

Multivariate analysis and geochemical signatures of groundwater in the agricultural dominated taluks of Jalandhar district, Punjab, India

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ABSTRACT

The present study is focused on the agriculturally dominated taluks of Nakodar, Shahkot and Phillaur in Jalandhar district, Punjab. Integrated multivariate technique along with geochemical signatures and vertical depth profiles of major ions were studied to assess the hydrogeochemical characteristics, processes influencing the aquifer chemistry and suitability appraisal for different uses. The analytical results revealed that the groundwater is hard to very hard in nature and their relative abundance of major ions are $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^- > \text{PO}_4^{2-}$ respectively. Elevated levels of NO_3^- (2 samples) in Phillaur taluk and F^- (1 sample in every three taluks) were observed in shallow aquifer of the study area. The overall results of the water quality index show that a major part of the study area possesses good water quality. The taluk wise WQI results depict that certain pockets fall in poor (3 samples in Phillaur, 1 in Shahkot) to very poor (1 sample of Nakodar) water classes. The chemical compositions of the study area were predominantly Ca^{2+} - Mg^{2+} - HCO_3^- followed by Ca^{2+} - Mg^{2+} - Cl^- - SO_4^{2-} facies. Both Nakodar and Shahkot taluk shows Na^+ - Mg^{2+} - HCO_3^- water type, while Phillaur taluk shows Mg^{2+} - HCO_3^- water type. The water type of the shallow aquifer is complex in nature showing Na^+ - Mg^{2+} - HCO_3^- type, further it changed to Na^+ - HCO_3^- in the intermediate zone. Interpretation of the geochemical signatures of the groundwater suggested that natural weathering and dissolution of silicate and carbonate minerals and ion exchange process are largely controlling the aquifer chemistry. Principal component analysis (PCA) extracts five principal components (PC's), where PC1, PC2 and PC4 are influenced by mixed factors i.e., lithogenic and anthropogenic inputs. PC3 is exclusively affected by anthropogenic factors like domestic sewage, fertilizer and irrigation return flow respectively and PC5 is mainly controlled by natural factors.

1. Introduction

Exponential population growth, industrialization, urbanization and poor waste management practices create immense stress on freshwater resource all over the world both in terms of quality and quantity (Santucci et al., 2018; Matta et al., 2018a, 2018b; Avtar et al., 2013; Jothiprakash and Mohan, 2004). Surface water sources are limited in nature. Changes in monsoon pattern and thrust of anthropogenic activities on inland freshwater bodies have increased the dependence on groundwater resource in India during the last two decades (Rao et al., 2017; Keesari et al., 2014). Adimalla and Venkatayogi (2018) suggested that 65% of groundwater is used for drinking, 20% for irrigation and 15% for industrial purposes in the world. Developing countries like

India used 88% potable water supplies from groundwater resource alone (Jain and Vaid, 2018; Jain et al., 2010). Groundwater quality deterioration has become a major issue especially in the arid and semi-arid regions of India and similar parts of the world (Keesari et al., 2014; Sharma et al., 2017). The quality of water is a serious concern since it is directly associated with human health (Matta et al., 2018a, 2018b; WHO, 2009). As per World Bank estimation, approximately 21% of communicable diseases are water-related and about 360 billion rupees per year are spent to combat such diseases that become a burden on India's economy (Shanmuganandan, 1999; DeNormandie and Sunitha, 2002).

Punjab is predominantly an agricultural state of India having 85% area under cultivation with an average cropping intensity of 190%, of

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which 71% of the total cultivated area is irrigated with groundwater (Pandey, 2016). During the green revolution, the change in cropping pattern has rapidly increased the demand for irrigation water which is fulfilled by groundwater till now (Singh et al., 2015). Groundwater is the foremost source of drinking water in both rural and urban areas. There are about 1.1 million tube wells abstracting groundwater for agricultural purpose and around 150 thousand tube wells are utilized for domestic and industrial purposes in urban and semi-urban areas (Lapworth et al., 2014). Over-abstraction of groundwater resource in the state further led to aquifer decline at an alarming rate of 0.7–1.2 m/year is not a very recent issue, but this problem may be even more worse in future (World Bank, 2010; Pant et al., 2017a; Pant et al., 2019). Therefore, the state witnessed approximately 78% (39,000 km²) area showing a declining trend in water level and around 80% area of the state is classified as an overexploited region (Rao et al., 2017; Gupta, 2009).

Jalandhar district is situated in central Punjab where 91% of the total area (2410 km²) is under cultivation with cropping intensity of 178%, also known as 'cultivated district' (CGWB, 2018). Around 86% of the total cultivated area is under rice and wheat crops. The population livelihood mainly depends on agricultural and its allied services as agriculture is the dominant land use land cover (LULC) class (Fig. 2). Three agricultural dominated taluks namely, Nakodar (275.13 km²), Shahkot (380 km²) and Phillaur (661.96 km²) are selected for the present study, located in Jalandhar districts of northeast Punjab. The study area belongs to the Indo-Gangetic alluvium plains which are known for its suitability for cultivation and huge reserve for groundwater. The net sown area is 1317.13 km², where approximately 80% of the total area has cropping intensity of 176% (CGWB, 2018). Among the three taluks, the groundwater gross draft in Phillaur is highest with 805 million cubic meters (mcm) for irrigation and 16.63 mcm for drinking and industrial uses followed by Nakodar and Shahkot according to the CGWB (2013). As per the report of CGWB (2018), there are 51,179 shallow and deeper tube wells operating in the area and categorized as "overexploited" (OE) region. The problem of groundwater draft is due to numerous groundwater abstraction units, overexploitation, cultivation of high water demanding crops (Rao et al., 2017). Expansion of agricultural land by converting forest area often illegally along with increase area in paddy cultivation led to tremendous stress in groundwater resource. Further, the shifting from organic farming method to synthetic chemical farming practices has led to tremendous impact on the ecology by releasing the harmful persistent chemicals in the surrounding water body, air and other non-target species (Abhilash and Singh, 2009). The study area is witnessed as one of the highest consumption of synthetic fertilizers 247 kg/ha as compared to the national average of 144 kg/ha. Therefore, prolonged use of fertilizers and pesticides in such semi-arid area will certainly release the water soluble chemical in irrigated water, thereby contaminating soil and groundwater (Brainerd and Menon, 2014; Pant et al., 2019). Therefore, monitoring of the alluvial aquifers is very important, especially in cultivated and urbanized zones due to their shallow character and high permeability as they are highly vulnerable to anthropogenic pollution (Kaur et al., 2019; Sidhu et al., 2013; Pant et al., 2017b; Herojeet et al., 2016). There also exist about 21 large & medium scale (such as tanneries, leather complex, metal processing and textile and paper industries) and 20,295 small-scale industries are functioning in the area (Statistical Abstract of Punjab, 2016). Both industrial and urban sectors not only utilize the available water but also discharge a large amount of untreated wastewater, which is another additional factor responsible for groundwater contamination in the study area (Naik et al., 2008; Aulakh et al., 2009).

Various researchers across the globe have adopted the chemometric techniques along with different water quality indices to understand the groundwater quality status and hydrogeochemical processes governing the aquifer chemistry (Adimalla et al., 2018; Khalid, 2019; Shi et al., 2018; Maurya et al., 2019; Islam et al., 2017; Thakur et al., 2016;

Purushothaman et al., 2014; Naik et al., 2009; Singh et al., 2005; Kim et al., 2005; Box et al., 1978). Groundwater quality is influenced by various latent natural and anthropogenic factors' thus water quality dataset is too intricate in nature and very difficult to derive meaningful information using simple techniques (Khanday et al., 2018; Herojeet et al., 2017). Therefore, in addition to the water quality index (WQI) and hydrogeochemical modelling, the chemometric statistical technique (principal component analysis) was used to extract significant hydrochemical information and probable source identification in the study area. These combined approaches of different techniques help to assess the hidden factors influencing groundwater hydrochemistry and produce more interpretable results for the efficient management of water resources (Simeonov et al., 2003; Singh et al., 2005). The present paper also elucidates the usefulness of chemometric technique and various geochemical signatures for the analysis and interpretation of water quality data for the emphatic management of groundwater resource in alluvial plains. The findings of this study shall provide significant information on groundwater quality of the study area and will help to adopt proper remedial management approach in the other agricultural prolific regions of Punjab.

2. Study area description

The area under investigation is geographically located between 30°59' to 31°37'N latitudes and 75°04' to 75°57'E longitudes in the intensively irrigated plain situated between River Beas and River Sutlej of the Punjab State (Fig. 1). The study area is characterized by semi-arid conditions having hot summer and mild winter with an average annual rainfall 606 mm. The area received 70% of the annual normal rainfall during south-west monsoon (July to September) which is unevenly distributed over the region (CGWB, 2018). The monsoon in the study area extends from June to mid-September. The temperature varies from 45 °C (May–June) to 2 °C (January). Agriculture is the main occupation and dominant land use land cover (LULC) class in the study area (Fig. 2). Wheat and rice are the principal crops grown in the region during Rabi and Kharif seasons respectively.

3. Geology and hydrogeology

The study area is a part of Satluj sub-basin of Indus Basin representing vast Indo-Gangetic alluvial plains and is drained by perennial River Satluj and its tributary (*East Bein*). The geological setup shows the area is part of Bist Doab tract comprised of Quaternary to Sub Recent alluvium type consisting of pebbles, gravel, fine to medium grained sand, clay and Kanker (Rao et al., 2017). The Older alluvium of Middle to Late Pleistocene age occurs all over the study area (Fig. 3). The Newer alluvium belongs to Upper Pleistocene to Recent age is light coloured and poor in the calcareous matter, whereas Older alluvium consists of pale reddish brown coloured beds of clay and rich in calcareous material (CGWB, 2012, 2016). Physiographically, the area is distinguished by two distinct features i.e. Satluj floodplain and vast upland plain (Rao et al., 2015; CGWB, 2018). The stratigraphic sequence of geological formations and the hydrogeological map of the study area are given in Table 1 and Fig. 4, respectively. Two types of soils namely, tropical arid brown and arid brown soils are found in the study area (CGWB, 2018). The fence diagram and 2-Dimension lithological sections of the study area are presented in Figs. 5 and 6, respectively. Three distinct aquifer groups (both unconfined and confined conditions) consisting of fine to coarse-grained sand separated by thick clay lenses of 5–20 m are present in the study area to the depth of 300 m below ground level (m bgl) (Figs. 5 and 6). The first aquifer is under unconfined conditions, while the second and the third aquifer groups are under semi-confined to confined conditions exists up to 115 m bgl, 130 to 195 m bgl and 215–300 m bgl, respectively (CGWB, 2012, 2016). These aquifer groups are characterized by highly permeable sand and gravel lenses interlayered with laterally discontinuous clay and kanker

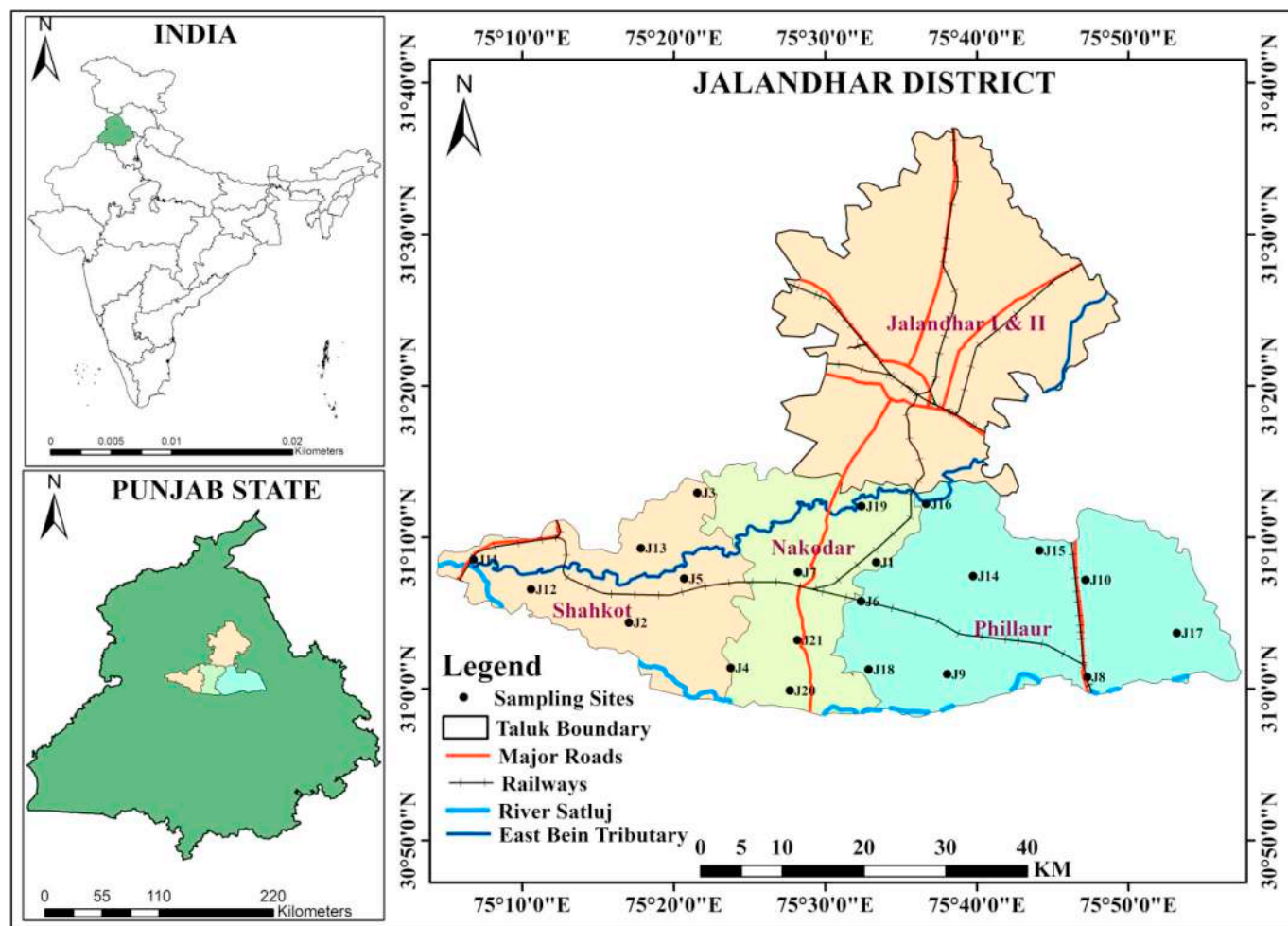


Fig. 1. The map of the study area with groundwater sampling locations.

deposited (Bonsor et al., 2017; Lapworth et al., 2017). The top sand beds are fine to medium grained while the lower ones are medium to coarse in texture (CGWB, 2018). Fig. 6 divulges that significant clay beds are prominent at Malsian, Sarih, Cheema khurd and Lasara locations. Whereas, Badli, Nakodar and Gulamgarh shows the variation in thickness i.e. thin clay layers inter bedded with sand layer, which indicate there may be vertical and lateral connectivity of different aquifers. Thus the over abstraction of groundwater from this particular region (shallow and deeper aquifer) for various purposes enhance the vertical leakage which led to the alteration in the regional groundwater flow. The overall flow of groundwater is toward south to south-west direction and water table elevation ranges from 205 m to 240 m above mean sea level (Rao et al., 2015; Lapworth et al., 2017; CGWB, 2018). The transmissivity value of the aquifer ranged from 1028 to 5750 m²/day and storativity value ranges from 0.001 to 0.006. The hydraulic conductivity value in the study area varies from 38 to 90 m/day and the value of storage coefficient ranged from 1.18×10^{-3} to 6.0×10^{-3} (CGWB, 2018). As per CGWB (2013), all the three taluks are categorized as 'overexploited'.

