/L	Mg^{2+} , mg/L	Na^+ , mg/L	K^+ , mg/L	HCO_3^- , mg/L	Cl^- , mg/L	NO_3^- , mg/L	SO_4^{2-} , mg/L	PO_4^{2-} , mg/L	DO, mg/L	BOD, mg/L	TC MPN/100 mL
SW1	Surajpur Chao D/S	7.78	428	281	166	25.23	34.35	6.6	1.3	76	3.98	0.38	9.92	0.01	2.50	1.00	32.00
SW2	Sirsa (Lahorandi)	7.57	554	354	232	58.87	42.24	9	1.5	102	5.96	0.56	10.21	0.05	5.80	1.00	210.0
SW3	Sirsa (Khokara)	7.07	725	469	140	23.55	28.41	12.3	1.8	122	8.95	2.30	10.5	0.01	6.40	5.20	40.00
SW4	Balad Nadi (Nariyanwala)	7.25	890	578	250	102.61	35.96	9.4	1.9	132	10.93	0.95	10.9	0.04	4.50	6.40	138.00
SW5	Sirsa (Thapal)	7.52	745	482	202	17.66	44.98	15.5	3.0	120	7.95	4.01	11.1	0.49	3.50	2.50	85.00
SW6	Sirsa (Sitalpur)	7.32	740	480	130	19.34	27.0	13.9	2.7	128	8.89	1.40	10.18	0.04	3.10	1.40	430.0
SW7	Sandholi Nala D/S (Baddi)	7.54	1490	969	261	79	44.41	130	9.0	145	17	17.89	23	0.03	0.00	280.0	1600.0
SW8	Sirsa (kaindawal)	7.42	1365	885	164	34.48	31.6	99	13.8	158	31.81	2.85	14.66	0.05	0.00	61.00	842.0
SW9	Sirsa (Beriyar)	7.64	1570	1037	202	33.64	41.08	245	8.70	130	40.75	1.96	14.72	0.09	0.00	22.00	260.0
SW10	Ratta Nadi D/S (Near Har Raipur)	7.49	1188	773	336	84.11	61.46	24.2	10.1	128	21.87	12.3	19.29	0.20	7.40	2.00	132.0
SW11	Sirsa (Chumi)	7.79	1555	1023	476	27.75	109.4	189	9.70	150	40.75	2.55	17.44	0.38	0.50	22.00	110.0
SW12	Phula Nadi (Manpura)	7.82	684	443	212	20.19	46.8	15.2	2.0	94	7.95	1.95	11.27	0.71	5.00	2.10	82.00
SW13	Confluence of Phula Nadi and Sirsa	7.75	1520	1001	156	26.07	31.7	143.1	9.6	152	38.77	2.21	18.62	0.20	5.80	7.20	46.00
SW14	Sirsa (Handi Kundi)	7.72	1389	903	174	41.21	32.4	148.5	8.2	138	36.78	3.72	20.18	0.16	5.10	0.60	24.00
SW15	Sirsa (Nahar Singh)	7.28	1350	872	236	31.96	49.79	197.1	6.6	134	33.8	3.52	22.35	0.16	5.80	1.50	46.00
SW16	Chikimi Nadi U/S (Palasta Nihla)	7.21	705	445	262	13.46	60.64	15.4	1.6	122	3.98	4.55	11.74	0.09	6.50	0.10	37.00
SW17	Chikimi Nadi D/S (Dhang Nihli)	7.5	1229	798	308	26.07	68.79	111.6	4.6	134	25.84	8.29	17.45	0.03	5.80	0.10	32.00
SW18	Sirsa (Sami Majra)	7.83	1311	853	236	31.96	49.79	162	6.1	126	30.81	2.42	16.28	0.08	5.10	0.60	24.00

U/S upstream, D/S downstream

Table 4 Analyzed result of surface water for post monsoon

S. no.	Locations	pH	EC, $\mu\text{S}/\text{cm}$	TDS, mg/L	TH, mg/L	Ca^{2+} , mg/L	Mg^{2+} , mg/L	Na^+ , mg/L	K^+ , mg/L	HCO_3^- , mg/L	Cl^- , mg/L	NO_3^- , mg/L	SO_4^{2-} , mg/L	PO_4^{2-} , mg/L	DO, mg/L	BOD, mg/L	TC MPN/100 mL
SW1	Surajpur Chao D/S	7.59	429	277	248	64.76	44.71	11.80	1.90	96	3.98	0.30	10.52	0.01	9.50	0.40	30.00
SW2	Sirsa (Lahorandi)	7.59	449	290	240	70.65	41.32	11.80	1.40	96	3.98	0.57	10.68	0.01	8.80	3.00	140.0
SW3	Sirsa (Khokara)	7.17	560	363	220	79.06	34.39	21.20	2.20	134	5.56	2.31	11.48	0.01	6.40	1.20	129.0
SW4	Balad Nadi (Nariyanwala)	7.50	454	293	242	51.30	46.53	20.70	2.70	92	11.93	0.93	10.99	0.04	7.10	1.50	88.0
SW5	Sirsa (Thapal)	7.29	534	345	300	76.54	54.53	20.90	2.30	112	6.69	4.05	11.04	0.03	6.80	1.50	176.0
SW6	Sirsa (Sitalpur)	7.45	522	337	214	61.40	37.24	21.50	2.20	114	6.96	1.36	11.02	0.04	8.40	1.80	120.0
SW7	Sandholi Nala D/S (Baddi)	7.54	1512	1014	261	79	44.41	130.0	9.00	145	17.00	18.0	23.0	0.03	0.00	170.0	765.0
SW8	Sirsa (kaindawal)	7.12	733	473	308	91.67	52.78	38.90	6.90	134	13.92	2.75	12.03	0.04	0.00	32.00	496.0
SW9	Sirsa (Beriyar)	7.25	998	645	288	67.20	56.32	118.4	7.60	156	24.85	2.01	13.51	0.09	4.80	8.00	408.0
SW10	Ratta Nadi D/S (Near Har Raipur)	7.40	796	516	250	103.45	35.76	26.60	3.20	130	14.91	12.13	12.55	0.01	6.70	0.60	60.00
SW11	Sirsa (Chumi)	7.33	967	624	228	84.95	34.91	98.80	7.30	144	24.85	2.51	13.91	0.07	5.30	8.00	50.00
SW12	Phula Nadi (Manpura)	7.43	616	398	290	28.60	63.78	32.20	3.50	110	10.93	1.91	13.35	0.01	6.30	0.10	36.00
SW13	Confluence of Phula Nadi and Sirsa	7.25	1015	658	290	61.40	55.78	77.60	7.80	144	24.90	2.13	13.99	0.09	7.00	2.60	140.00
SW14	Sirsa (Handi Kundi)	7.25	966	625	160	62.24	23.85	119.2	7.10	142	23.86	4.10	13.56	0.05	5.90	0.30	24.00
SW15	Sirsa (Nahar Singh)	7.21	954	616	268	74.01	47.33	113.2	6.30	150	25.84	3.60	13.28	0.08	5.10	0.10	80.00
SW16	Chikimi Nadi U/S (Palasta Nihla)	7.59	750	485	238	37.01	49.04	37.2	5.00	120	14.91	4.59	12.31	0.04	7.70	0.10	36.00
SW17	Chikimi Nadi D/S (Dhang Nihli)	7.62	713	460	210	41.34	41.15	41	4.80	164	14.91	8.26	12.32	0.05	6.70	0.10	27.00
SW18	Sirsa (Sami Majra)	7.35	888	574	162	42.05	29.27	103.2	6.80	134	21.87	2.06	13.12	0.07	5.50	0.50	45.00

U/S upstream, D/S downstream

Table 5 Statistics of surface water chemistry for drinking purpose

S no.	Parameters	Prescribed limits		Post monsoon												
		No. of samples	IS:10500:1991	Pre monsoon						Post monsoon						
				Desirable	Permissible	Range	Mean	Median	Std. dev (SD)	No of sample above desirable limit (%)	No of sample above permissible limit (%)	Range	Mean	Median	Std. dev (SD)	No of sample above desirable limit (%)
1.	pH	18	6.5	8.5	7.07–7.83	7.53	7.53	0.23	NIL	NIL	7.12–7.62	7.38	7.38	0.16	NIL	NIL
2.	EC	18	1500		428–1570	1079.89	1208.50	387.56	16.67		429–1512	769.78	741.50	276.26	5.56	
3.	TDS	18	500	2000	281–1037	702.56	785.50	256.06	61.11		277.1014	499.61	479.00	184.61	44.44	
4.	TH	18	200	600	130–476	230.17	222.00	83.08	66.67		160–308	245.39	245.00	42.71	88.89	
5.	Ca ²⁺	18	75	200	13.46–102.61	38.73	29.86	25.39	16.67		28.6–103.45	64.81	63.50	19.86	33.33	
6.	Mg ²⁺	18	30	100	27–109.37	46.71	43.33	19.64	83.33		23.85–63.78	44.06	44.56	10.46	100	
7.	Na ⁺	18	200		6.6–245.7	85.97	61.60	81.05	5.56		11.8–130	58.01	38.05	43.51	NIL	
8.	K ⁺	18	12		1.3–13.8	5.68	5.35	3.89	5.56		1.4–9.00	4.88	4.90	2.48	NIL	
9.	HCO ₃ ⁻	18	500		76–158.0	127.28	129.00	20.45	NIL		92–164.0	128.72	134.00	21.49	NIL	
10.	Cl ⁻	18	250	1000	3.98–40.75	20.93	19.44	13.94	NIL		3.98–25.84	15.14	14.91	7.75	NIL	
11.	SO ₄ ²⁻	18	200	400	9.82–23.0	14.98	14.69	4.47	NIL		10.52–23.0	12.93	12.44	2.77	NIL	
12.	NO ₃ ⁻	18	45		0.38–17.89	4.1	2.98	4.49	NIL		0.3–18.0	4.09	2.41	4.5	NIL	
13.	PO ₄ ³⁻	18	-		0.01–0.71	0.16	0.09	0.19	-		0.01–0.09	0.04	0.04	0.03	-	
14.	DO	18	>6 mg/L		BDL–7.40	4.04	5.05	2.47	16.67		BDL–9.50	6.00	6.55	2.52	61.11	
15.	BOD	18	<2 mg/L		0.10–280.0	23.15	2.05	65.79	44.44		0.10–170.0	12.88	1.35	39.92	33.33	
16.	TC	18	100 MPN/100 ml		24.0–1600.0	231.67	83.50	396.49	44.44		24.0–765.0	158.33	84.00	199.22	44.44	

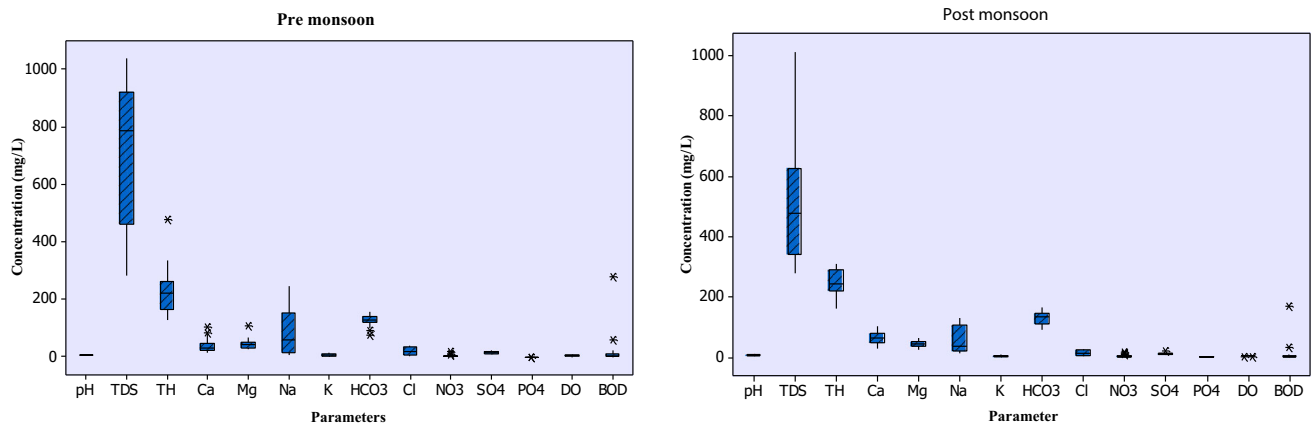


Fig. 3 Box plot of different parameter concentration in the study area (cross outlier, whisker line median, vertical line maximum and minimum and box third and first quartiles)