4. Materials and methods

4.1. Analytical procedures

A well tested systematic random sampling technique was adopted to collect the groundwater sample in the study area. Total twenty one groundwater samples (9 from Phillaur, 5 from Nakodar and 7 from Shahkot) were collected using Global Positioning System (GPS) during

the pre-monsoon season (May 2017) from tube wells (TW) and hand pump (HP) which were used for domestic and irrigational purposes. The specific depth, source and ownership of each sampling location are listed in Table 3. The samples were collected after 10–15 min pumping of TW/HP to ensure the original composition of water in 1 L high-density polyethylene (HDPE) bottles pre-washed with 10% nitric acid (HNO₃) and rinsed with deionized water. Sterilized bottles were thoroughly rinsed 2–3 times with the water to be sampled to avoid unpredictable changes in characteristics as per standard procedures. pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured in the field by using a multiparameter water quality meter (Hanna HI98194). Two sets of groundwater samples were collected from each sampling locations. The groundwater samples were filtered through 0.45 μm Whatman filter paper and preserved by acidifying with HNO₃ to pH ~2. Samples were kept at a temperature of 4 °C until analysis. All water samples were analyzed for major cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) and major anions (HCO₃⁻, CO₃²⁻, SO₄²⁻, PO₄³⁻, F⁻, Cl⁻ and NO₃⁻) according to the standard methods (APHA, 2005). The geographical sites of all sampling locations are shown in Fig. 1. The systematic research design for the appraisal of groundwater quality of the study area is presented in Fig. 7. Geospatial analyst tool in ArcGIS 10.2.1 software developed by Environmental Systems Research Institute (ESRI) was used to prepare maps and Inverse distance weighted (IDW) algorithm interpolation method was used to generate spatial interpolation maps of various groundwater quality parameters. This technique of interpolation estimates the values of the pixels by averaging the known data (Mueller et al., 2004). It is an effective algorithm extensively used in the mapping of spatial interpolation of groundwater

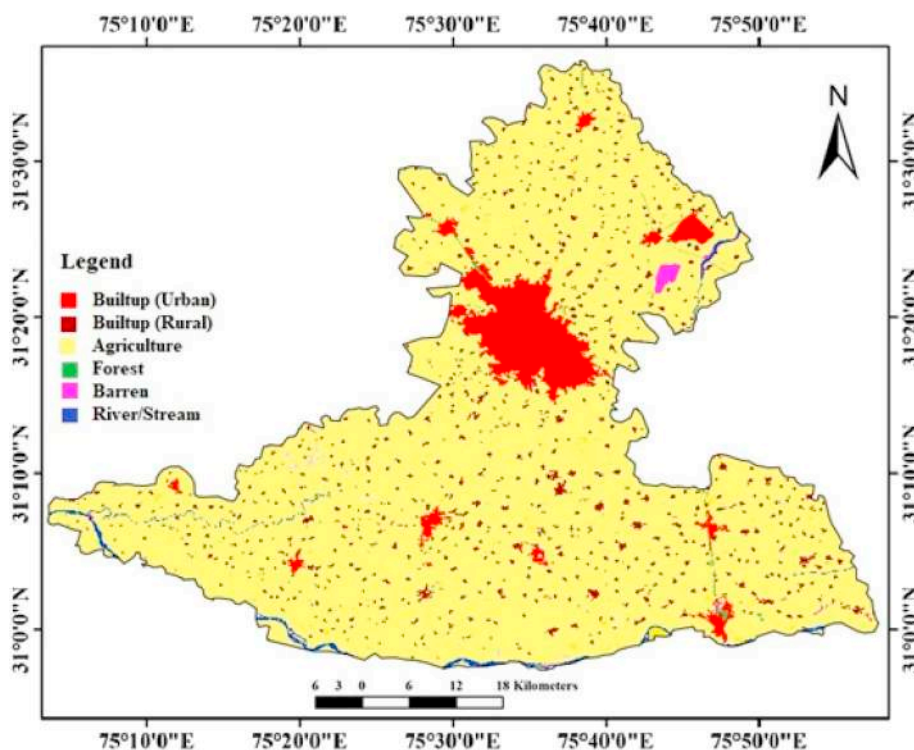


Fig. 2. LULC map of the Jalandhar district.

quality parameters (Shakerkhatibi et al., 2019). The accuracy of the chemical ion data was examined using charge balance error (CBE) equation and values were within the acceptable limit of ± 5% (Hounslow, 1995).

$$CBE\% = \frac{(Cations)meq/L - (Anions) meq/L}{(Cations)meq/L + (Anions) meq/L} * 100 \quad (1)$$

4.2. Appraisal of water quality index (WQI)

WQI is an efficacious method to evaluate the suitability of water for drinking purpose (Khalid, 2019; Horton, 1965). It is an effective mathematical tool which communicates information on the overall quality of water by examining individual water parameter (Herojeet et al., 2016). WQI was calculated by adopting the weighted arithmetical

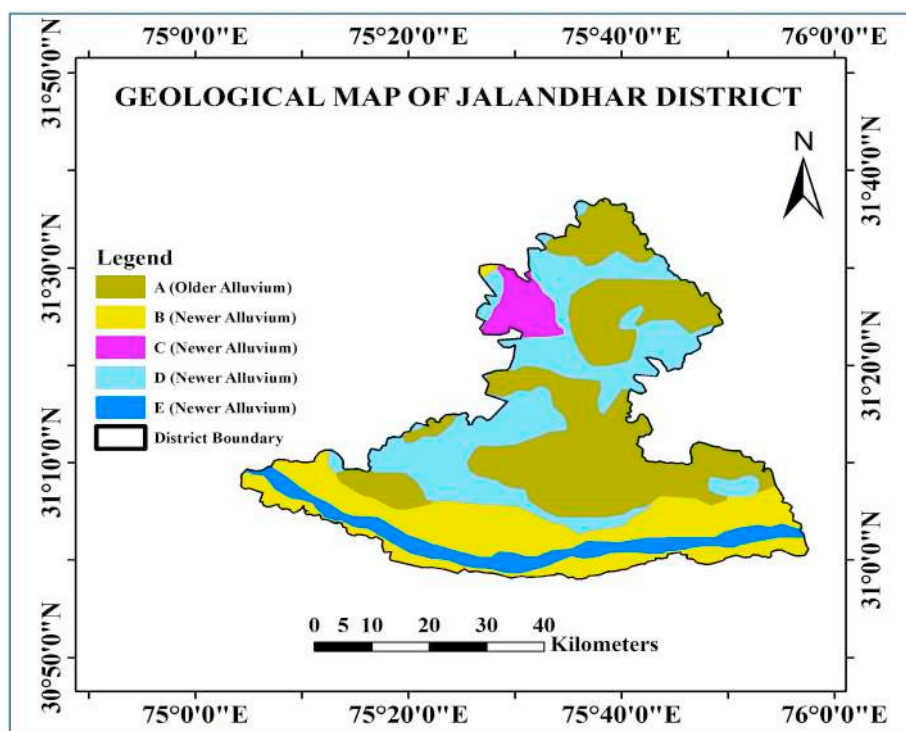


Fig. 3. Geological map of the Jalandhar district (After GSI).

Table 1
Stratigraphic sequence of geological formations of the study area.

Age	Formation	Lithology
Upper Pleistocene to Recent age	Newer alluvium	B Blue grey to light grey micaceous sand with interbeds of purple red clay
		C Undifferentiated semi consolidated and stabilised older dunes with kankar and some carbonaceous material
		D Undifferentiated Aeolian flat/sand sheet and newer dunes
		E Loose grey micaceous sand along the stream courses (Recent)
		A Red drift sand to loam with kankar, sticky clay, grey medium to coarse micaceous sand with kankar, subrounded to subangular unsorted pebbles, gravel and cobble in adjoining foothills
Middle to late pleistocene	Older alluvium	

index method. Ten water quality parameters were considered for estimating WQI namely, pH, TDS, TH, Ca^{2+} , Mg^{2+} , HCO_3^- , F^- , Cl^- , SO_4^{2-} and NO_3^- . Bureau of Indian Standards (BIS, 2012) were used for the computation of WQI. The equation used in the present study to calculate WQI is developed by Tiwari and Mishra (1985). Table 2 describes the relative weights of physicochemical parameters used for WQI calculation.

$$\text{WQI} = \sum q_n W_n / W_n \quad (2)$$

where, W_n = unit weight of n^{th} parameters, is calculated by the equation

$$W_n = K/S_n \quad (3)$$

and K, is the proportionality constant obtained from,

$$K = \left[\frac{1}{\sum_{i=1}^n \frac{1}{S_i}} \right] \quad (4)$$

where, S_n and S_i are the BIS standard values of the water quality parameter.

$$q_{ni} = 100 \times \frac{V_a - V_i}{V_s - V_i} \quad (5)$$

q_{ni} is the Quality rating of the i^{th} parameter for a total of n water quality parameters where, V_a = value of the water quality parameter obtained from laboratory analysis, V_i = ideal value (for pH = 7 and 0 for other parameters) and V_s = BIS standard value of water quality

parameters.

4.3. Evaluation of hydrogeochemical signatures of groundwater

To understand the hydrogeochemical characteristics of groundwater, various plots were used namely, Piper (1944), Durov (1948), Scholler (1965), Giggenbach (1988), Gibbs (1970) and scatter diagrams. These plots graphically represent the relationship defining various geochemical signatures in a set of groundwater samples. The Geochemist's Workbench Student Edition 12.0 was used to prepare the Piper diagram, Durov and Schoeller plot, while Giggenbach plot was prepared by using AquaChem 2011 software.

4.4. Evaluation of groundwater for irrigation purposes

The irrigation water quality may affect plant growth and agriculture production. Agriculture being the main LULC class in the study area and most of the irrigational water demand is met by the groundwater. Therefore, it is essential to evaluate the groundwater quality for irrigation use. The suitability appraisal of groundwater for irrigational purpose is determined by various irrigation indices namely, sodium adsorption ratio (SAR), percent sodium (%Na), residual sodium carbonate (RSC), magnesium hazard, (MH), potential salinity (PS) and permeability index (PI). Therefore, the above-mentioned indices are calculated using the following equations:

$$\text{SAR} = \text{Na}^+ / \sqrt{\text{Ca}^{2+} + \text{Mg}^{2+}/2} \quad (\text{Richard 1954}) \quad (6)$$

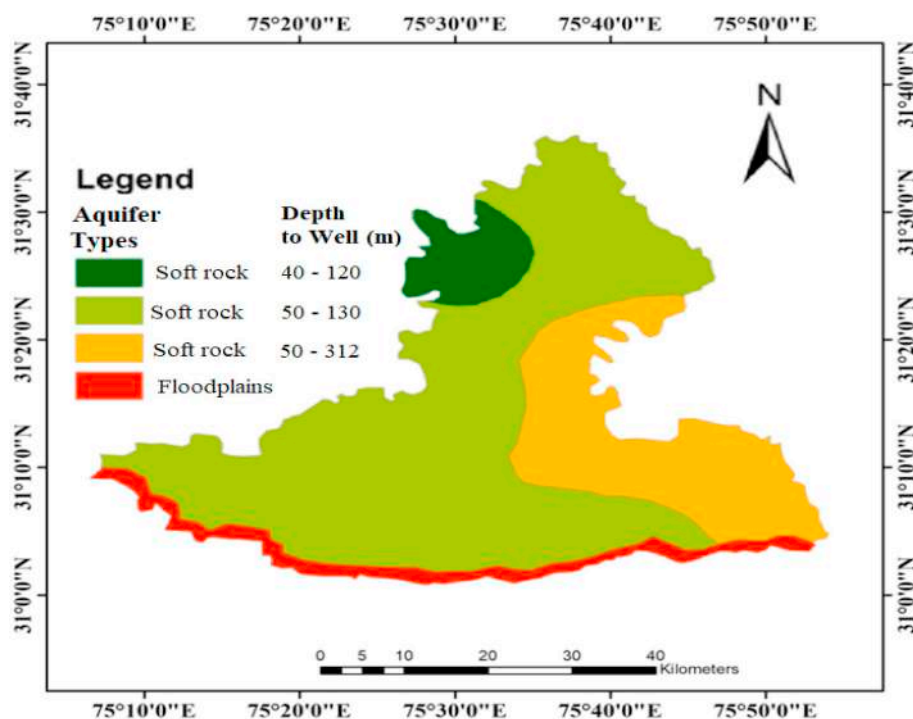


Fig. 4. Hydrogeological map of the Jalandhar district (After CGWB, 2012).

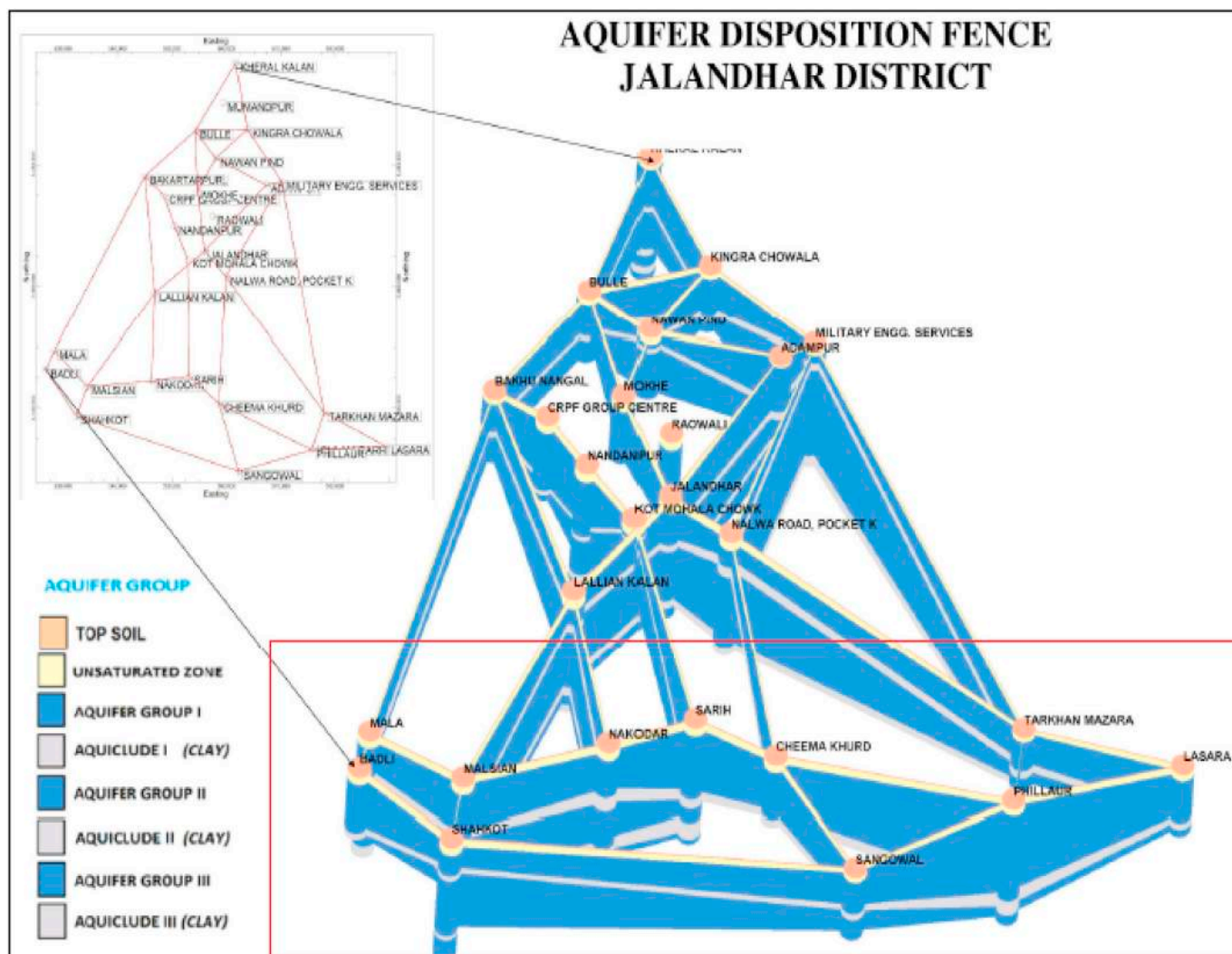


Fig. 5. Fence diagram of the Jalandhar district (Modified after CGWB, 2018).

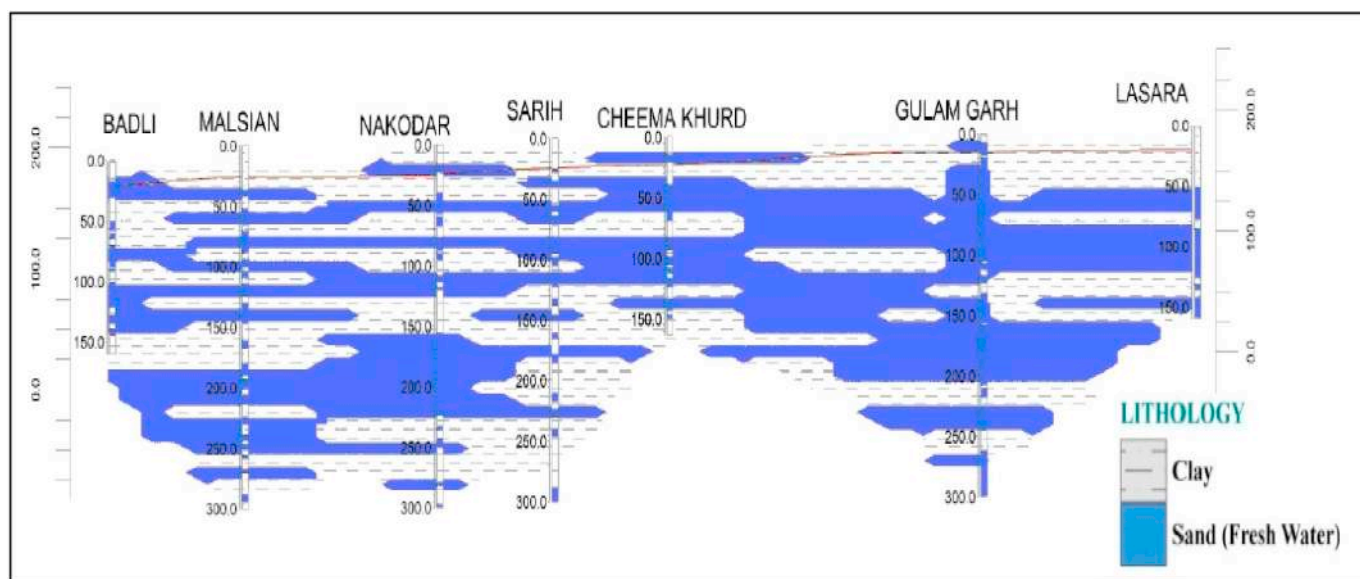


Fig. 6. 2-Dimension lithological section of the study area (Modified after CGWB, 2018).

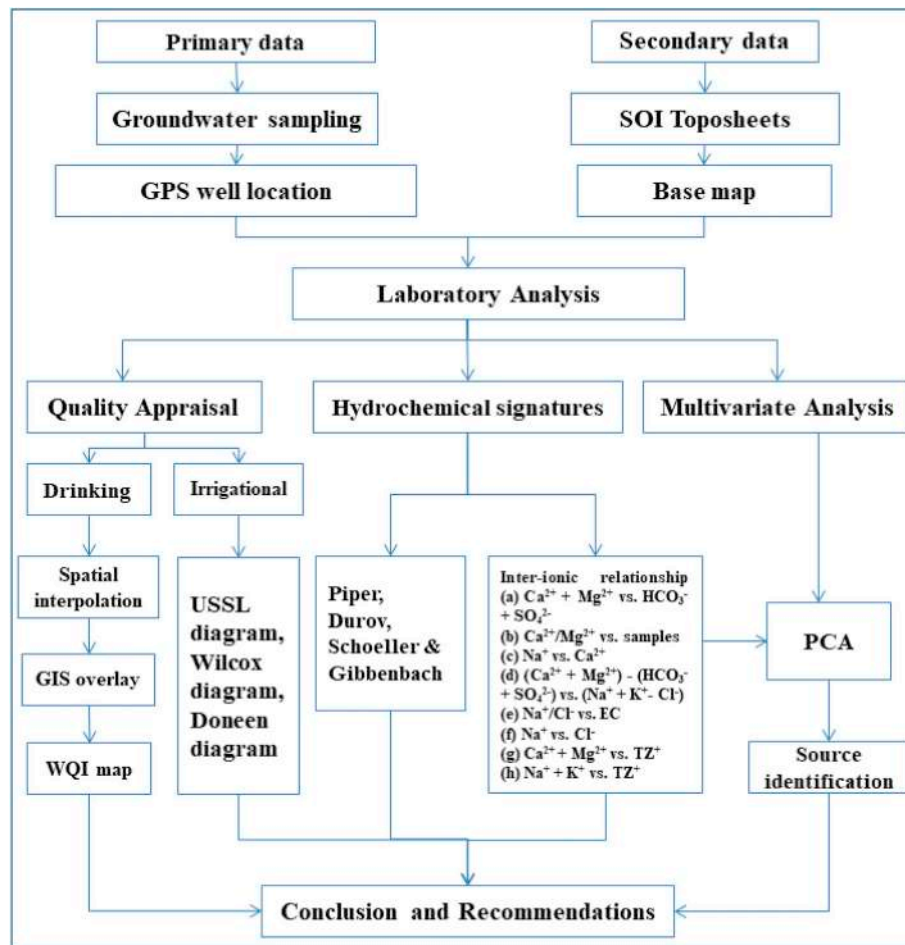


Fig. 7. Systematic research design for the appraisal of groundwater quality of the study area.