$\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{PO}_4^{3-}$ that contribute on an average concentrations (mg/L) of all the anions for pre monsoon (76.01, 12.50, 8.95, 2.45 and 0.09%) and post monsoon (79.99, 9.41, 8.03, 2.54 and 0.03%), respectively. Among anions, 83.33 and 100% samples are characterized as HCO_3^- water indicating the dominant ion for both seasons and 16.67% samples for pre monsoon plotted near the central zone have no dominant anion (Fig. 4a, b; Table 9). The entire samples of HCO_3^- , Cl^- , SO_4^{2-} and NO_3^- concentrations are well within the permissible limits of 500, 1000, 400 and 45 mg/L (BIS 2012).

Biological parameters (DO, BOD, TC)

The content of DO in surface water ranged from BDL (below detectable limit)—7.40 mg/L and BDL—9.50 mg/L for pre and post monsoon. The DO values fall to zero at SW8 and SW9 during the investigation period depicts not even fit to support aquatic life. DO values <6 indicate pollution (WHO 2011), cannot be use for domestic purposes. 16.67 and 61.11% samples, respectively, are above the permissible limit of >6 mg/L (BIS 2012) for both seasons. BOD concentration varies from 0.10 to 280.0 mg/L during pre monsoon and 0.10 to 170.0 mg/L for post monsoon. Lower DO and higher BOD are accounted in pre monsoon (Anshu et al. 2011) when river flows are slow and high temperatures increase the organic decomposition discharge from untreated sewage and agricultural runoff. The study area also lacks proper drainage system and modern sanitation facilities where domestic sewage and wastewater directly enter the Sirsa river and its tributaries. TC content in the samples ranged between 24–1600 and 27–765 MPN/100 mL during pre and post monsoon, respectively. Highest value of TC, BOD and low DO is observed at SW7 for both seasons where Sandholi nala is an effluent channel for sewage and agricultural runoff.

Majority of samples are above the permissible limits of BOD (<2 mg/L) and TC (100 MPN/100 mL) indicating unfit for domestic purpose (BIS 2012).

Classification of surface water for designated use

CPCB (2007) classified surface water in five quality class based on combine assessment of primary water parameters namely TC, DO, BOD, pH and EC for specific designated purpose (Table 8). It is important to note that evaluation of mutli-parameter provide concrete result rather than individual parameter. Surface water samples of the study area for both seasons are classified as per the guidelines of water quality criteria (CPCB 2007). Based on Table 8, the number of samples fall in class A, B, C, D and E, respectively, are 1, 7, 8, 11, 18 for pre monsoon indicates that maximum number of samples are suitable for namely, propagation of wildlife and fisher and irrigation, industrial cooling and controlled disposal. Whereas during post monsoon 4, 10, 14, 16, 18 samples belong to class A, B, C, D and E, respectively, indicating majority of samples are best suitable for more purposes, i.e., Outing bathing, drinking water source with conventional treatment, propagation of wildlife and fisher and irrigation, industrial cooling and controlled disposal. It is evident that significant temporal variation of surface water quality representing post monsoon season has better water quality as per the guidelines of water quality criteria (CPCB 2007). Such variation may be attributed to the increased volume of water and dilution from precipitation and self purification capacity of lotic system.

Hydrochemical facies

Hydrochemical facies reveals the analogies, dissimilarities and different types of water in the particular area

Table 6 Suitability of water based on conductivity for irrigation (Source: CGWB and CPCB 1999)

Class	Conductivity (µmhos/cm)	Suitability or otherwise for irrigation	Number of samples			
			Pre monsoon	Percentage	Post monsoon	Percentage
1.	Below 250	Entirely safe	NIL	NIL	NIL	NIL
2.	250–750 (moderately Saline)	Safe practically under all conditions	7	38.89	10	55.56
3.	750–2250 (medium to high saline)	Safe with permeable soils and moderate leaching	11	61.11	8	44.44
4.	2250–4000 (high salinity)	Used on soils with good permeability and with special leaching for salt tolerant crops	NIL	NIL	NIL	NIL
5.	4000–6000 (very high salinity)	Used only on highly permeable soils with frequent leaching with plants of high salt tolerance	NIL	NIL	NIL	NIL
6.	Above 6000 (excessive Salinity)	This class represents water that is unfit for irrigation	NIL	NIL	NIL	NIL

Table 7 Different degree of hardness in water (Source: Durfor and Becker 1964)

S. no.	Hardness (mg/L)	Characteristics	Number of samples			
			Pre monsoon	Percentage	Post monsoon	Percentage
1.	0–60	Very soft	NIL	NIL	NIL	NIL
2.	61–120	Moderately soft	NIL	NIL	NIL	NIL
3.	121–180	Hard	6	33.33	2	11.11
4.	>180	Very hard	12	66.67	16	88.89

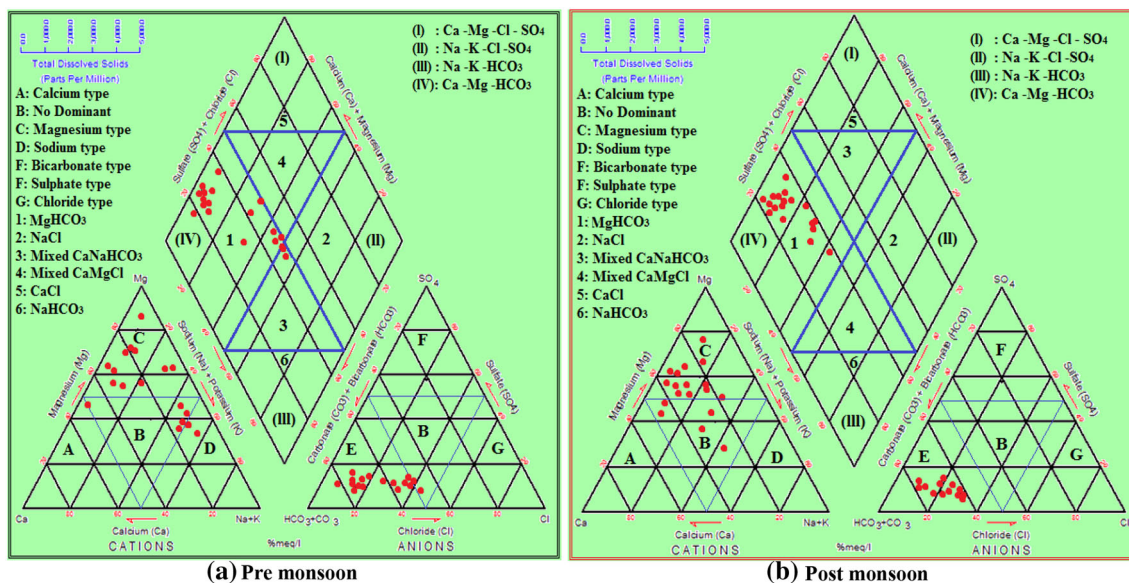


Fig. 4 Piper classification diagram illustrating the chemical composition of surface water

representing different characteristics belonging to any genetically related system. The graphical representations of facies are useful in identifying chemical processes and

detecting the effects of mixing water within different lithological framework (Todd 1980). Various workers namely Collins (1923), Piper (1944, 1953), Black (1960),

Table 8 Designated best use classification of surface water Source: Guidelines for water quality monitoring, MINARS/2007–08 (CPCB 2007)

Designates best use	Quality class	Primary water quality criteria	No of sample	
			Pre monsoon	Post monsoon
Drinking water source without conventional treatment but with chlorination	A	TC (MPN ^a /100 mL) shall be 50 or less DO 6 mg/L or more BOD 2 mg/L or less	1	4
Outing bathing (organized)	B	TC (MPN ^a /100 mL) shall be 500 or less DO 5 mg/L or more BOD 3 mg/L or less	7	10
Drinking water source with conventional treatment	C	TC (MPN ^a /100 mL) shall be 5000 or less DO 4 mg/L or more BOD 3 mg/L or less	8	14
Propagation of wildlife and fisheries	D	DO 4 mg/L or more	11	16
Irrigation, industrial cooling and controlled disposal	E	pH between 6.5 and 8.5 Electrical conductivity less than 2250 μ S/cm	18	18

^a MPN most probable number

Walton (1970) and Chadha (1999) proposed the concept of graphical methods of representation of chemical analysis of water. In present study, Piper (1944) and Chadha (1999) diagrams were employed by plotting the concentration of major cations and anions for hydrochemical characterization of surface water. Rockworks 16 and Microsoft Excel 2007 software were used to construct Piper and Chadha diagram, respectively.

Piper trilinear diagram

The ionic concentrations were plotted in Piper diagram (Piper 1944) to characterize the hydrochemistry of the surface water in the study area (Fig. 4a, b; Table 9). Piper diagram shows that 83.33% of samples in $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$ facies belong to temporary hardness while the remaining samples (16.67%) fall under $\text{Na}^+\text{-K}^+\text{-HCO}_3^-$ facies due to base ion exchange processes exhibit sodium bicarbonate type wherein carbonate primary salinity during pre monsoon. All the surface water samples fall in $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$, resulting MgHCO_3^- is the dominant facies in post monsoon. The graph also indicates that alkaline earth elements ($\text{Ca}^{2+}+\text{Mg}^{2+}$) and weak acids ($\text{CO}_3^{2-} + \text{HCO}_3^-$) exceeded over the alkaline elements ($\text{Na}^+ + \text{K}^+$) and strong acids (SO_4^{2-} and Cl^-) resulting Mg^{2+} and HCO_3^- are the principal cation and anion in surface water. Majority of surface water samples (83.33 and 100.00%) for both seasons fall in the field of $\text{Mg}^{2+}\text{-HCO}_3^-$ water types having secondary salinity exceeding 50% which indicates inverse or reverse ion exchange

(Davis and Dewiest 1966; Tay 2012). Remaining 16.67% sample for pre monsoon is $\text{Ca}^{2+}\text{-Na}^+\text{-HCO}_3^-$ where types of water samples cannot be classified as neither cation- nor anion-dominant hydrochemical facies (Todd and Mays 2005; Herojeet et al. 2016).

Chadha's plot

Chadha's diagram is modified as well as improved version of Piper trilinear diagram (1944) and the expanded Durov diagram (1948). Chadha's diagram (1999) is used to identify the evolution of hydrochemical processes of surface water. In Chadha's diagram, the difference in milliequivalent percentage (percentage reacting values) between alkaline earths (calcium plus magnesium) and alkali metals (sodium plus potassium) is plotted on the X axis and the difference between weak acidic anions (carbonate plus bicarbonate) and strong acidic anions (chloride plus sulfate) is plotted on the Y-axis. The four quadrant suggested by Chadha's graph explained mixing of natural water or recharging water, reverse ion exchange water, end seawater (saline water) and base ion exchange water. The upper right quadrant formed recharging water ($\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$) where surface runoff or standing water percolates to subsurface aquifers carrying dissolved CO_3^{2-} or HCO_3^- and geochemically mobile Mg^{2+} or Ca^{2+} ions. Reverse ion exchange waters are less easily defined and less common, but represent groundwater where $\text{Ca}^{2+}\text{-Mg}^{2+}$ is in excess to $\text{Na}^+\text{-K}^+$ either due to the preferential release of Ca^{2+} and Mg^{2+} from mineral weathering of