Table 2
Unit weight of water quality parameters for WQI.

Parameters	Unit weight (W _n)
pH	0.1420
TDS	0.0006
TH	0.0020
Ca ²⁺	0.0060
Mg ²⁺	0.0121
HCO ₃ ⁻	0.0020
NO ₃ ⁻	0.0268
F ⁻	0.8043
Cl ⁻	0.0012
SO ₄ ²⁻	0.0030
Σ W _n	1.0000

$$\%Na = Na^+ + \frac{K^+}{Ca^{2+}} + Mg^{2+} + Na^+ + K^+ \times 100 \quad (\text{Richard 1954}) \quad (7)$$

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (\text{Eaton 1950}) \quad (8)$$

$$MH = Mg^{2+}/(Ca^{2+} + Mg^{2+}) \times 100 \quad (\text{Szabolcs and Darab 1964}) \quad (9)$$

$$PI = (Na^+ + \sqrt{HCO_3^-})/(Ca^{2+} + Mg^{2+} + Na^+) \times 100 \quad (\text{Doneen 1961}) \quad (10)$$

$$PS = Cl^- + \sqrt{SO_4^{2-}} \quad (\text{Doneen 1961}) \quad (11)$$

where, all ions concentrations are expressed in meq/L.

4.5. Chemometric techniques

The chemometric approach has been extremely used as unbiased methods for attaining significant information from the hydrochemical dataset in the groundwater system (Li et al., 2018; Islam et al., 2017; Herojeet et al., 2017; Singh et al., 2005; Box et al., 1978). Chemometric technique namely principal component analysis (PCA) was carried out to understand the geochemical processes and the sources of major anions and cations in the groundwater. PCA is a statistical technique to reduce original data variables into a small number of principal components for better interpretation of data (Simeonov et al., 2003; Singh et al., 2005). The first principal component (PC1) explains the most variance present in the data set, each subsequent component explaining progressively less variance (Vieira et al., 2012). Prior to application of PCA, therefore, standardization (z-scale) of the chemical parameters is carried out to render each of them dimensionless in order to eliminate potential bias toward a particular parameter of the different unit with high concentrations (Simeonov et al., 2004; Herojeet et al., 2016). Varimax rotation method was used to extract the principal components (PCs) considering eigenvalues > 1 as significant for interpretation (Kaiser, 1960). According to Liu et al. (2003) factor loading is classified corresponding to absolute loading values as 'strong' (> 0.75), 'moderate' (0.75–0.50) and 'weak' (0.50–0.30), respectively. All the statistical analyses were performed by using the Microsoft Excel 2010, Minitab 17 software.

Table 3
Analytical results of groundwater samples.

S. no.	Taluk	Depth (m)	Source	Ownership	pH	EC $\mu\text{S}/\text{cm}$	mg/L													
							TDS	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	F ⁻	Cl ⁻	PO ₄ ³⁻	SO ₄ ²⁻	
J1	Nakodar	50	TW	Private	8.3	487	302	147	26	20	23	4	35	107	6.2	1.20	42	0.02	38	
J2	Shahkot	57	TW	Private	8.6	635	394	136	23	19	45	15	59	125	5.3	0.31	54	0.07	48	
J3	Shahkot	60	TW	Private	8.8	1348	836	222	26	38	150	11	82	286	21.0	0.50	123	0.02	98	
J4	Shahkot	73	TW	Private	7.6	715	443	247	41	35	28	13	0	143	2.4	0.07	35	0.03	145	
J5	Shahkot	48	TW	Private	8.3	827	513	103	18	14	106	23	12	196	3.2	0.39	55	0.11	85	
J6	Phillaur	47	TW	Private	7.7	782	485	228	35	34	38	11	0	183	45.0	0.58	49	0.01	89	
J7	Nakodar	70	TW	Private	8.2	624	387	208	29	33	25	7	23	177	3.2	0.55	39	0.07	50	
J8	Phillaur	37	HP	Private	8.5	929	576	211	30	33	61	6	59	226	55.0	1.01	48	0.05	57	
J9	Phillaur	43	TW	Private	8.6	790	490	168	26	25	62	13	47	174	21.0	0.52	55	0.03	66	
J10	Phillaur	38	HP	Private	8.7	635	394	201	26	33	27	9	35	153	8.9	0.90	49	0.04	52	
J11	Shahkot	73	TW	Private	7.6	661	410	199	32	29	18	13	5	156	26.2	0.30	43	0.04	92	
J12	Shahkot	75	TW	Private	8.2	1037	643	348	24	70	49	6	15	285	23.7	0.40	117	0.18	53	
J13	Shahkot	35	HP	Private	8.0	694	430	128	23	17	56	12	5	215	5.3	1.10	39	0.03	62	
J14	Phillaur	40	HP	Private	8.7	723	448	146	27	19	51	15	15	186	15.3	0.90	24	0.06	95	
J15	Phillaur	53	TW	Private	8.6	795	493	217	21	40	39	19	19	242	7.2	0.70	15	0.04	90	
J16	Phillaur	50	TW	Private	8.7	795	493	146	27	19	60	17	25	225	5.3	0.40	36	0.05	78	
J17	Phillaur	60	TW	Private	8.4	597	370	196	19	36	21	13	21	172	7.8	0.50	21	0.07	59	
J18	Phillaur	67	TW	Private	8.3	782	485	214	18	41	40	24	10	192	6.9	0.90	59	0.06	93	
J19	Nakodar	47	TW	Private	8.5	763	473	178	35	22	52	15	47	177	14.0	0.45	49	0.02	62	
J20	Nakodar	50	TW	Private	7.8	429	266	158	32	19	13	4	0	119	6.0	0.03	47	0.01	26	
J21	Nakodar	52	TW	Private	8.2	637	395	195	32	28	32	11	10	180	15.0	0.15	38	0.02	49	

5. Results and discussion

5.1. General parameters of groundwater

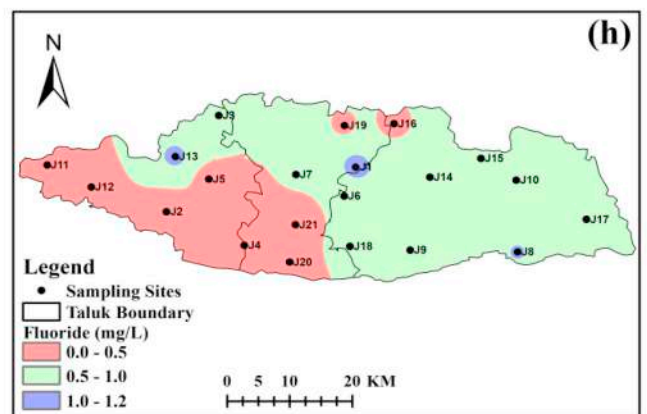
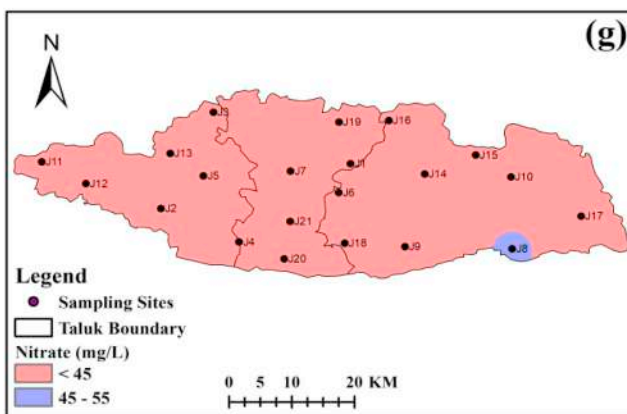
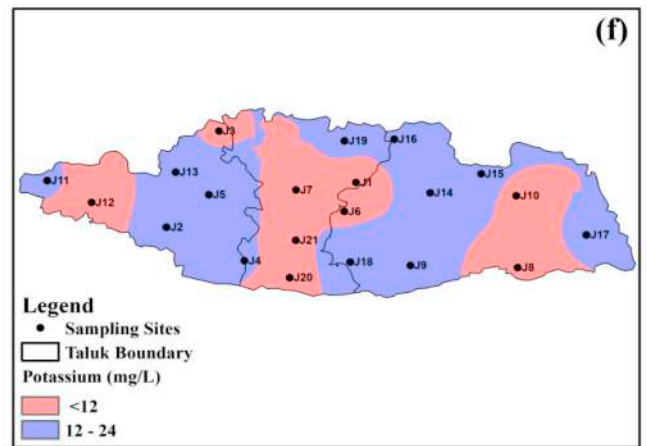
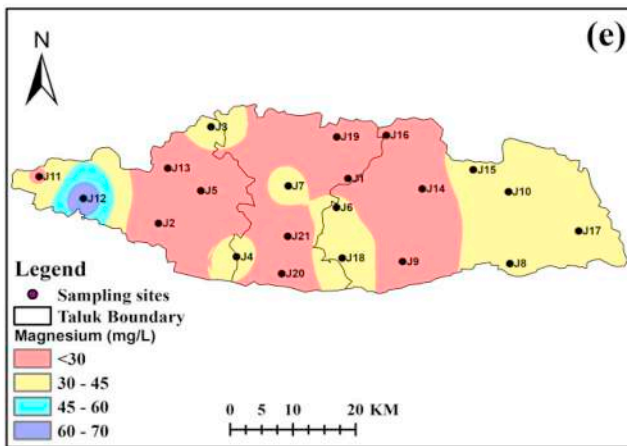
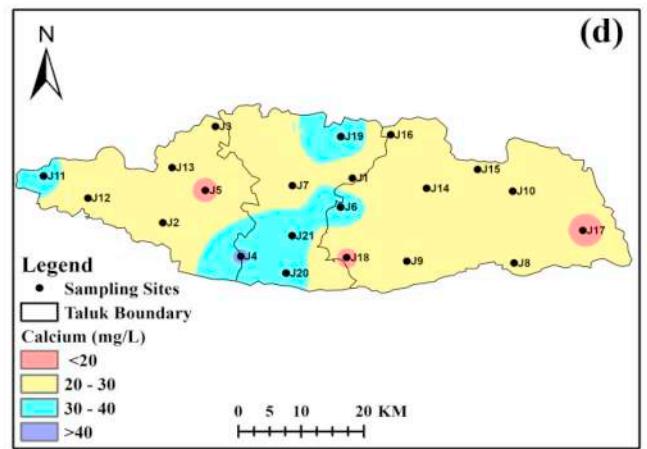
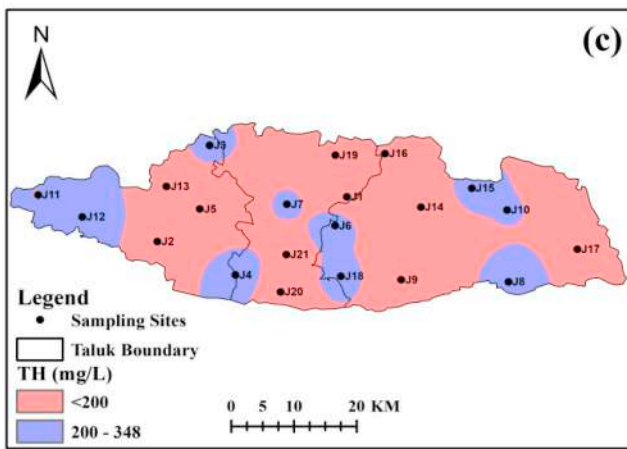
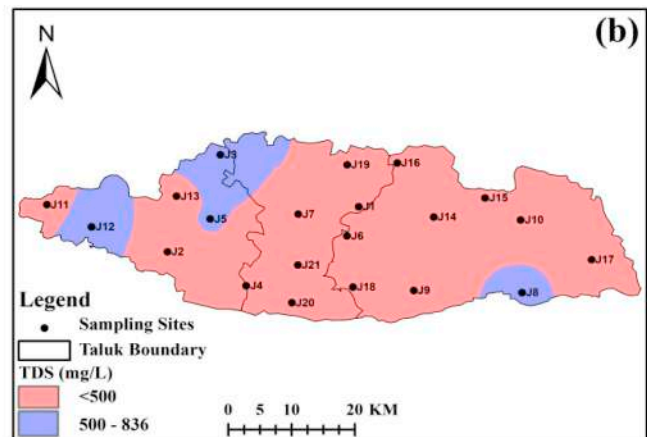
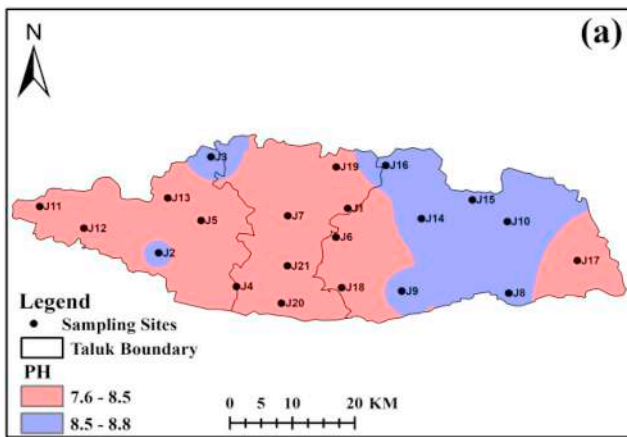
The results of the physicochemical analysis of the groundwater sampled from the study area are given in Table 3. The statistical description of groundwater samples such as maximum, minimum, mean, standard deviation, median are enlisted in Table 4. The concentrations of the analyzed parameters of groundwater were compared with the drinking water standards of Bureau of Indian Standards (BIS, 2012) and World Health Organization Standards (WHO, 2011), respectively. The

spatial distribution maps of some important analyzed parameters of groundwater are illustrated in Fig. 8 (a to h). Further Box and Whisker plot is used to study the order of dominance ions among cations ($\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$) and anions ($\text{HCO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^- > \text{PO}_4^{3-}$) (Fig. 9 (a and b)). The groundwater of the study area is slightly alkaline in nature with 38% (2 Shahkot, 6 Phillaur) samples are above the permissible limit (6.5–8.5) of BIS (2012) and WHO (2011). The Na^{2+} (varied from 13 to 150 mg/L) was dominant among cations, while HCO_3^- (ranged from 107 to 286 mg/L) dominated among the anions. The NO_3^- content in the groundwater varied from 2.4 to 55 mg/L with two samples of Phillaur

Table 4
Statistical summary of physicochemical parameters of groundwater of the study area.

Parameter	Mean \pm SD	Range	Median	BIS (2012) standards		% of sample above BIS (2012) standards		WHO (2011) standards	% of sample above WHO (2011) standards	Undesirable effect produced beyond MPL (summarized from published reports)
				DL	PL	DL	PL	DL	DL	
Physical parameters										
pH	8.3 \pm 0.37	7.6–8.8	8.3	6.5–8.5	38			6.5–8.5	38	Taste effects, mucus membrane
EC	746.9 \pm 193.5	429–1348	723	–	1500	Nil	Nil	1500	Nil	High concentration laxative effect on human
TDS	463 \pm 120.0	266–836	448	500	2000	19	Nil	1000	Nil	Gastrointestinal irritation
TH	190 \pm 52.3	103–348	196	200	600	43	Nil	500	Nil	Calcification at arteries, gastrointestinal irritation
Major cations										
Ca ²⁺	27.1 \pm 6.0	18–41	26	75	200	Nil	Nil	300	Nil	May cause kidney and bladder problems and urination disorder
Mg ²⁺	29.7 \pm 12.4	14–70	29	30	100	48	Nil	100	Nil	Laxative effect
Na ⁺	47.4 \pm 31.4	13–150	40	–	–	–	–	200	Nil	High Blood Pressure
K ⁺	12.4 \pm 5.5	4–24	13	–	–	–	–	12	48	Bitter taste, laxative effects on human digestive and nervous system
Major anions										
CO ₃ ²⁻	25 \pm 22.7	0–82	19	–	–	–	–	–	–	
HCO ₃ ⁻	186.6 \pm 47.9	107–286	180	–	500	–	Nil	500	Nil	Combined with Ca ²⁺ and Mg ²⁺ forms carbonate hardness
NO ₃ ⁻	14.4 \pm 13.9	2.4–55	7.8	45	NR	5	Nil	50	5	Methemoglobinemia in infants
F ⁻	0.6 \pm 0.3	0.03–1.2	0.5	1	1.5	14	Nil	1.5	Nil	Fluorosis, dental caries
Cl ⁻	49.4 \pm 26.1	15–123	47	250	1000	Nil	Nil	250	Nil	Injurious to people with heart and kidney ailment
PO ₄ ³⁻	0.04 \pm 0.03	0.01–0.18	0.04	–	–	–	–	–	–	
SO ₄ ²⁻	70.8 \pm 26.8	26–145	62	200	400	Nil	Nil	250	Nil	Gastrointestinal irritation along with Mg or Na, can have a cathartic effect on users

Note: Unit in mg/L, Except EC ($\mu\text{S}/\text{cm}$) and pH.



(caption on next page)

Fig. 8. Spatial distributions maps of some important water quality parameters. a) pH, b) TDS, c) TH, d) Calcium, e) Magnesium, f) Potassium, g) Nitrate and h) Fluoride.

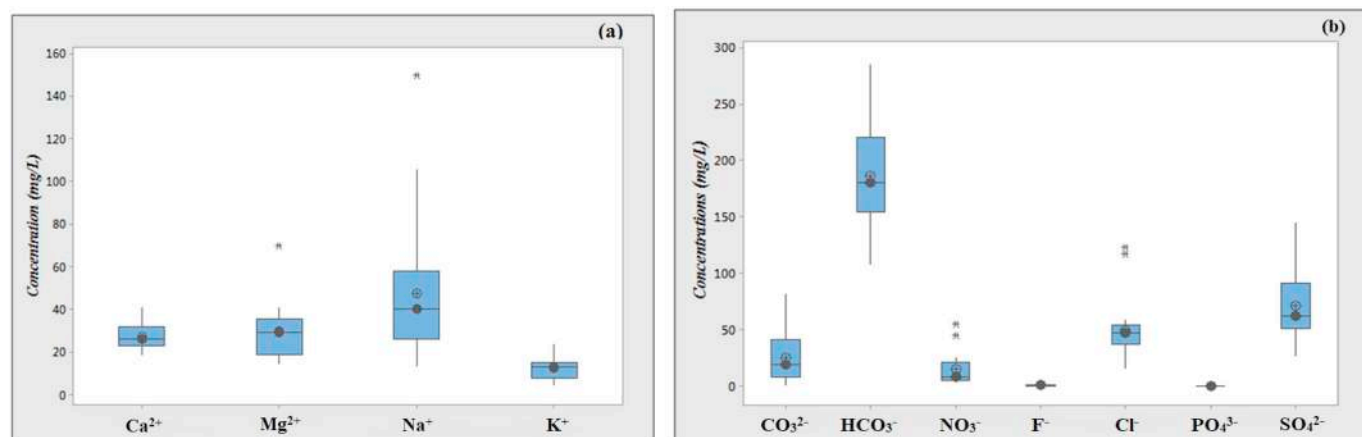


Fig. 9. (a and b) Box plots of the major cations and anions of groundwater of the study area.

taluk (J8 (55mg/L) and J6 (45.3 mg/L)) was found above the permissible limit of WHO (2011) and BIS (2012). Leaching of the agrochemical, mineralization of soil organic matter and seepage from septic tanks may be responsible for the elevated level of NO_3^- in the study area (Kumar et al., 2018). Around 14.28% (One sample in each studied taluks) samples are above the desirable limit of F^- (1.0 mg/L) of BIS (2012). Consumption of F^- rich water causes dental fluorosis followed by skeletal fluorosis (Keesari et al., 2016). As per the classification of CGWB and CPCB (1999) on the basis of electrical conductivity (Table 5), it is observed that 52.30% of groundwater samples are practically suitable for irrigation in all crops types. Around 47.61% of groundwater samples fall under moderate to the high saline category, which indicates that groundwater can be used for permeable soil with moderate leaching. Davis and DeWiest (1966) classification of groundwater for drinking and irrigation purposes based on TDS values indicates that 81% (4 Shahkot, 5 Nakodar and 8 Phillaur) of the samples fall in desirable (< 500 mg/L) and 19% (3 Shahkot and 1 Phillaur) of samples belong to permissible (500–1000 mg/L) for drinking purposes class (Table 6). According to Hounslow (1995), the mean value of TDS < 500 mg/L, depicts that silicate weathering is the major mechanism involved in groundwater chemistry in the study area. Higher concentration of TDS may cause gastrointestinal irritation in human (Herojeet et al., 2013). The classifications of groundwater based on the degree of hardness (Sawyer and McCarthy, 1967) shows that 66.7% (3

Shahkot, 4 Nakodar and 7 Phillaur) samples fall in hard, 28.6% (3 Shahkot, 1 Nakodar and 2 Phillaur) samples fall under moderately hard water type and remaining 4.7% (1 Shahkot) samples falls in very hard category (Table 6). Long-term consumption of very hard water is linked with some cancer and cardiovascular diseases (urolithiasis, anencephaly) (Sidhu et al., 2013).

The contamination of shallow aquifer by the agriculture and industrial activities has reported by various researchers (Kaur et al., 2019; Singh et al., 2019; Lapworth et al., 2017; Sharma et al., 2017; Keesari et al., 2016, 2014; Thakur et al., 2016; Rao et al., 2015; CGWB 2014; Srinivasamoorthy et al., 2014). The groundwater abstraction units of three taluks are divided into shallow (35–50 m bgl) to intermediate (50–75 m bgl) with an average depth of 54 m to understand the relationship between the distribution of ions and depth of the aquifers. The vertical distribution of major ions in the groundwater at different depths is shown in Fig. 10. It is clearly evident from the plots (Fig. 10) that wide variations in the ionic content were observed up to a depth of 35–60 m bgl. However, the maximum concentration of Ca^{2+} (J4), Mg^{2+} (J12), Na^+ (J3), HCO_3^- (J3), Cl^- (J3), SO_4^{2-} (J4) in Shahkot taluk and K^+ (J18) in Phillaur taluk are recorded at intermediate zone ranged between 60 and 75 m bgl (Fig. 10 and Table 3). This may be due to the long residence time of percolating water interacting with the aquifer materials, ion exchange and weathering of minerals. Whereas, the highest concentrations of NO_3^- (J8) and F^- (J1) are observed in

Table 5
Suitability of water based on conductivity for irrigation (Source: CGWB and CPCB, 1999).

Class	Conductivity ($\mu\text{S}/\text{cm}$)	Suitability or otherwise for irrigation	No. of samples	% of samples
1	Below 250	Entirely safe	Nil	Nil
2	250–750 (moderately saline)	Safe practically under all conditions	11	52.38
3	750–2250 (medium to high saline)	Safe with permeable soils and moderate leaching	10	47.61
4	2250–4000 (high salinity)	Used on soils with good permeability and with special leaching for salt tolerant crops	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
6	Above 6000 (excessive salinity)	This class represents water that is unfit for irrigation	Nil	Nil

Table 6
Classification of groundwater based upon TH (Sawyer and McCarthy, 1967) and TDS (Davis and DeWiest, 1966).

TH (as CaCO_3 mg/l)	Water classification	% of samples	TDS (mg/l)	Water classification	% of samples
< 75	Soft	Nil	< 500	Desirable for drinking	81
75–150	Moderately hard	28.5	500–1000	Permissible for drinking	19
150–300	Hard	66.6	1000–3000	Useful for irrigation	Nil
> 300	Very hard	4.76	> 3000	Unfit for drinking and irrigation	Nil

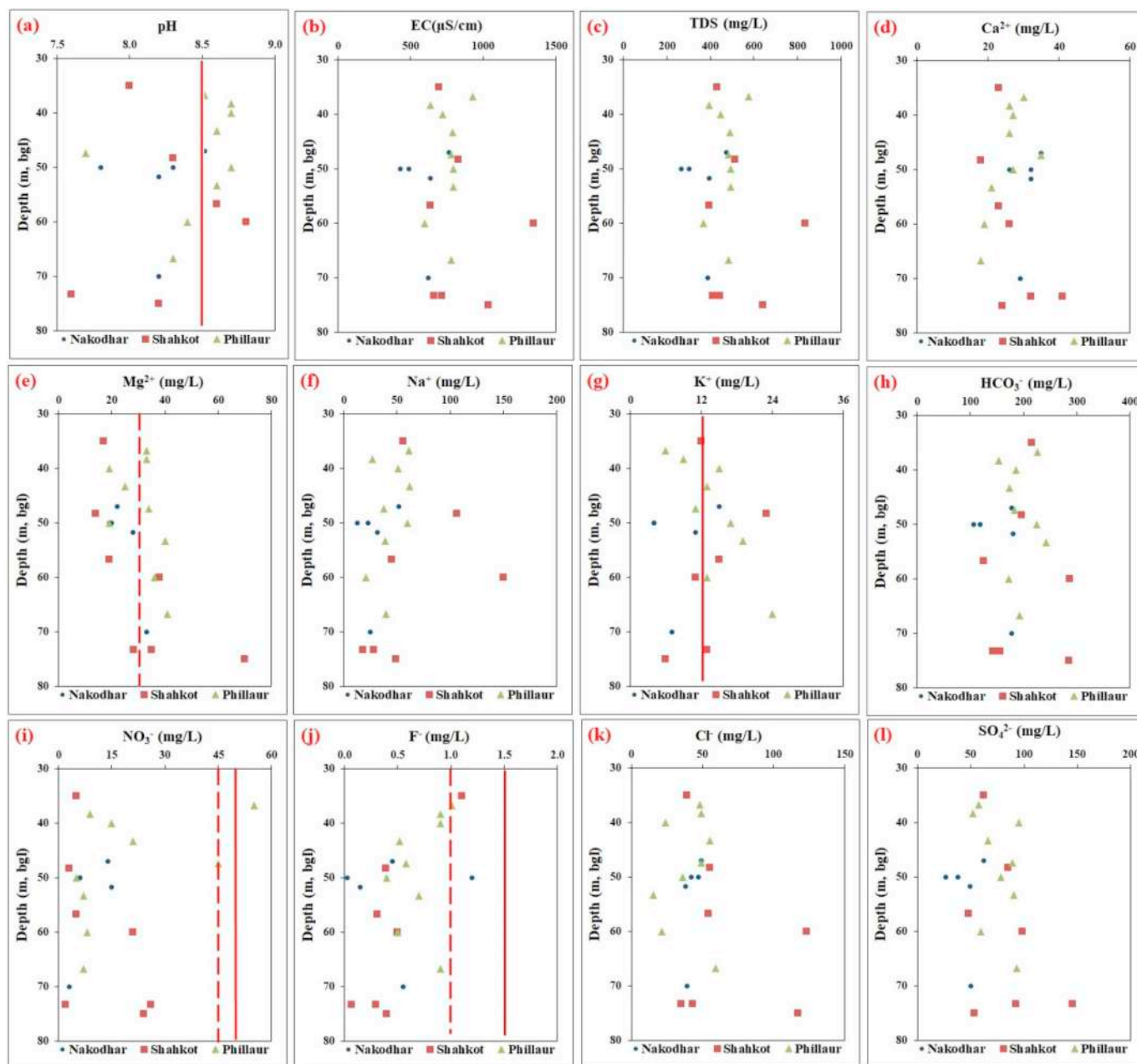


Fig. 10. The vertical distribution of major ions in the groundwater of the study area a) pH, b) EC, c)TDS, d) Ca^{2+} , e) Mg^{2+} , f) Na^+ , g) K^+ , h) HCO_3^- , i) NO_3^- , j) F^- , k) Cl^- , l) SO_4^{2-} . Solid red line represents the desirable limits prescribed by the WHO, 2011 and dashed red line represents the desirable limits prescribed by the BIS, 2012 for drinking water.

Phillaur and Nakodar taluk, respectively in the shallow aquifer at the depth of 37 m bgl and 50 m bgl (Fig. 10). Also, NO_3^- contents above 45 mg/L and F^- levels above 1.0 mg/L are found within the depth of 35–50 m bgl (Table 3). The presence of higher concentration of these ions in the shallow region may be attributed to the anthropogenic activities. Such similar finding was earlier suggested by Lapworth et al. (2017) in the Bist Doab region may be influenced by intensive agricultural activities to the shallow groundwater system. NO_3^- is the study area may be mainly derived from agricultural sources due to the application of significant quantity (247 kg/Ha) of synthetic fertilizers such as nitrogen, phosphate and potash during the farming seasons (Singh et al., 2019; Statistical Abstract of Punjab, 2016). The major variation in the concentration of Cl^- was also reported in shallow aquifer except for few samples in deeper zone (Fig. 10), as the area lacks proper sewerage and drainage system. In addition to this,

industrial and municipal effluents and leakage from the septic tanks may also contaminate the shallow aquifer. The maximum variation in the F^- content was also observed in the shallow zone (35–50 m bgl). Apart from natural sources, some anthropogenic sources such as application of fluoride based fertilizers, industrial activities like brick kiln and seepage of untreated sewage water may be responsible for the elevated concentrations of F^- in the study area (Khalid, 2019). Groundwater mining and vertical seepage of pollutants may further contaminate the deeper aquifer of the region.

5.2. Water quality index (WQI) evaluation

The computed WQI values of groundwater in the study area ranged from 15.0 to 77.0 with mean value 43.1 (Table 7). Spatial distribution map of WQI classification is depicted in Fig. 11. As per the classification

Table 7
Calculation of WQI for individual groundwater samples.

S. no.	Depth (m)	Taluk	WQI value	WQI class
J1	50	Nakodar	77	Very poor
J2	57	Shahkot	33	Good
J3	60	Shahkot	46	Good
J4	73	Shahkot	16	Excellent
J5	48	Shahkot	34	Good
J6	47	Phillaur	46	Good
J7	70	Nakodar	42	Good
J8	37	Phillaur	72	Poor
J9	43	Phillaur	45	Good
J10	38	Phillaur	58	Poor
J11	73	Shahkot	33	Good
J12	75	Shahkot	34	Good
J13	35	Shahkot	69	Poor
J14	40	Phillaur	66	Poor
J15	53	Phillaur	44	Good
J16	50	Phillaur	29	Good
J17	60	Phillaur	37	Good
J18	67	Phillaur	50	Good
J19	47	Nakodar	40	Good
J20	50	Nakodar	15	Excellent
J21	52	Nakodar	20	Excellent
Min			15	
Max			77	
Mean			43	

of WQI (Tiwari and Mishra, 1985), 14% and 62% of groundwater samples fall under the excellent and good category for drinking purposes, respectively, whereas 19% and 5% groundwater samples belong to poor and very poor water category for drinking purposes, respectively (Table 8). In Shahkot taluk, majority of the sample (5 samples) falls in good class followed by excellent (1 sample) and poor (1 sample) class (Fig. 11 and Table 7). The groundwater of Nakodar taluk shows one sample fall in very poor class, while the remaining four samples fall under excellent and good class. In Phillaur taluk, 6 groundwater samples fall in good class and 3 samples belong to the poor class. The overall results of the WQI showed that a major part of the study area possesses good water quality. But, certain pockets of these three taluks fall in poor to very poor water classes may be attributed to the extensive agricultural and industrial activities. Therefore, proper regular monitoring and assessment of groundwater quality is prerequisite to understand further contamination.

Table 8
Water quality index classification.

S. no.	WQI value	WQI class	No. of samples				Overall	
			Nakodar	Shahkot	Phillaur	Total	% of samples	
1	0–25	Excellent	2	1	Nil	3	14	
2	26–50	Good	2	5	6	13	62	
3	51–75	Poor	Nil	1	3	4	19	
4	76–100	Very poor	1	Nil	Nil	1	5	
5	> 100	Unfit for drinking	Nil	Nil	Nil	Nil	Nil	

5.3. Hydrogeochemical classification and groundwater type

The hydrochemical facies are the functions of the lithology, solute kinetics and flow pattern of the aquifers (Singh et al., 2005). Piper (1944) was constructed to evaluate the hydrochemical facies of the groundwater. The results of Piper plot (Fig. 12) indicated that alkaline earth elements (Ca^{2+} and Mg^{2+}) and weak acids (CO_3^{2-} and HCO_3^-) exceeded over the alkalis elements (Na^+ and K^+) and strong acids (SO_4^{2-} and Cl^-) resulting in Mg^{2+} (61.90%) and HCO_3^- (66.66%) as the principal cation and anion in the groundwater of the study area. The elevated concentration HCO_3^- is may be due to the weathering of silicate minerals by carbonic acid in the groundwater (Kumar et al., 2006). Fig. 12 and Table 9 indicates that 42.85% (3 Shahkot, 2 Nakodar and 4 Phillaur) samples fall in the fields of $Ca^{2+}-Mg^{2+}-HCO_3^-$ suggesting temporary hardness and 38.09% (1 Shahkot, 3 Nakodar and 4 Phillaur) samples belong to $Ca^{2+}-Mg^{2+}-Cl^-SO_4^{2-}$ facies indicating permanent hardness (Herojeet et al., 2016). Only one sample (J5) of Shahkot taluk located along with the East Bein drainage fall in $Na^+-K^+-Cl^-SO_4^{2-}$ facies. This may be related to the elevated concentration of Na^+ and Cl^- ions in groundwater due to seepage from sewage water and nearby septic tanks and irrigation return flow (Williams et al., 2000). About 14.28% (2 Shahkot and 1 Phillaur) samples fall in the $Na^+-K^+-HCO_3^-$ facies. Majority of groundwater samples fall in the field of $Mg^{2+}-HCO_3^-$ water (carbonate hardness) types having secondary alkalinity exceeding 50%, indicated that cation exchange process involved in the study area (Herojeet et al., 2016; Davis and DeWiest, 1966). The groundwater of Nakodar and Shahkot taluk shows $Na^+-Mg^{2+}-HCO_3^-$ facies, while groundwater of Phillaur taluk shows $Mg^{2+}-HCO_3^-$ facies. The water types of shallow aquifer in the study area is complex in nature showing $Na^+-Mg^{2+}-HCO_3^-$ type, further it changed to

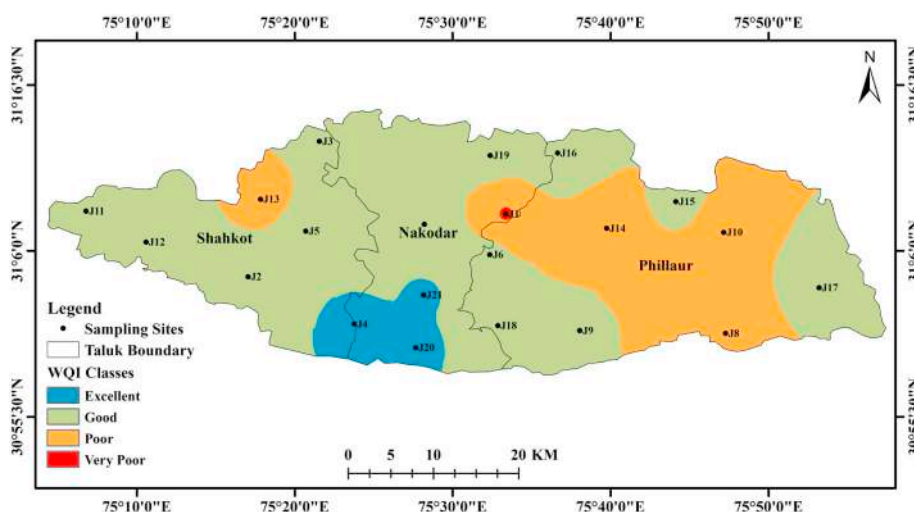


Fig. 11. Spatial Distribution map of the DWQI.