Table 9 Surface water samples characterization based on Piper diagram

Class	Groundwater types corresponding subdivisions of facies	Samples in the different category			
		Pre monsoon		Post monsoon	
		No. of samples	Percentage	No. of samples	Percentage
I	Ca ²⁺ -Mg ²⁺ -Cl ⁻ -SO ₄ ²⁻	NIL	NIL	NIL	NIL
II	Na ⁺ -K ⁺ -Cl ⁻ -SO ₄ ²⁻	NIL	NIL	NIL	NIL
III	Na ⁺ -K ⁺ -HCO ₃ ⁻	3	16.67	NIL	NIL
IV	Ca ²⁺ -Mg ²⁺ -HCO ₃ ⁻	15	83.33	18	100
A	Calcium type	NIL	NIL	NIL	NIL
B	No dominant (cations)	5	27.78	5	27.78
C	Magnesium type	11	61.11	13	72.22
D	Sodium type	2	11.11	NIL	NIL
E	Bicarbonate type	15	83.33	18	100
B	No dominant (anions)	3	16.67	NIL	NIL
F	Sulfate type	NIL	NIL	NIL	NIL
G	Chloride type	NIL	NIL	NIL	NIL
1	HCO ₃ ⁻ -CO ₃ ²⁻ and Ca ²⁺ -Mg ²⁺ (temporary hardness); magnesium bicarbonate type (carbonate hardness exceeds 50%)	15	83.33	18	100
2	Cl ⁻ -SO ₄ ²⁻ and Na ⁺ -K ⁺ (saline); sodium chloride type (non-carbonate alkali exceeds 50%)	NIL	NIL	NIL	NIL
3	Mixing Zone (Ca ²⁺ -Na ⁺ -HCO ₃ ⁻); Base ion exchange processes	3	16.67	NIL	NIL
4	Mixing Zone (Ca ²⁺ -Mg ²⁺ -Cl ⁻); reverse ion exchange processes	NIL	NIL	NIL	NIL
5	Cl ⁻ -SO ₄ ²⁻ and Ca ²⁺ -Mg ²⁺ (permanent hardness); calcium chloride type (non-carbonate hardness exceeds 50%)	NIL	NIL	NIL	NIL
6	HCO ₃ ⁻ -CO ₃ ²⁻ and Na ⁺ -K ⁺ (alkali carbonate); sodium bicarbonate type (carbonate alkali exceeds 50%)	NIL	NIL	NIL	NIL

exposed bedrock or possibly reverse base cation exchange reactions of Ca²⁺-Mg²⁺ into solution and subsequent adsorption of Na⁺ onto mineral surfaces. The upper left quadrant represents base ion exchange of water from Ca²⁺-HCO₃⁻ fresh water type mixed with Na⁺-Cl⁻ salinity water type to produce Na⁺-HCO₃⁻ (carbonate primary salinity) through ion exchange processes. Finally, the lower left quadrant indicate seawater types are commonly occurred to the coastal or bay or estuaries region with Na⁺-Cl⁻ (non carbonate primary salinity) dominant ions resulting seawater mixing. To define the primary character of water, the rectangular field is divided into eight sub-fields, each of which represents a water type (Table 10).

The results of Chadha’s classification for surface water observed that during pre monsoon season 12 samples (66.67%) fall in recharge water Group 5 (Ca²⁺-Mg²⁺-HCO₃⁻ type or Ca²⁺-Mg²⁺ dominant HCO₃⁻ type or HCO₃⁻ dominant Ca²⁺-Mg²⁺ type) indicates temporary hardness and six samples (33.33%) in base ion exchange Group 8 (Na⁺-K⁺-HCO₃⁻ type or Na⁺-K⁺ dominant HCO₃⁻ type or HCO₃⁻ dominant Na⁺-K⁺ type) depicts alkali carbonate enrichment water type by dissolution or

Table 10 Summarized results of Chadha’s classification

Classification/type	Surface water	
	No. of samples	
	Pre monsoon	Post monsoon
Group 1 (Ca ²⁺ -Mg ²⁺ -Na ⁺ -K ⁺)	12 (66.67%)	16 (88.89%)
Group 2 (Na ⁺ -K ⁺ -Ca ²⁺ -Mg ²⁺)	6 (33.33%)	2 (11.11%)
Group 3 (HCO ₃ ⁻ -Cl ⁻ -SO ₄ ²⁻)	18 (100%)	18 (100%)
Group 4 (SO ₄ ²⁻ -HCO ₃ ⁻ -Cl ⁻)	NIL	NIL
Group 5 (Ca ²⁺ -Mg ²⁺ -HCO ₃ ⁻)	12 (66.67%)	16 (88.89%)
Group 6 (Ca ²⁺ -Mg ²⁺ -Cl ⁻ -SO ₄ ²⁻)	NIL	NIL
Group 7 (Na ⁺ -K ⁺ -Cl ⁻ -SO ₄ ²⁻)	NIL	NIL
Group 8 (Na ⁺ -K ⁺ -HCO ₃ ⁻)	6 (33.33%)	2 (11.11%)

weathering of halite mineral characterize primary salinity (Ravikumar and Somashekar 2015) (Fig. 5a). However, 16 samples (88.89%) fall in recharge water Group 5 (Ca²⁺-Mg²⁺-HCO₃⁻) except for 2 samples (11.11%) which belong to base ion exchange Group 8 (Na⁺-K⁺-HCO₃⁻ type) during post monsoon (Fig. 5b). It is evident from Chadha’s diagram that there is temporal variation in