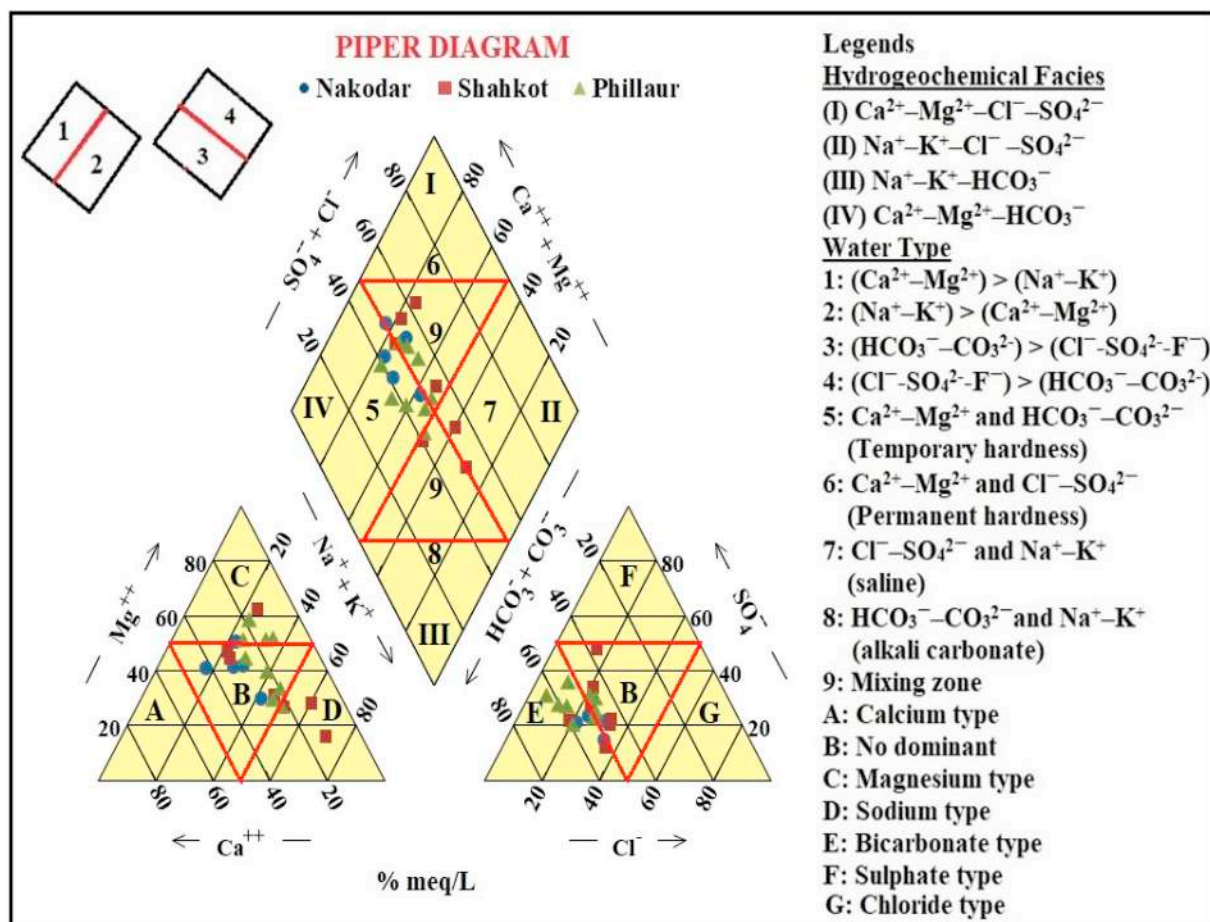


Fig. 12. Piper diagram representing hydrogeochemical facies of groundwater of the study area.

$\text{Na}^{+}\text{-HCO}_3^{-}$ in the intermediate zone due to the ion exchange process. Durov diagram is an important graphical form which provides better information on the hydrochemical characterization and possible geochemical processes (mixing, cation exchange, reverse ion exchange dissolution) influencing the groundwater quality of the area. Fig. 13 shows that there are three geochemical processes that may have

affected the water genesis in the study area. According to the classification of Lloyd and Heathcote (1985); 47.62% (4 Shahkot, 2 Nakodar and 4 Phillaur) of the groundwater samples belongs to mixed zone with no dominance of major anions or cations indicating dissolution or mixing influence (Fig. 13). Such similar finding was concluded by Thakur et al. (2018), suggested that the geochemical processes in

Table 9

Hydrochemical facies of the groundwater of the study area derived from piper diagram.

Class	Groundwater types corresponding subdivisions of facies	No. of samples	Percentage
I	$\text{Ca}^{2+}\text{-Mg}^{2+}\text{-Cl}^{-}\text{-SO}_4^{2-}$	8	38.09
II	$\text{Na}^{+}\text{-K}^{+}\text{-Cl}^{-}\text{-SO}_4^{2-}$	1	4.76
III	$\text{Na}^{+}\text{-K}^{+}\text{-HCO}_3^{-}$	3	14.28
IV	$\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^{-}$	9	42.84
1	Alkaline earths ($\text{Ca}^{2+}\text{-Mg}^{2+}$) exceed alkalis ($\text{Na}^{+}\text{-K}^{+}$)	17	80.95
2	Alkalis exceed alkaline earths	4	19.04
3	Weak acids ($\text{HCO}_3^{-}\text{-CO}_3^{2-}$) exceed strong acids ($\text{Cl}^{-}\text{-SO}_4^{2-}\text{-F}^{-}$)	11	52.38
4	Strong acids exceed weak acids	10	47.62
5	$\text{Ca}^{2+}\text{-Mg}^{2+}$ and $\text{HCO}_3^{-}\text{-CO}_3^{2-}$ (temporary hardness); magnesium bicarbonate type (carbonate hardness (secondary alkalinity) exceeds 50%)	8	38.09
6	$\text{Ca}^{2+}\text{-Mg}^{2+}$ and $\text{Cl}^{-}\text{-SO}_4^{2-}$ (permanent hardness); calcium chloride type (non-carbonate hardness (secondary salinity) exceeds 50%)	Nil	Nil
7	$\text{Cl}^{-}\text{-SO}_4^{2-}$ and $\text{Na}^{+}\text{-K}^{+}$ (saline); sodium chloride type (non-carbonate alkali (primary salinity) exceeds 50%)	1	4.76
8	$\text{HCO}_3^{-}\text{-CO}_3^{2-}$ and $\text{Na}^{+}\text{-K}^{+}$ (alkali carbonate); sodium bicarbonate type (carbonate alkali (primary alkalinity) exceeds 50%)	Nil	Nil
9	None of the cation and anion pairs exceed 50%	12	57.14
A	Calcium type	Nil	Nil
B	No dominant (cations)	11	52.38
C	Magnesium type	6	28.57
D	Sodium type	4	19.04
E	Bicarbonate type	14	66.67
B	No dominant (anions)	7	33.34
F	Sulphate type	Nil	Nil
G	Chloride type	Nil	Nil

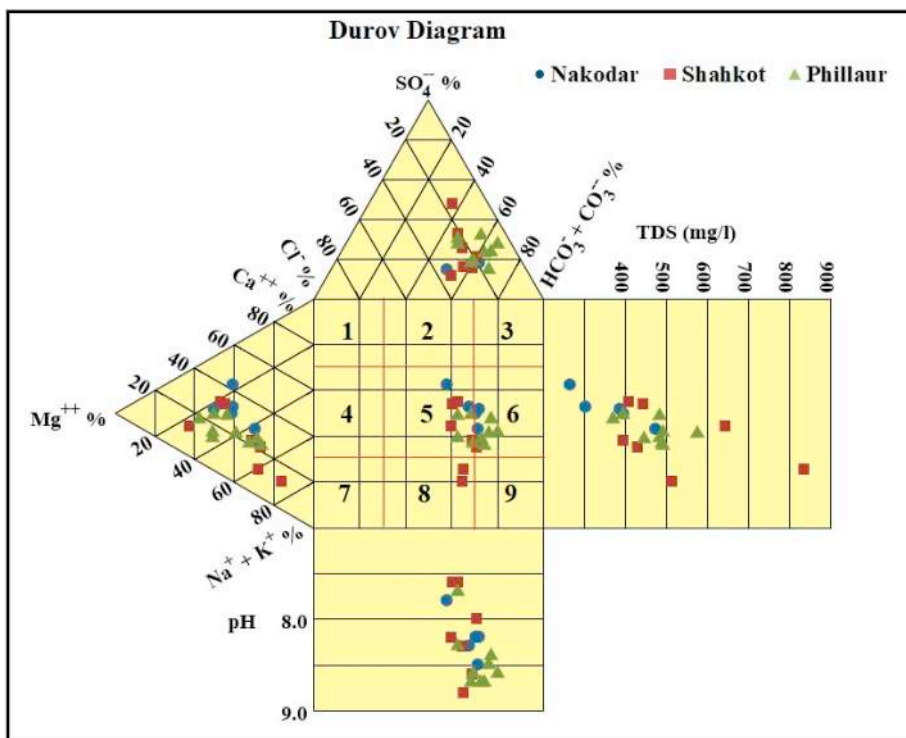


Fig. 13. Durov diagram showing the hydro-chemical facies involved in the study area. 1. Cl⁻ and Ca²⁺ dominant. 2. SO₄²⁻ dominant or anions indiscriminate and Ca²⁺ dominant. 3. HCO₃⁻ and Ca²⁺ dominant. 4. Cl⁻ dominant and no dominant cation. 5. No dominant anions or cations. 6. HCO₃⁻ and Mg²⁺ dominant. 7. Cl⁻ and Na⁺ dominant. 8. SO₄²⁻ dominant or anions indiscriminate and Na⁺ dominant. 9. HCO₃⁻ and Na⁺ dominant.

groundwater are controlled by recent fresh recharge water exhibiting simple dissolution or mixing. Remaining 42.8% (1 Shahkot, 3 Nakodar and 5 Phillaur) samples belong to Mg²⁺ and HCO₃⁻ dominant type of water, indicating the partial ion exchange processes. Two groundwater samples (J2 and J5) of Shahkot taluk fall under Na⁺ and SO₄²⁻ dominant water field that is not frequently encountered reflecting probable mixing or uncommon dissolution (Ramadain et al., 2018). Majority of the groundwater samples of Phillaur taluk fall in 6th field of the plot indicating HCO₃⁻ and Mg²⁺ dominant type of water. The Schoeller diagram represents the relative abundance of the major

cations and anions. Fig. 14 divulges that HCO₃⁻ is the dominant anion followed by SO₄²⁻ and Cl⁻ and among cations, Na⁺ is dominant cation followed by Mg²⁺ and Ca²⁺ ions in the groundwater samples of the study area. Giggenbach (1988) (Fig. 15) revealed that all the groundwater samples of the three studied taluks fall at the base of the triangle indicating the occurrence of immature water in the study area (Msika et al., 2014). The findings of various hydrochemical approaches conclude that majority of the groundwater sample have Ca²⁺-Mg²⁺-HCO₃⁻ water type influenced by dissolution and freshwater recharge mixing through interaction with aquifer matrix.

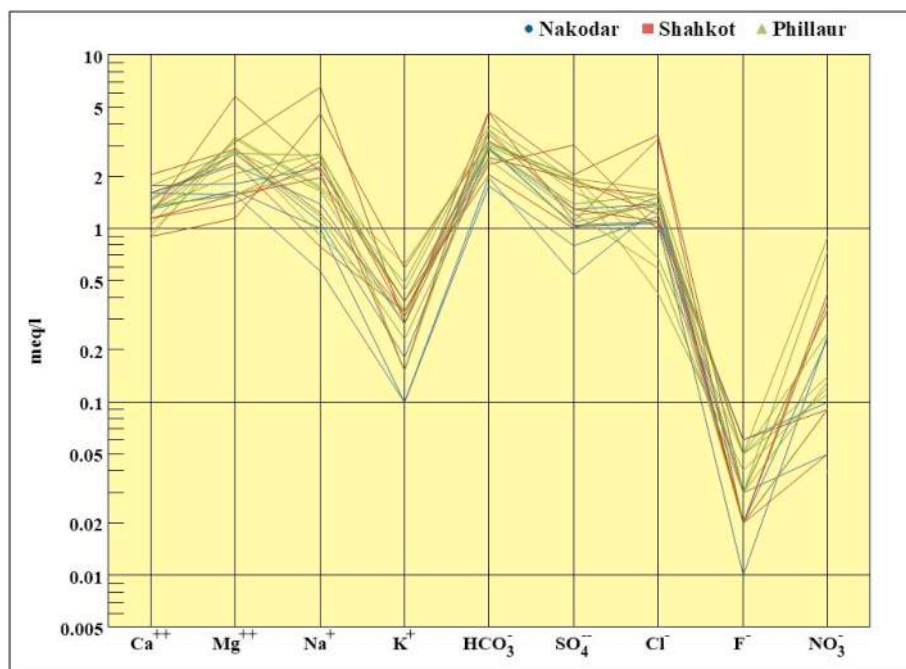


Fig. 14. Schoeller diagram of groundwater samples of the study area.

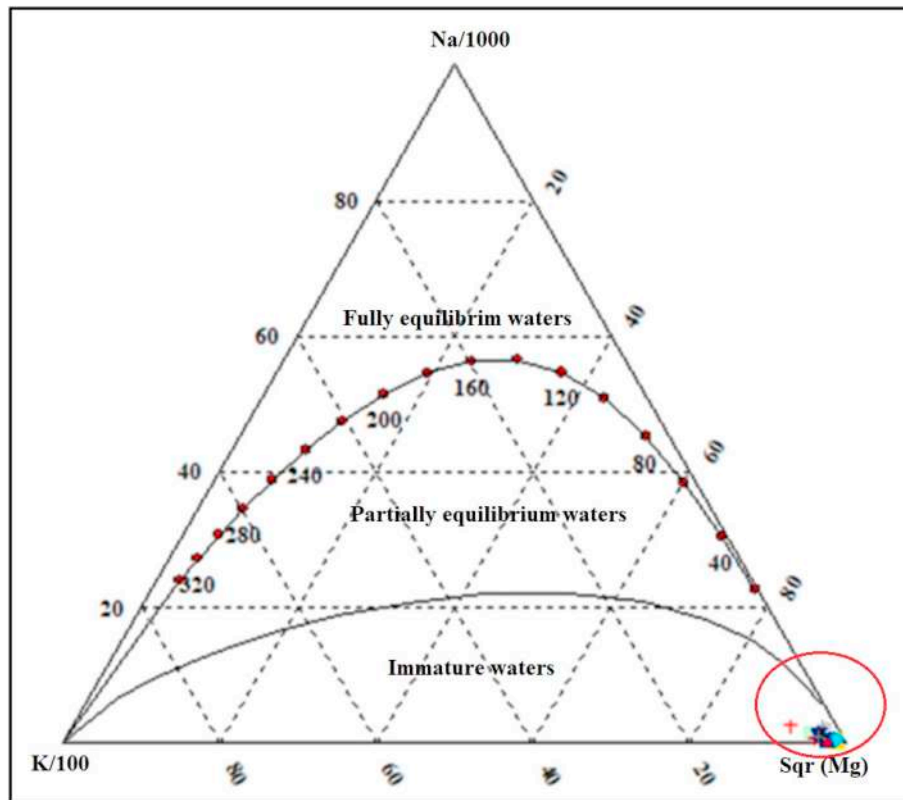


Fig. 15. Giggenbach triangle representing the rock-water equilibrium.

5.4. Groundwater classification

Based on Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-} concentrations (Soltan, 1998, 1999; Herojeet et al., 2013) samples were classified as normal chloride (< 15 meq/L), normal sulphate (< 6 meq/L) and normal carbonate and bicarbonate (2–7 meq/L) water types. All the groundwater samples of the three studied taluks are categorized as normal chloride, normal sulphate and normal carbonate and bicarbonate type (Table S1). Base-exchange indices (r1) and Meteoric genesis indices (r2) proposed by Soltan (1998, 1999) were also employed to study the groundwater type using Eqs. (12) and (13).

$$Base - exchange\ indices\ (r1) = (Na^+ - Cl^-)/SO_4^{2-} \tag{12}$$

$$Meteoric\ genesis\ indices\ (r2) = [(Na^+ + K^+ - Cl^-)]/SO_4^{2-} \tag{13}$$

where all the ionic concentrations are expressed in meq/L. If $r1 > 1$ and $r2 > 1$, the groundwater sources are of $Na^+ - HCO_3^-$ type and shallow meteoric type, $r1 < 1$ and $r2 < 1$, indicates the sources are of $Na^+ - SO_4^{2-}$ type and deep meteoric type. Based on the base-exchange indices (Fig. 16) 19% of groundwater samples of the study area are classified as $Na^+ - HCO_3^-$ type and rest of the samples (81%) is of $Na^+ - SO_4^{2-}$ type. Meteoric genesis indices indicate that 29% of groundwater samples belong to shallow meteoric water percolation type and 71%

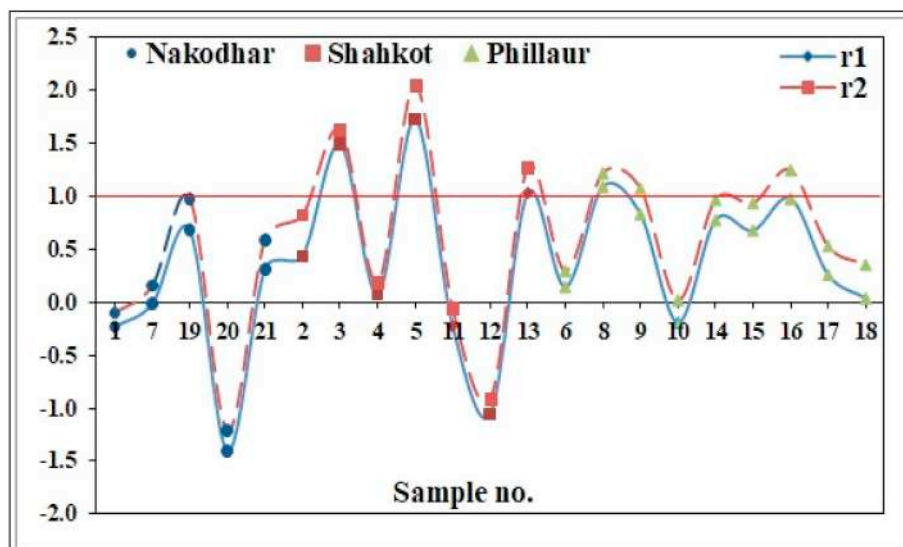


Fig. 16. Base-exchange indices (r1) and Meteoric genesis indices (r2) of the groundwater of the study area.