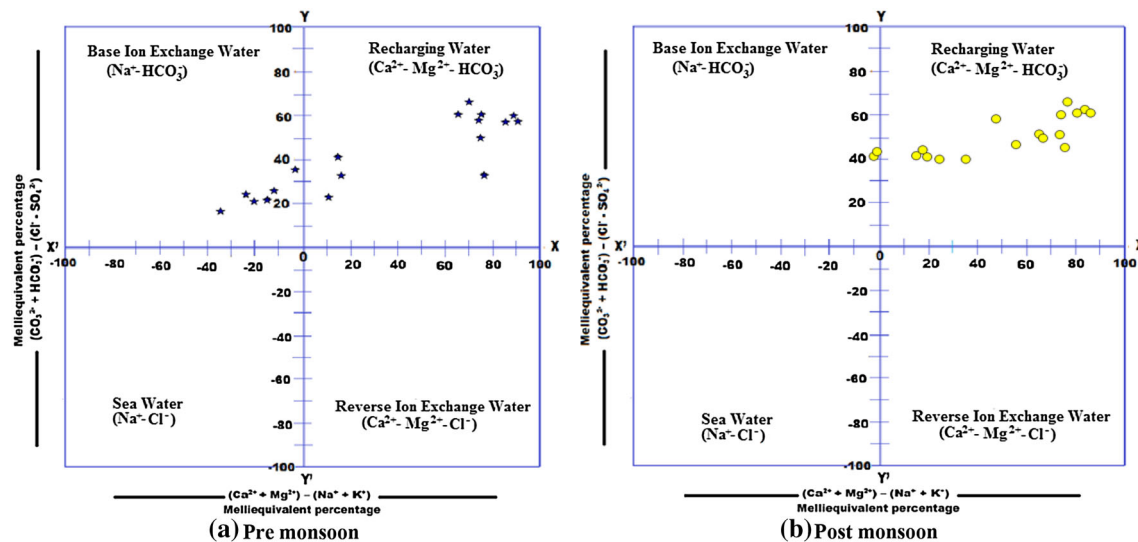


Fig. 5 Diagram showing Chadha's classification of surface water

surface water chemistry as certain samples contain a high concentration of bicarbonate ions to precipitate Ca^{2+} and Mg^{2+} ions which may deposit residual sodium carbonate in irrigation use and cause foaming problems during pre monsoon and post monsoon.

The output of Piper trilinear diagram is confirmed with the Chadha's plot that maximum samples for surface water belong to alkaline earths and weak acidic anions exceed alkali metals and strong acidic anions, as Ca^{2+} – Mg^{2+} – HCO_3^- water type for both seasons, respectively. Only few samples of surface water fall in alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions as indicated by Na^+ – HCO_3^- type of water.

Pollution source identification of surface water

Multivariate statistical techniques such as PCA and CA have been applied on the analyzed parameters of surface water to distinguish the pollution sources during pre and post monsoon seasons, respectively.

Principal components (PCs) are extracted by the scree plot method considering the eigenvalues more than 1 (Shrestha and Kazama 2007). The calculated component loadings, cumulative percentage and percentages of variance explained by each factor are listed in Table 11. Principal components (PC's) corresponding to absolute loading values of >0.75 (marked bold in the table) and additionally second level of interpretation (bold plus italics) are taken into consideration as statistically significant in the interpretation by PCA. Four PCs were extracted by varimax rotation methods (Singh et al. 2004, 2005; Herojeet et al. 2016) which explains about 81.2 and 83.6% of the total variance, respectively, for pre and post monsoon seasons.

During pre monsoon, PC1 explains 42.2% of total variance that has strong positive loadings on Na^+ , K^+ , HCO_3^- , Cl^- and SO_4^{2-} and moderately with BOD which are controlled by lithogenic factors and various hydro-geochemical processes resulting in high EC and TDS scores (mineralized water). This condition can be associated with weathering of silicate, limestone, halite and pyrite dissolution (Okiongbo and Douglas 2015; Ravikumar and Somashekar 2015). The strong loading of Na^+ and K^+ with HCO_3^- , Cl^- and SO_4^{2-} ions indicates natural weathering of rock minerals and various ion exchange processes in the water system (Srivastava and Ramanathan 2008). The high positive loading of HCO_3^- and SO_4^{2-} is attributed to the reaction of feldspar, pyroxene, amphiboles and biolite minerals with carbonic acid in the presence of water (Amadi et al. 1987; Elango et al. 2003). SO_4^{2-} ions associated with higher concentration of Na^+ may cause laxative and gastric disorder (Herojeet et al. 2015a, 2016). Moreover, moderate BOD score indicates natural water quality and least intervention from human activities.

PC2 accounts for 18.0% of the total variance with strong negative weight on BOD and TC and moderate negative score with Ca^{2+} and NO_3^- . This may be attributed to anthropogenic factor linked to domestic wastewater discharge and surface runoff from river catchment containing soil minerals and nitrogen species which increased the biological activity. Esakkimuthu et al. (2015) have reported that strong absolute loadings on BOD and TC indicate organic pollution from human activities. Surface water contaminated with TC causes cholera, diarrhea, dysentery and skin, eye, and throat infections (Hammer 1986; WHO 1993). PC3 is responsible for 12.2% of the total variance, strong positive score on TH and Mg^{2+} and may be attributed to natural factor from the dissolution of silicate and

Table 11 Varimax rotated component matrix of analyzed water samples

Variables	Component (pre monsoon)				Component (post monsoon)			
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4
pH	0.274	0.439	0.092	-0.612	-0.312	-0.332	-0.547	0.607
EC	0.970	0.141	-0.143	0.085	0.977	0.026	-0.112	0.075
TDS	0.968	0.148	-0.146	0.074	0.976	-0.004	-0.124	0.080
TH	0.419	0.280	0.801	0.098	0.082	-0.482	0.829	0.095
Ca ²⁺	0.223	-0.516	0.309	0.316	0.218	-0.324	0.075	-0.836
Mg ²⁺	0.362	0.452	0.729	0.002	-0.019	-0.332	0.795	0.485
Na ⁺	0.829	0.327	-0.257	-0.057	0.878	0.369	-0.070	0.064
K ⁺	0.889	0.020	-0.161	-0.023	0.927	0.260	0.097	0.100
HCO ₃ ⁻	0.795	-0.063	-0.185	0.291	0.758	0.366	0.013	-0.109
Cl ⁻	0.842	0.433	-0.289	0.083	0.745	0.605	0.109	0.064
SO ₄ ²⁻	0.859	-0.014	0.095	0.225	0.868	-0.336	-0.222	0.198
NO ₃ ⁻	0.505	-0.545	0.479	0.121	0.607	-0.501	-0.412	-0.012
PO ₄ ³⁻	-0.054	0.479	0.370	-0.436	0.541	0.684	0.305	0.157
DO	-0.446	0.248	0.146	0.691	-0.798	0.304	-0.197	0.205
BOD	0.514	-0.744	0.169	-0.303	0.689	-0.650	-0.210	0.089
TC	0.451	-0.807	0.021	-0.326	0.653	-0.609	0.209	-0.060
Eigen value	6.7898	2.8765	1.9543	1.5246	7.7694	2.9799	2.1166	1.47.5
Cumulative % of variance	42.4	60.4	72.6	82.1	48.6	61.2	74.4	83.6
% of variance	42.4	18.0	12.2	9.5	48.6	18.6	13.2	9.2