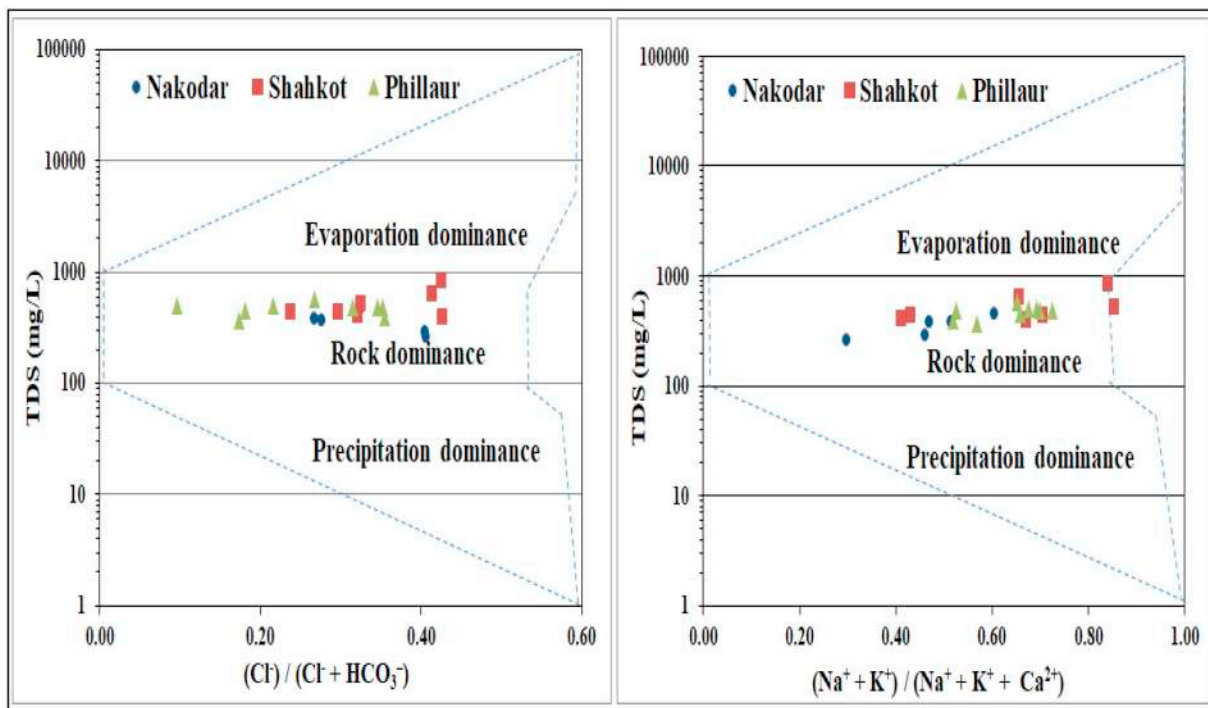


Fig. 17. Gibbs diagram representing controlling factors of groundwater quality.

samples fall in deep meteoric water percolation type (Fig. 16). All the samples of Nakodar taluk showed $r_1 < 1$ and $r_2 < 1$ indicating the groundwater are of $\text{Na}^+ \text{-SO}_4^{2-}$ and deep meteoric type.

5.5. Mechanisms controlling the hydrochemistry of the study area

Gibb's diagram is used to identify the mechanisms controlling groundwater chemistry, namely precipitation, rock-water and evaporation. The hydrochemical data of groundwater samples were plotted in Gibbs diagram which employs ratio of $((\text{Na}^+ + \text{K}^+) / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}))$ vs TDS and $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ vs TDS. A perusal of Fig. 17 revealed that water samples of all the three taluks are fall in rock dominance zone. Therefore, the geochemical process such as precipitation-dissolution; oxidation-reduction and ion exchange are the main governing factors of groundwater chemistry in the study area. This result is consistent with the previous study by Rao et al. (2015). Thus, Giggenbach triangle results coherent with the Gibbs diagram as well.

5.5.1. Ion exchange process and dissolution of silicate and carbonate minerals

The ion exchange and chemical weathering profile of the groundwater of the study area was studied through various scatter plots. Chloro-Alkaline Indices proposed by Scholler (1965, 1967) were employed to assess the possibility of ion exchange and reverse ion exchange among groundwater and aquifer materials during their residence or circulation time were evaluated using Eqs. (14) and (15).

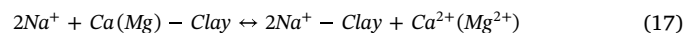
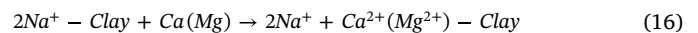
$$\text{CAI} - \text{I} = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) / \text{Cl}^- \quad (14)$$

$$\text{CAI} - \text{II} = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) / (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-) \quad (15)$$

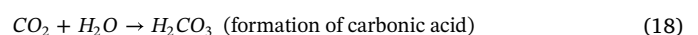
All the ionic concentrations are expressed in meq/L.

If Ca^{2+} and Mg^{2+} ions in groundwater are exchanged with Na^+ and K^+ ions present in the aquifer material (as expressed in Eq. (16)), the value of both chloro-alkaline indices is negative, indicate chloro-alkaline disequilibrium. However, in the reverse ion exchange reaction (as shown in Eq. (17)), the value of both CAI-I and CAI-II are positive (Scholler, 1967). Accordingly, 81% samples show negative values in

each CAI-I and CAI-II indicating the prevalence of cation exchange reaction in the aquifer system (Fig. 18 and Table S1). During this process, the host rock or aquifer materials are the principal sources of dissolved solids in water (Herojeet et al., 2015). Two samples in each Nakodar (J1, J20) and Shahkot (J11, J12) taluks show the positive value of both CAI-I and CAI-II, indicating chloro-alkaline disequilibrium.



The bivariate plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs $\text{HCO}_3^- + \text{SO}_4^{2-}$ is used to identify the parent rock responsible for ion exchange process in the groundwater system (Maurya et al., 2019; Srinivasamoorthy et al., 2008). The abundance of $\text{Ca}^{2+} + \text{Mg}^{2+}$ over $\text{HCO}_3^- + \text{SO}_4^{2-}$ indicate carbonate weathering, whereas, the dominance of $\text{HCO}_3^- + \text{SO}_4^{2-}$ reflect silicate weathering as the primary process of ion exchange (Elango and Kannan, 2007; Barzegar et al., 2016). Fig. 19(a) shows that majority of samples were below and along the equiline, depicting silicate weathering is the major geochemical process responsible for the increased HCO_3^- and SO_4^{2-} concentration in groundwater (Datta and Tyagi, 1996; Varol and Davraz, 2014). On the other hand, ~24% samples (3 samples of Nakodar and one sample of each Shahkot and Phillaur taluk) were above the equiline indicating carbonate weathering is responsible for reverse ion exchange (Okiongbo and Douglas, 2015; Rao et al., 2015). Consequently, the study area is a part of the alluvial aquifer, which is rich in feldspars and kankars (calcium-rich encrustations) react with carbonic acid that may contribute to these ions namely, Ca^{2+} , Na^+ and HCO_3^- and H_4SiO_4 in groundwater (Guo and Wang, 2005). Silicate weathering is the result from the reaction of feldspar minerals with carbonic acid in the groundwater, identified by higher HCO_3^- values in the groundwater samples of the study area (Lakshmanan et al., 2003; Rao et al., 2013). The dissolution of carbonate and silicate minerals in the groundwater saturated carbonic acid with CO_2 is an intensive process. Such type of water readily dissolve the minerals available in its percolating path.



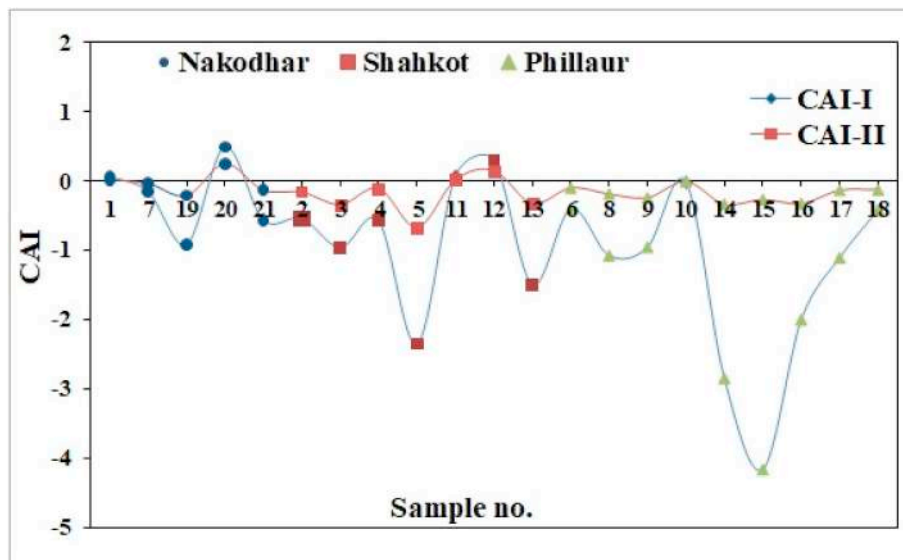
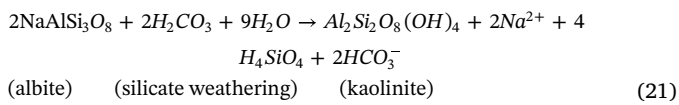
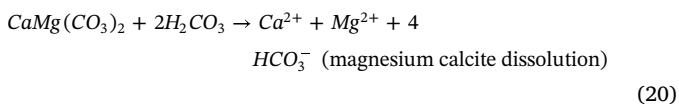
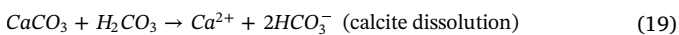


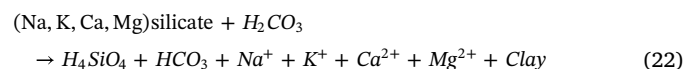
Fig. 18. Chloro-Alkaline Indices of the groundwater of the study area.



Further, Ca/Mg ratio is also derived to evaluate the influence of carbonate and silicate weathering on the groundwater chemistry. The Ca/Mg ratio equal to one indicates the dissolution of dolomite, while the ratio more than one depicts the sources of these ions from the dissolution of calcite rocks (Mayo and Loucks, 1995). Ca/Mg > 2 represents the dissolution of silicate minerals in the groundwater (Katz et al., 1997). Table 3 and Fig. 19(b) depicted that dissolution of dolomite is largely responsible for the contribution of Ca^{2+} and Mg^{2+} in the groundwater of the study area (Eq. (20)). Few samples (J19 and J20) from Nakodar taluk showed ratio equal to unity indicates the dissolution of carbonate from the kankar layer is contributing to the Ca and Mg in the groundwater. The scatter plot of Na^+ vs Ca^{2+} (Fig. 19(c)) indicated the dominance of Na^+ over Ca^{2+} ions in the groundwater. Such conditions may prevail due to the weathering of silicate containing rocks in combination with ion exchange, increases the Na^+ level in the groundwater (Lakshmanan et al., 2003). Majority of the groundwater samples of Nakodar taluk shows the dominance of Ca^{2+} over Na^+ indicating carbonate weathering, whereas majority samples of both Shakhkot and Phillaur taluk show the dominance of Na^+ over Ca^{2+} ions suggesting the silicate weathering.

The scatter plot of $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$ vs $[(\text{Na}^+ + \text{K}^+) - \text{Cl}^-]$ was used to evaluate the cation exchange activity involved in the aquifer. The concentration of Ca^{2+} and Mg^{2+} that may have been involved in cation exchange processes were corrected by subtracting equivalent concentrations of anions (SO_4^{2-} and HCO_3^-) that could have originated from other processes (eg. silicate or carbonate weathering and dissolution of gypsum). Similarly, the alkalis (Na^+ and K^+) that may be derived from the aquifer can be accounted for by assuming that contributions of meteoric origin would be balanced by equivalent concentrations of Cl^- (Jalali and Jalali, 2016; Kortatsi et al., 2008). The slope of this bivariate plot should be -1 if cation exchange activity taking place in the aquifer (McLean et al., 2000). It is clear from the Fig. 19(d) that cation exchange geochemical

process is controlling the hydrochemistry with slope $y = -1.1955 \times$ ($R^2 = 0.8422$) in the study area (Wanda et al., 2011; Jalali and Jalali, 2016). The Na^+/Cl^- molar ratio was used to identify the source of salinity in groundwater (Fig. 19(e)). If Na^+/Cl^- ratio is equal to 1 then the source of Na^+ is due to halite dissolution, if Na^+/Cl^- ratio is > 1, the source of Na^+ is silicate weathering (Meybeck, 1987). In the present study, the molar ratio of Na^+/Cl^- for groundwater samples varied from 0.43 to 4.01 with most of the samples (71%) have Na^+/Cl^- ratio is equal to or above 1, indicating the prevalence of cation exchange reaction and dissolution of silicate containing minerals (Table 3). 28.5% of groundwater samples have shown the Na^+/Cl^- molar ratio below 1, indicating halite dissolution. Majority of the samples of Phillaur and Shakhkot taluks shows silicate weathering, whereas in Nakodar taluk majority of the samples shows halite dissolution. Furthermore, the scatter plot of Na^+/Cl^- vs EC (Fig. 19(e)) revealed that Na^+/Cl^- showed a decreasing trend with increases in EC in Shakhkot and Phillaur taluks, which further supported that Na^+ is derived from the silicate weathering process and rock-water interaction (Purushothaman et al., 2014). In Nakodar taluk, the plot of Na^+/Cl^- vs EC (Fig. 19(e)) depicted the trend of Na^+/Cl^- increases with increasing EC as the role of evaporation is significant in the aquifer system over ion exchange process or halite dissolution (Hamzah et al., 2017). Further, the plot of $\text{HCO}_3^-/\text{Na}^+$ vs $\text{Ca}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{Na}^+$ vs $\text{Ca}^{2+}/\text{Na}^+$ distinguishes mineral weathering and dissolution in groundwater (Brindha et al., 2017). Fig. 19(f) and (g) depicted that the silicate weathering is largely influencing the hydrochemistry. The general reaction for the dissolution of silicate weathering with carbonic acid (Das and Kaur, 2001) is shown in Eq. (22).



The ratio of $\text{SO}_4^{2-}/\text{Cl}^-$ ions was used as a marker to identify the potential pyrite dissolution in groundwater. $\text{SO}_4^{2-}/\text{Cl}^-$ ratio > 0.5, indicates pyrite oxidation (Okiongbo and Douglas, 2015). Table 3 shows that 91.5% of samples have $\text{SO}_4^{2-}/\text{Cl}^-$ ratios ≥ 0.5 indicating pyrite dissolution in the study area.

5.6. Contribution of anthropogenic factors to the groundwater chemistry

Anthropogenic influences on the shallow aquifers are generally characterized by high levels of NO_3^- , NH_4^+ , Cl^- and Na^+ ions. In this section, the impacts of anthropogenic inputs such as agricultural,

urbanization and industrialization in groundwater of the three taluks have been discussed. The Na^+ vs. Cl^- plot (Fig. 19(h)) revealed that the majority of the samples (76%) lie above the equiline (1:1). It suggested that besides silicate weathering Na^+ may be attributed to some anthropogenic sources such as sewage, domestic and animal waste and septic tanks (Stallard and Edmond, 1983; Kumar et al., 2006; Nematollahi et al., 2018; Williams et al., 2000). On the other hand, few groundwater samples i.e., two samples each of Nakodar and Shakhot taluk and one sample of Phillaur taluk have shown the dominance of Cl^- over the Na^+ indicating aquifer contamination by anthropogenic activities. The higher content of Cl^- in the groundwater may be attributed to the discharges of the untreated municipal and industrial effluents and leakage from the septic tanks. The scatter plots of $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. TZ^+ (Total cations) (Fig. 19(i)) shows that all the water samples of three taluks are below the theoretical line (1:1), resulting the weathering of non-carbonate minerals somehow

contributing Ca^{2+} and Mg^{2+} ions and the increasing concentration of alkalis in the water samples may be attributed to anthropogenic input mainly from application of fertilizer in agriculture land (Rao and Devadas 2003). Similarly, the relationship between $\text{Na}^+ + \text{K}^+$ vs. TZ^+ shows that the samples are plotted well below the 1:1 equiline (Fig. 19(j)). This suggests that silicate weathering and anthropogenic inputs in soil salts which contributes mainly Na^+ and K^+ ions to the water system (Stallard and Edmond, 1983; Sarin et al., 1989; Datta and Tyagi, 1996). Furthermore, the concentration of NO_3^- was also found higher in the shallow aquifer of the study area (Fig. 10). Anthropogenic inputs like fertilizers, domestic wastewater, poultry farming and septic tank system contain significant amount of organic nitrogen and ammonia. Ammonia is easily adsorbed over the clay particles and becomes immobilized (Raju and Singh, 2017). Due to anoxic condition on the clay particles, it expedites the denitrification of ammonia by bacterial activities as expressed in Eqs. (23) and (24), which results in the