PC principal component

magnesium bearing minerals. Among the cations, Mg²⁺ is the dominant ions contributing hardness in water. Additionally, 9.5% of the total variance is explained by PC4 that indicates positive score with DO (moderate) and negatively correlated with pH (moderate), reflects natural water system to support aquatic life. It may be noted that increased pH (slightly alkaline conditions) and high DO are the favorable environment to sustain aquatic animals.

For post monsoon, PC1 explains that 48.6% of the total variance has strong positive correlation on EC, TDS, Na⁺, K⁺, HCO₃⁻ and SO₄²⁻, moderate positive score on Cl⁻, NO₃⁻, PO₄²⁻, BOD and TC, and negative loading on pH (weak) and DO (moderate). The combination of EC, TDS, Na⁺, K⁺, HCO₃⁻, Cl⁻ and SO₄²⁻ ions, indicates weathering of minerals (lithogenic factor) associated with hydrochemistry (Okiongbo and Douglas 2015). The chemical species NO₃⁻ and PO₄²⁻ stimulates increased BOD and TC level, which may be due to industrial and domestic effluent and agricultural runoff (Iscen et al. 2008; Dinkaa et al. 2015). The negative loading of pH and DO represents the organic contamination from human activities (Muangthong and Shrestha 2015; Hamid et al. 2016). Kim et al. (2003, 2005) suggested that negative loading of pH and DO is due to organic contamination, resulting in the formation of ammonia and organic acids thereby decreasing pH and affecting aquatic life. Hence, it can be inferred that PC1 is controlled by mixed factor (lithogenic and

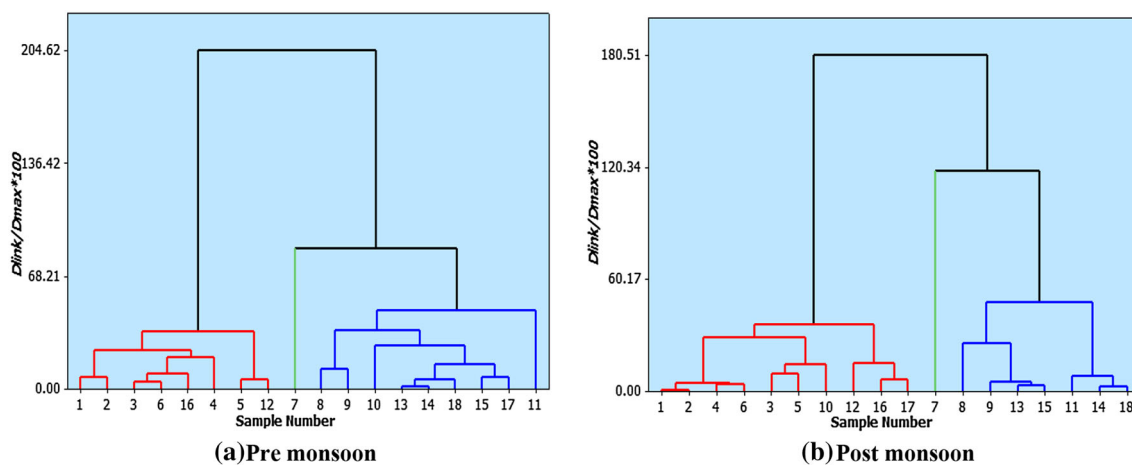
anthropogenic). PC2 accounts for 18.6% of the total variance and moderate positive loading on Cl⁻ and PO₄²⁻ and negative score (moderate) with NO₃⁻, BOD and TC. The significant inverse relationship between Cl⁻ and PO₄²⁻ and NO₃⁻ could be due to different source of chemical origin. Increase in nutrient concentration, primarily PO₄²⁻ and NO₃⁻, enhanced biological metabolism thereby decreasing dissolved oxygen (Hickman and Gray 2010; Nyamangara et al. 2013). It is noted that the study area lacks proper sewage drainage system and also encounters tremendous surface/urban runoff (effluent) during monsoon season. This component is attributed to anthropogenic factor (agricultural runoff and domestic sewage). PC3 is responsible for 13.2% of the total variance with strong positive loading on TH and Mg²⁺, which are controlled by lithogenic factor. Boyd and Tucker (1998) depict that the degree of water hardness increased with the elevated concentration of Mg²⁺ ions. Lastly, 9.2% of the total variance is explained by PC4 that indicates positive loading on pH (moderate) and negative weight with Ca²⁺ (strong), represent natural water quality formed due to rock water interaction. Alkaline pH enables Ca²⁺ to precipitate as calcium carbonate.