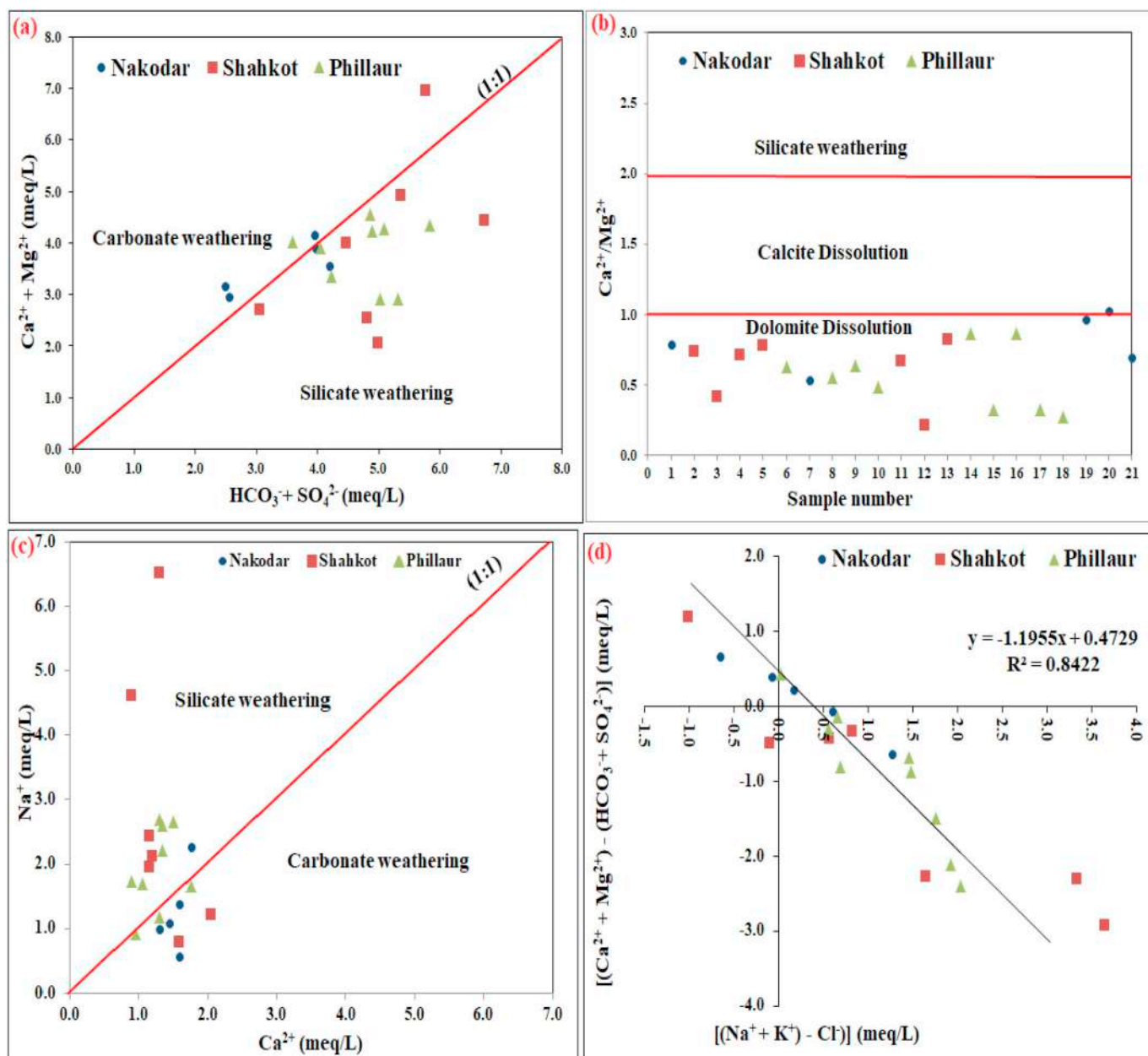


Fig. 19. Identification of mineral weathering in groundwater through major inter ionic relationship: (a) $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. $\text{HCO}_3^- + \text{SO}_4^{2-}$, (b) $\text{Ca}^{2+}/\text{Mg}^{2+}$ vs. Samples (c) Na^+ vs. Ca^{2+} (d) $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$ vs. $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ (e) Na^+/Cl^- vs. EC (f) $\text{HCO}_3^-/\text{Na}^+$ vs. $\text{Ca}^{2+}/\text{Na}^+$ (g) $\text{Mg}^{2+}/\text{Na}^+$ vs. $\text{Ca}^{2+}/\text{Na}^+$ (h) Na^+ vs. Cl^- (i) $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. TZ^+ (j) $\text{Na}^+ + \text{K}^+$ vs. TZ^+ for groundwater in the study area.

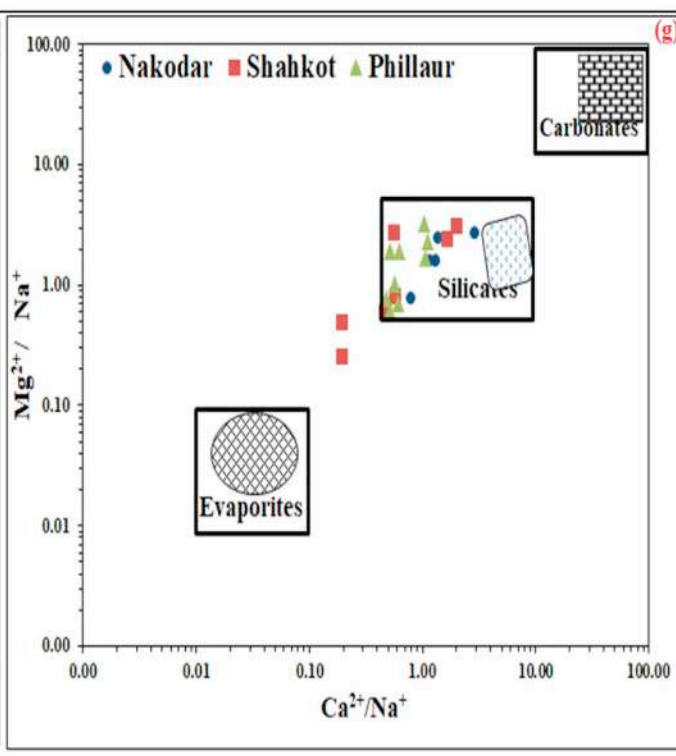
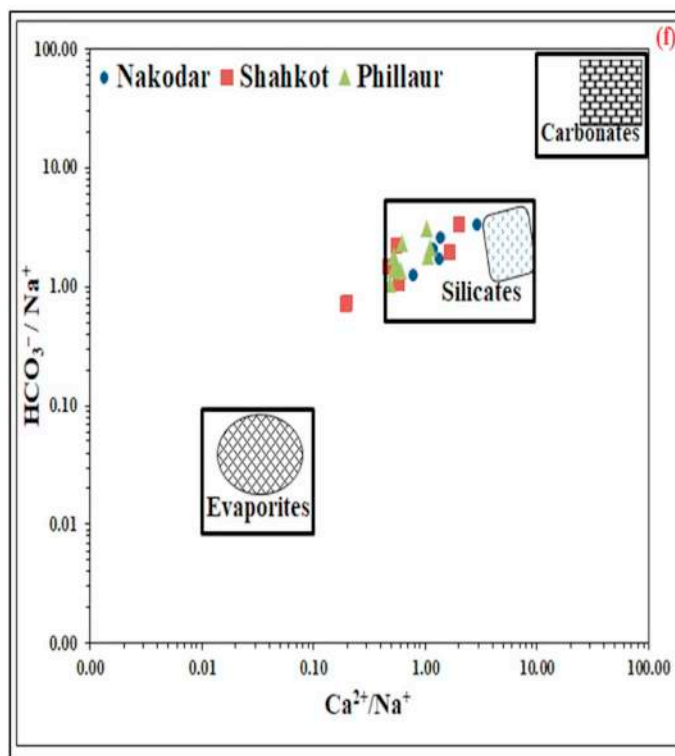
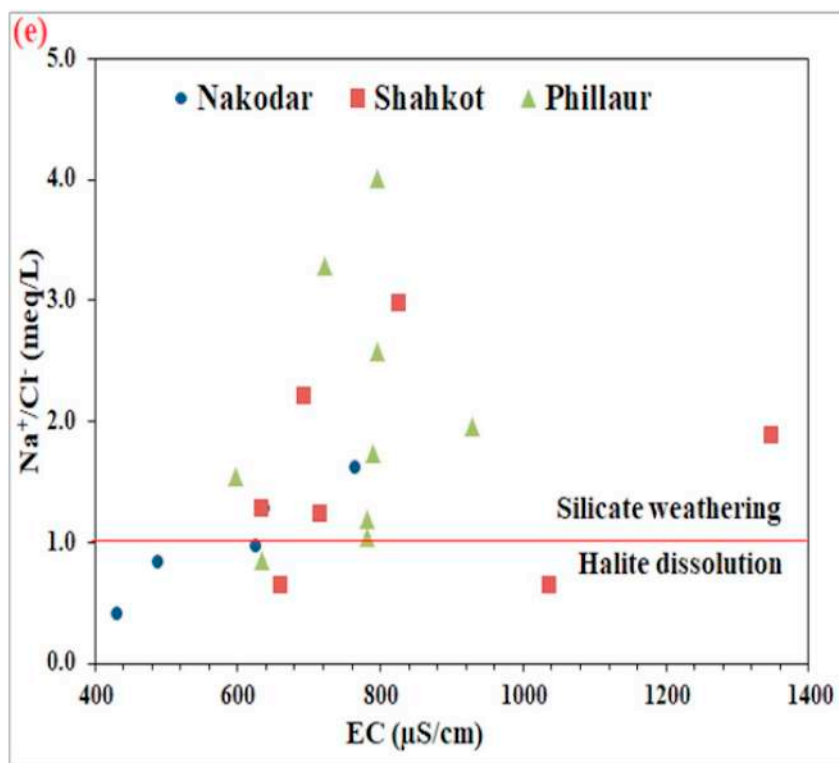
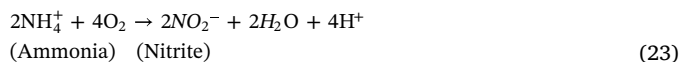


Fig. 19. (continued)

leaching of NO_3^- to the shallow aquifer. It is cleared from the results that anthropogenic activities are strongly affecting the hydro-geochemistry of the shallow aquifers.



5.6.1. Correlation among different anions

Correlation among different anions was also studied for the present research. F^- showed an increasing trend with an increase in pH and HCO_3^- as evident from the (Fig. 20 (a) and (b)). This may be attributed

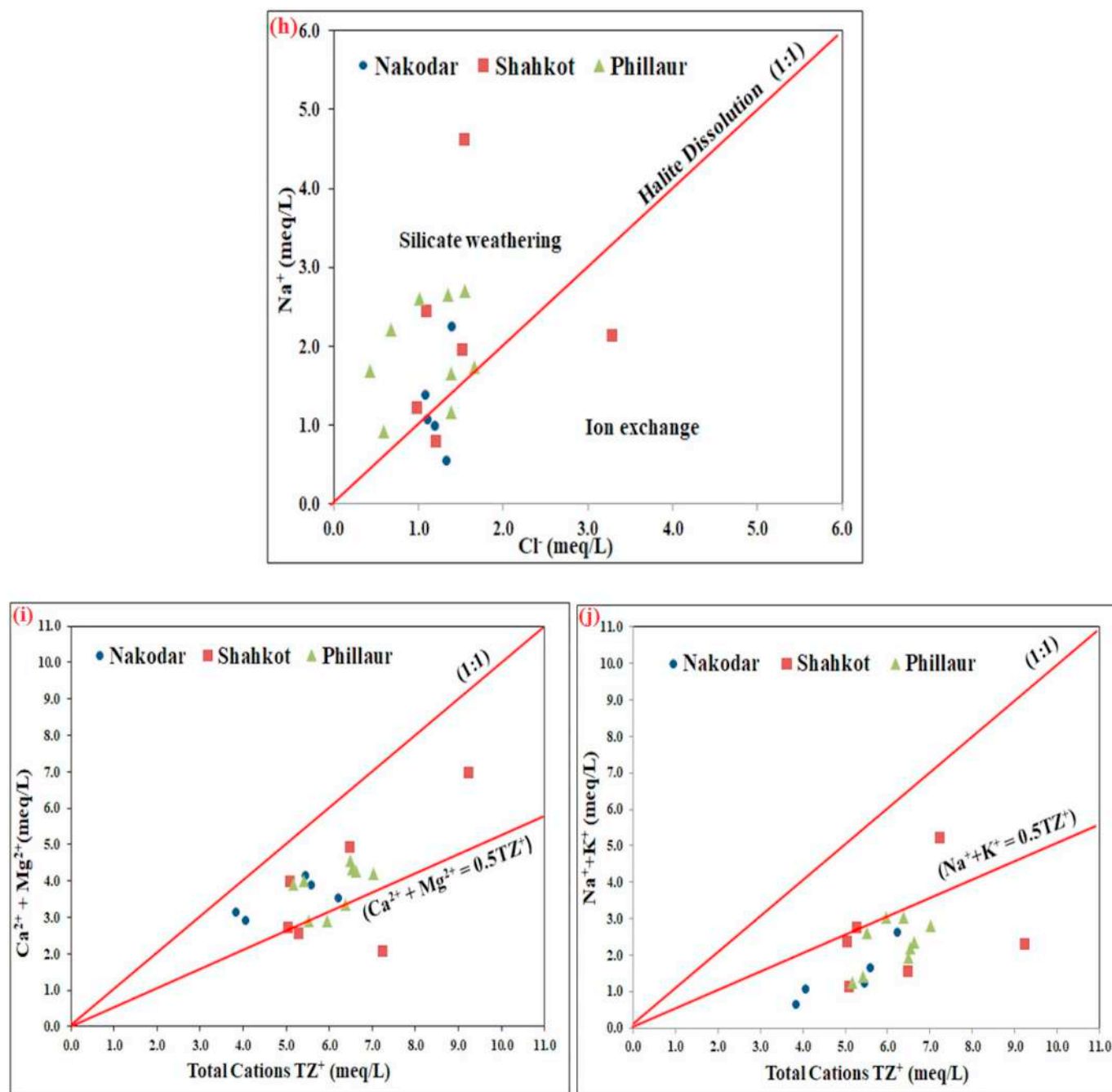


Fig. 19. (continued)

to the ion exchange processes and identical ionic radii of F^- and OH^- ions which occur at higher pH. Further, F^- ions are also adsorbed by the clay particles at higher pH and alkalinity; on the other hand, OH^- ions displace the F^- ions resulting in an increase of F^- ion content in the groundwater (Genxu and Guodong, 2001). As already discussed in above section (general parameters of groundwater of results and discussion part) several conditions like alkaline pH, higher alkalinity and low level of Ca in the groundwater of the study area provides favorable conditions for fluoride enrichment. F^- ion also showed an increasing trend with HCO_3^- (Fig. 20 (b)) indicating the multiple sources of F^- in groundwater including geogenic as well as anthropogenic sources such as application of fluoride-based fertilizers and brick kiln activities in the study area. A significant positive correlation was observed between NO_3^- and Cl^- at certain sampling sites suggesting similar source of

these ions (Fig. 20 (c)). The elevated level or increasing trend of NO_3^- with Cl^- concentration in the shallow aquifer is directly related to anthropogenic inputs such as domestic sewage, seepage from septic tank systems, organic and inorganic fertilizers and agricultural runoff. Such similar findings were reported by McQuillan (2004) and Marghade et al. (2012). The scatter plot between SO_4^{2-} vs. Cl^- (Fig. 20 (d)) showed a positive correlation indicated the effect of anthropogenic inputs on the aquifer chemistry, particularly irrigation return flow; since application of gypsum (CaSO_4) is a common practice in the agricultural fields of the study area to improve the quality of the soils. Certain sampling sites exhibited decreasing trend of SO_4^{2-} with increase in Cl^- content (Fig. 20 (d)). Suthar et al. (2009) concluded that it may be attributed to the fertilizers, wastewater and animal excreta.

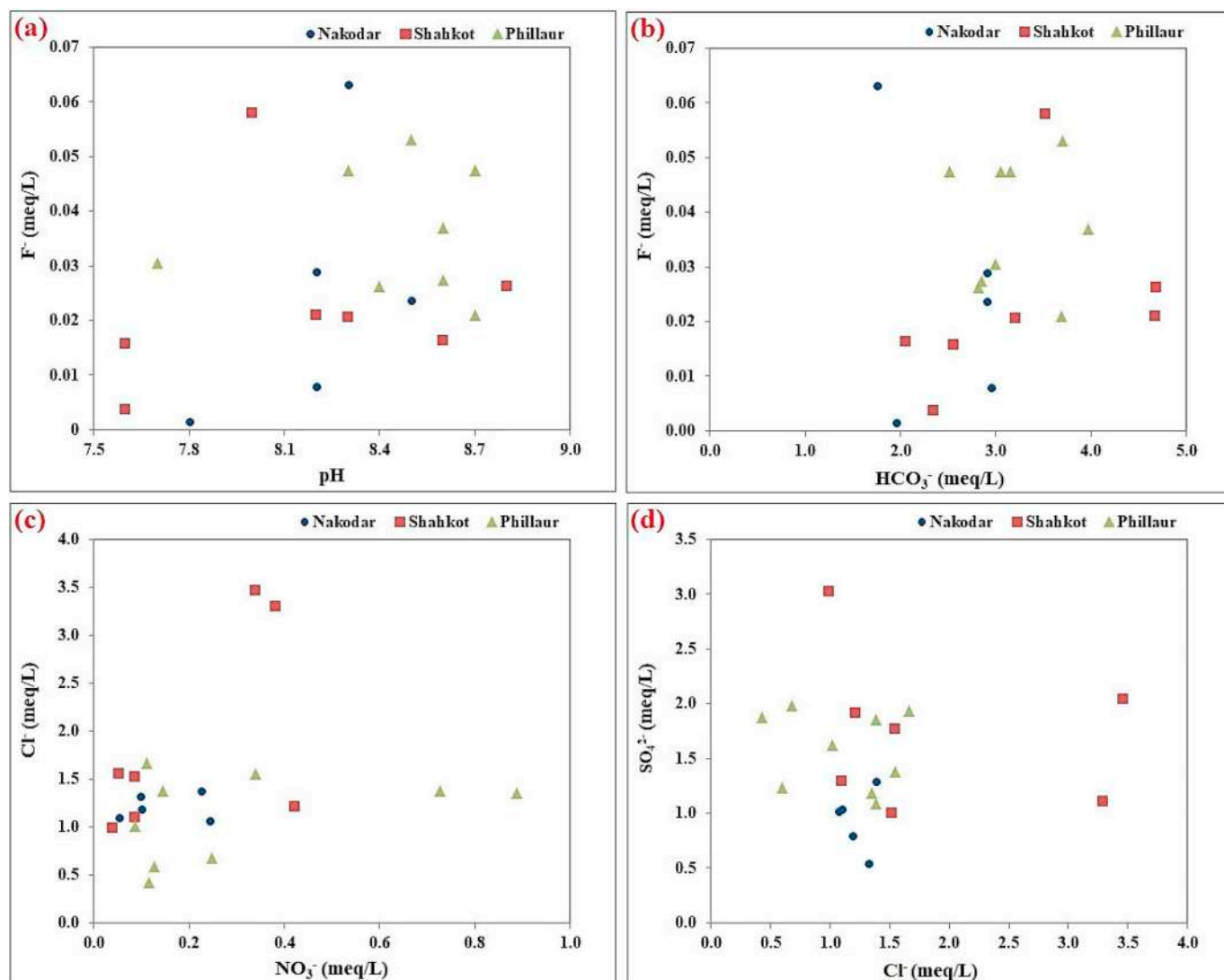


Fig. 20. Correlation among different anions, a) F^- vs. pH, b) F^- vs. HCO_3^- , c) Cl^- vs. NO_3^- and d) SO_4^{2-} vs. Cl^- .