CA is employed to sort out the similarities and differences between the 18 sampling locations of surface water by dendrogram. The clustering pattern formed by each cluster cannot be explained by considering certain special

Table 12 Average values of the water quality parameters for each cluster

Cluster parameter	Pre monsoon			Post monsoon		
	Cluster 1 (1, 2, 3, 6, 16, 4, 5, 12)	Cluster 2 (7)	Cluster 3 (8, 9, 10, 13, 14, 18, 15, 17, 11)	Cluster 1 (1, 2, 4, 6, 3, 5, 10, 12, 16, 17)	Cluster 2 (7)	Cluster 3 (8, 9, 13, 15, 11, 14, 18)
pH	7.44	7.54	7.60	7.46	7.54	7.25
EC	683.66	1490.00	1386.33	582.30	1512.00	931.57
TDS	441.50	969.0	905.00	376.40	1014.00	602.14
TH	199.25	261.0	245.22	245.20	261.00	243.43
Ca ²⁺	35.11	79.0	37.47	61.41	79.00	67.65
Mg ²⁺	40.05	44.41	52.89	44.85	44.41	42.89
Na ⁺	12.16	130.00	146.69	24.49	130.00	95.61
K ⁺	1.98	9.00	8.60	2.92	9.00	7.11
HCO ₃ ⁻	7.32	17.00	33.46	9.54	17.00	22.87
Cl ⁻	112.00	145.00	138.89	116.80	145.00	143.43
SO ₄ ²⁻	2.01	17.89	4.42	3.64	18.00	2.74
NO ₃ ⁻	10.72	23.00	17.89	11.63	23.00	13.34
PO ₄ ³⁻	0.15	0.03	0.18	0.03	0.03	0.07
DO	4.66	0.00	3.94	7.44	0.00	4.80
BOD	2.46	280.00	13.00	1.03	170.00	7.36
TC	131.76	1600.00	168.44	84.20	765.00	178.43

Bold indicates the highest average value paramters among different clusters

**Fig. 6** Hierarchical dendrogram of sampling locations in the study area

parameters only. Therefore, specific tracers for each pattern representing individual cluster need to be identified by calculating the average value of each parameter belonging to the individual clusters. Dendrogram reveals three statistically significant clusters $(D_{link}/D_{max}) \times 100 < 70$ (pre monsoon) and $(D_{link}/D_{max}) \times 100 < 60$ (post monsoon) for water samples, respectively, and their average values are listed in Table 12 and Fig. 6a, b.

During pre monsoon, Cluster 1 (C1) confirms a pattern with the highest level of DO and low tracer pH, corresponds well with PC4. The sampling locations belonging to

C1 (1, 2, 3, 6, 16, 4, 5, 12) indicate natural water quality. The smallest cluster 2 (C2) is represented by single sample (7) and the highest levels of EC, TDS, TH, Ca²⁺, K⁺, Cl⁻, SO₄²⁻ NO₃⁻, BOD and TC, which may be attributed to the mixed factor (anthropogenic and lithogenic). C2 correlates fairly well with PC1 and PC2. The largest group of sampling locations (8, 9, 10, 13, 14, 18, 15, 17, 11) belonging to cluster 3 (C3) confirms the highest level of pH, Mg²⁺, K⁺ and HCO₃⁻ and embodies lithogenic factor (weathering and leaching of minerals) controlling the hydrochemistry as in PC3.

The dataset obtained in post monsoon also displayed 3 clusters. The first cluster C1 is the largest group of sampling locations (1, 2, 4, 6, 3, 5, 10, 12, 16, 17) forms a pattern of highest level of Mg^{2+} and DO indicate natural water attributed to dissolution of minerals and favourable for the existence of aquatic life. C1 fairly correlates with PC3. The intermediate cluster C2 (7) confirms the highest level of pH, EC, TDS, TH, Ca^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- , BOD and TC, and corresponds well with PC1 and PC4. It signifies that the sampling location is polluted from lithogenic and anthropogenic factors. Lastly, Cluster 3 (C3) is distinguished by the highest level of HCO_3^- and PO_4^{3-} , which correlates well with PC2. The sampling locations group of C3 (8, 9, 13, 15, 11, 14, 18) may be attributed to the anthropogenic factor (domestic sewage and agricultural runoff) (Nyamangara et al. 2013).

CA has been incorporated to assess the relationships and validate the sources identified by PCA.

The sampling locations group in C1 are influenced by lithogenic factor, whereas C2 by mixed factor, respectively, for both seasons. However, C3 sampling locations are controlled by lithogenic factor for pre monsoon, whereas during post monsoon by anthropogenic factor. Few sampling locations (10, 17) of C3 during pre monsoon are grouped under C1 of post monsoon. The remaining sampling locations grouped in C3 (8, 9, 13, 15, 11, 14, 18) for both seasons are influenced by different sources. It indicates that same sampling locations are influenced by temporal variation of pollution sources, changing human activities related to seasonality like agriculture and excessive surface runoff often loaded with industrial and domestic effluents during monsoon and post monsoon period. The area also lacks proper drainage system where effluents are directly discharged into local tributaries and enters Sirsa river. CA supported by PCA confirms that the surface water chemistry is strongly controlled by natural factors such as weathering of minerals, ion exchange processes and anthropogenic factors. Hence, a good relation between the two statistical techniques (PCA and CA) is elucidated from the analyzed datasets of water samples.

Conclusion

This paper highlights the application of multivariate statistical analysis and conventional graphical hydrochemical representation to assess the hidden factor controlling hydrochemistry and geochemical evolution processes of water system. The physicochemical parameters are within the permissible limits of BIS (2012) and WHO (2011), except for EC (both seasons), Mg^{2+} , Na^+ and K^+ (pre monsoon), respectively. However, the biological indicators namely BOD and TC show majority of the samples are

above the prescribed limits of BIS (2012) indicating organic pollution. The irrigation suitability for EC values falls moderately to high saline whereas TDS values belong to fresh water class. The result of Piper plot and Chadha's classification confirms that majority of samples for both seasons fall under $Ca^{2+}-Mg^{2+}-HCO_3^-$ water types indicating temporary hardness and remaining few samples belong to $Ca^{2+}-Na^+-HCO_3^-$ or $Na^+-HCO_3^-$ forms by base ion exchange processes. Based on the conventional hydrochemical study, the influence of ion exchange processes attributes the dominance of alkaline earth metals over the alkali metals and weak acidic anions over strong acidic anions in the study area. PCA and CA identify the surface water chemistry is strongly controlled by natural factors such as weathering of minerals, ion exchange processes and anthropogenic factors like agricultural runoff and discharge of industrial and domestic effluent. Thus, the holistic approach of PCA and CA modeling will help to plan the future design through optimal sampling locations based on seasons without losing any outcome significance and develop remedial measures for the restoration of water resources.

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