5.7. Irrigation water quality appraisal

The quality of groundwater for irrigation purpose is important because it influences both the soil and plant health (Richards, 1954; Todd and Mays, 2005). The irrigation suitability was evaluated by EC, TDS, SAR, %Na, RSC, MH, PI and PS and the results based on various irrigation indices are summarized in Table 10. On the basis of EC (Richards, 1954), 52.38% (4 samples in each Nakodar and Shahkot and 6 samples of Phillaur) of the groundwater samples fall in good category and rest 47.62% (1, 3 and 6 samples of Nakodar, Shahkot and Phillaur, respectively) are in permissible category (Table 10). The high TDS content in irrigation water leads to the accumulation of salts around the crop root zone, which further affects the plant growth and crop yield (Ayers and Westcot, 1994). As per the classification of Ayers and Westcot (1994) and UCCC (1974) (Table 10) based on TDS values, 52.38% of groundwater samples (4 samples in each Nakodar and Shahkot and 6 samples of Phillaur) was suitable for agricultural use. Whereas remaining 47.62% (1, 3 and 6 samples of Nakodar, Shahkot and Phillaur, respectively) of samples were moderately suitable for the irrigational purpose. SAR is generally considered as a robust index for irrigation water evaluation (Ayers and Westcot, 1985) and it is calculated by Eq. (6). The high content of sodium in irrigational water leads to alkali hazard and reduces soil permeability (Domenico and Schwartz, 1990; Nagarajah et al., 1988). The SAR values of the groundwater were

ranged from 0.45 and 4.5 with mean value of 1.5. All the samples of the studied taluks have SAR value < 10, thus groundwater can be considered as excellent quality for irrigation purpose (Table S2). The SAR versus EC values of groundwater samples were plotted in the USSS diagram (1954). Fig. 21, reveals that 52.38% of the samples (4 samples in each Nakodar and Shahkot and 6 samples of Phillaur) fall in the C2-S1 (medium salinity with low sodium hazard) and 47.62% samples (1, 3 and 6 samples of Nakodar, Shahkot and Phillaur, respectively) fall in C3-S1 (high salinity with low sodium hazard) category. High salinity may cause nutritional disorder and also affects crop growth (Ragunath, 1987). Based on the USSS classification, the groundwater of the study area can use for irrigation purpose in almost all types of soils.

The value of %Na ranges from 15.1% to 69.0% with the mean value of 33.4% in the study area. Table 10 shows that 95% of samples belong to excellent to permissible class for irrigation uses, while one sample of Shahkot taluk falls under doubtful class. Wilcox diagram is used to understand the combined effect of EC and %Na (Wilcox, 1948). Fig. 22, shows that only one sample of Nakodar taluk fall in permissible to doubtful class and rest are in excellent to permissible class for irrigation use. It is cleared from the figure that 1, 3 and 6 groundwater samples of Nakodar, Shahkot and Phillaur, respectively fall in good to permissible class of Wilcox diagram. The remaining three samples in each taluks fall under the excellent to good class. Residual sodium carbonate (RSC) index and magnesium ratio (MR) are important parameters to estimate

Table 10
Classification of groundwater of the study area based upon various irrigational indices.

Parameters	Range	Water class	% of samples
EC ($\mu\text{S}/\text{cm}$) (Richards, 1954)	< 250	Excellent	Nil
	250–750	Good	52.38
	750–2000	Permissible	47.62
	2000–3000	Doubtful	Nil
	> 3000	Unsuitable	Nil
TDS	< 450	Suitable	52.38
	450–2000	Moderate	47.62
Alkalinity hazard (SAR) (Richards, 1954)	> 2000	Unsuitable	Nil
	< 10	Excellent (S1)	100
	10–18	Good (S2)	Nil
Salinity hazard (EC values in $\mu\text{S}/\text{cm}$) (Richards, 1954)	18–26	Doubtful (S3)	Nil
	> 26	Unsuitable (S4)	Nil
	< 250	Excellent (C1)	Nil
	250–750	Good (C2)	52.38
% Na (Wilcox, 1955)	750–2250	Doubtful (C3)	47.62
	> 2250	Unsuitable (C4)	Nil
	< 20	Excellent	19
	20–40	Good	48
RSC (Richards, 1954; Eaton, 1950)	40–60	Permissible	28
	60–80	Doubtful	5
	> 80	Unsuitable	Nil
	< 1.25	Good	76
Magnesium ratio (MR) (Ragunath, 1987)	1.25–2.5	Doubtful	19
	> 2.5	Unsuitable	5
	< 50	Suitable	Nil
Permeability Index (Doneen, 1961)	> 50	Unsuitable	100
	Class I	Max. permeability	38
	Class II	75% of max. permeability	62
Potential Salinity (Doneen, 1961)	Class III	25% of max. permeability	Nil
	< 5	Excellent to good	100
	5–10	Good to injurious	Nil
	> 10	Injurious to unsatisfactory	Nil

the alkalinity hazard in the irrigation water. The RSC value varied from –2.62 to 2.96 with mean value 0.06 in the groundwater samples. The negative value of RSC indicates the incomplete precipitation of Ca^{2+} and Mg^{2+} (Adimalla and Venkatayogi, 2018). 76% of groundwater samples (5 samples in each Nakodar and Shahkot and 7 samples in Phillaur) were found good for the irrigation on the basis Lloyd and Heathcote (1985) classification (Table 10), while remaining 19%

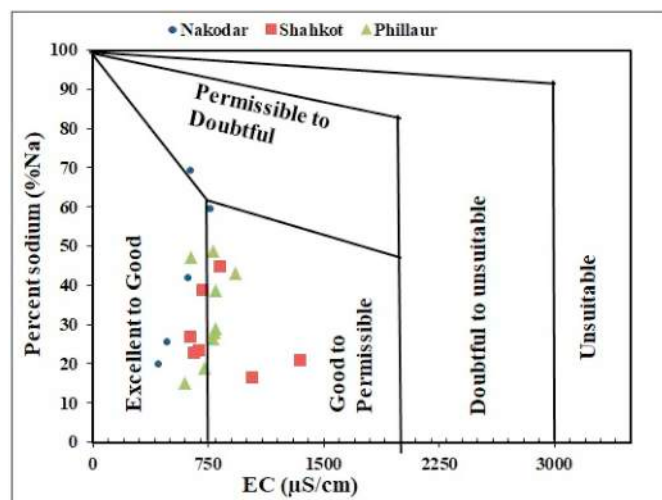


Fig. 22. Wilcox diagram indicating the suitability of groundwater for irrigation.

samples (2 samples in each Shahkot and Phillaur) were found doubtful class indicating poor quality of water for irrigation. One sample of Shahkot taluk was found unsuitable for irrigation as per the classification.

High Mg^{2+} content in irrigational water may increase soil alkalinity affecting crop yields. MH values ranged from 50 meq/L to 83 meq/L with the mean value of 63 meq/L. As per Szabo and Darab (1964) and Ragunath (1987), all the groundwater samples of the study area were found unsuitable for irrigation with Mg^{2+} hazard ratio > 50 meq/L (Table 10). The permeability of the soil is also affected by long-term use of irrigational water containing Na^+ , Ca^{2+} , Mg^{2+} and HCO_3^- ions. Doneen (1964) develop the permeability index and potential salinity to study the irrigational water quality and is computed as per Eqs. (10) and (11), respectively. PI value ranged from 24.7 to 37.8 (mean value of 30.9) in the study area. Schwartz and Domenico (1990) classify three water classes based on permeability index (Table 10), where 38% and 62% of groundwater samples fall under class I and class II, respectively thus groundwater of all the taluks are suitable for the irrigation purpose (Fig. 23). The concentration of highly soluble salt and the frequency of successive irrigation increases the soil salinity. The PS value ranged from 1.7 to 4.9 meq/L, with a mean value of 2.6 meq/L. Based upon potential salinity classification (Table 10), all the groundwater samples of the study area fall in excellent to good class, depicting the groundwater suitability for irrigation purpose. From the above indices of

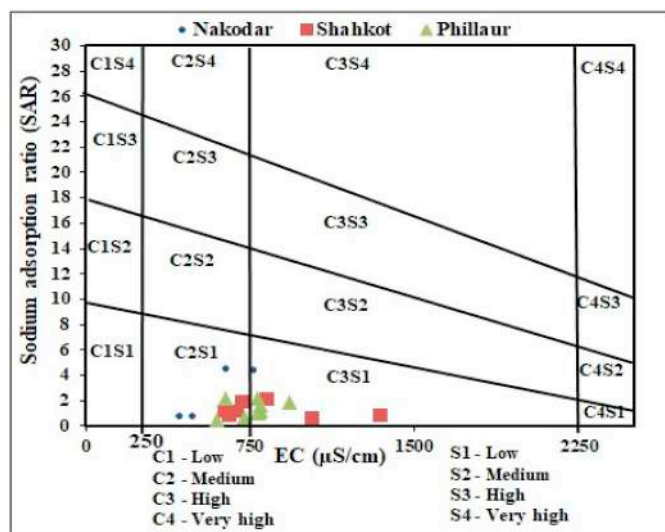


Fig. 21. USSR diagram indicating the suitability of groundwater for irrigation.

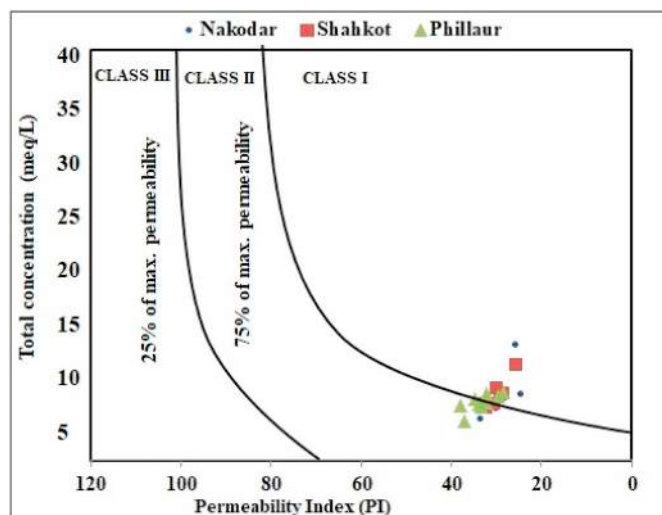


Fig. 23. Doneen diagram of groundwater for irrigation water suitability.

Table 11
Varimax rotation of physicochemical parameters.

Variable	PC1	PC2	PC3	PC4	PC5	Communality
pH	0.606	0.23	-0.414	0.177	0.388	0.773
EC	0.861	-0.414	0.059	-0.281	0.044	0.997
TDS	0.862	-0.413	0.058	-0.28	0.044	0.997
TH	0.055	-0.925	0.216	0.01	-0.095	0.915
Ca ²⁺	-0.171	0.019	0.85	0.01	-0.373	0.891
Mg ²⁺	0.104	-0.952	-0.028	0.011	0.011	0.918
Na ⁺	0.919	0.084	-0.107	-0.242	-0.025	0.922
K ⁺	0.097	0.23	-0.465	-0.769	0.015	0.87
CO ₃ ²⁻	0.785	0.193	0.031	0.378	0.172	0.826
HCO ₃ ⁻	0.633	-0.541	-0.131	-0.27	0.185	0.818
NO ₃ ⁻	0.272	-0.366	0.626	0.07	0.34	0.72
F ⁻	0.034	0.049	-0.073	0.068	0.925	0.869
Cl ⁻	0.691	-0.484	-0.022	0.208	-0.263	0.824
PO ₄ ³⁻	0.089	-0.606	-0.635	0.043	-0.087	0.788
SO ₄ ²⁻	0.127	-0.101	0.205	-0.896	-0.105	0.882
Eigen value	4.3406	3.2956	2.0372	1.9117	1.4263	
Variance %	28.9	22	13.6	12.7	9.5	
Cumulative variance (%)	28.9	50.9	64.5	77.2	86.7	
Source	Mixed factor i. Natural input like silicate and halite dissolution; ii. Anthropogenic input namely irrigation return flow and aquifer salinity.	Mixed factor (dolomite and carbonate weathering and application of agrochemical and domestic sewage)	Anthropogenic factor namely domestic sewage, fertilizer and irrigation return flow	Dissolution of silicate rocks like potassium feldspar, potash minerals and inorganic sulphides pyrite.	Natural factor	

Significant factor loadings are bold faced.

irrigation water quality, it can be concluded that the groundwater of all the three taluks is suitable for irrigation purposes except for magnesium hazard that could increase the soil alkalinity to certain extent hereby affecting the crop production in the study area.

6. Source identification of groundwater

PCA has been employed on the analyzed parameters to distinguish the geochemical processes and pollution sources influencing the groundwater regime in the study area. Principal components (PCs) corresponding to absolute loading values of > 0.75 (bold) and additionally second level of interpretation (bold italics) were considered statistically significant, and therefore, taken for interpretation by PCA. Five PCs were extracted by the varimax rotation method (Herojeet et al., 2017) that explains 86.7% of the total variance in the analyzed water samples (Table 11). The rotation makes the PCs easier to interpret by maximizing the differences between the variables (Invernizzi and de Oliveira, 2004). Principal component 1 (PC1) defined 28.9% of the total variance, that shows positive weight on Na⁺ and CO₃²⁻ (strong) and pH, HCO₃⁻ and Cl⁻ (moderate) influenced by lithogenic and several hydrogeochemical processes resulting in high EC and TDS loadings. The strong correlation of HCO₃⁻ and CO₃²⁻ with Na⁺ and weak correlation with Ca²⁺ and Mg²⁺ indicates input from parent rock material (Srivastava and Ramanathan, 2008). The main source of HCO₃⁻, CO₃²⁻ and Na⁺ may be attributed to the reaction of carbonic acids with silicate minerals (Amadi et al., 1987; Lakshmanan et al., 2003) as discussed in Eqs. (19) and (22). Earlier, Na⁺/Cl⁻ ratio confirmed that both Na⁺ and Cl⁻ ions are released from silicate and halite dissolution. Perttu et al. (2011) suggested that the positive correlation between Na⁺ and Cl⁻ is due to halite dissolution. However, the plot Na⁺ + K⁺ vs TZ⁺ depicts that in addition to silicate mineral, anthropogenic inputs are also another key factor led to increasing Na⁺ ion in the aquifer. The aquifer salinity is entirely related to sodium and chloride contents. Further, alkaline pH enables the Na⁺ ion to precipitate as sodium carbonate. PC2 illustrates 22.0% of the cumulative variance with a strong negative score on TH and Mg²⁺ and moderate negative loading on HCO₃⁻ and PO₄³⁻. The common source of Mg²⁺ and HCO₃⁻ is dolomite and carbonate dissolution (Guo and Wang

2004; Brindha et al., 2017). The degree of water hardness increased with an elevated concentration of Mg²⁺ ions. The high loading between Mg²⁺ with HCO₃⁻ and weak loading correlation with Ca²⁺, Na⁺ and K⁺ may be contributed by rock-water interaction. The moderate correlation of PO₄³⁻ suggested the application of fertilizers and pesticides in the agricultural area (Datta and Tyagi, 1996). Since the study area is an extensively cultivated region. Moreover, irrigation returns flow and domestic sewage may also be another possible source of PO₄³⁻ in groundwater. Hence, PC2 is influenced by mixed factors (dolomite and carbonate weathering and application of fertilizer and domestic sewage). PC3 accounts 13.6% of the overall variance with strong loading on Ca²⁺, a moderate positive score on NO₃⁻ and a moderate negative weight on PO₄³⁻. The kankars deposits (limestone) react with carbonic acid are the main source contributing to Ca²⁺ (Calcite dissolution) in groundwater. The significant inverse relationship between NO₃⁻ and PO₄³⁻ could be due to different anthropogenic factor. It is also noted that the study area lacks proper drainage and sewage system suggesting the major source for NO₃⁻ in groundwater beside fertilizers (Nyamangara et al., 2013; Purushothaman et al., 2014). The lack of clear relations of PO₄³⁻ with other chemical ions ignores the possible contribution from rock minerals. The application of phosphate fertilizers and irrigation return flows from agricultural land is the potential source for PO₄³⁻ ion in groundwater. The fourth component (PC4) is the negative weight on K⁺ and SO₄²⁻, explained 12.7% of the entire variance which indicates weathering of parent rocks. It is important to note that the concentration of K⁺ ion is least among the cations (Ca²⁺ > Mg²⁺ > Na⁺ > K⁺) in the groundwater. It indicates that potassium minerals like potassium feldspar and potash rock are least affected by weathering processes (Datta and Tyagi, 1996). The plot of Ca²⁺ + Mg²⁺ versus HCO₃⁻ + SO₄²⁻ and SO₄²⁻/Cl⁻ ratio indicates silicate weathering and inorganic sulphides pyrite-bearing minerals are the main source of SO₄²⁻ in groundwater (Barzegar et al., 2016; Okiongbo and Douglas, 2015). Lastly, 9.5% of the total variance is explained by PC5 that indicate strong positive loading on F⁻. Insignificant loading in PC5 indicates negligible anthropogenic influence on groundwater chemistry. Purushothaman et al. (2014) identified the same principal component and concluded that the possible source of F⁻ in the study area is geogenic.

7. Conclusion

This study provides significant information on groundwater quality of Nakodar, Shahkot and Phillaur taluks of Jalandhar district, Punjab. The result of this study revealed that groundwater in the study area is neutral to slightly alkaline and hard to very hard in nature. The parameters like Ca^{2+} , HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} and PO_4^{3-} are well within desirable limits of BIS (2012) and WHO (2011) for drinking purposes except for NO_3^- and F^- respectively. The result of WQI suggests that certain pockets of the studied taluks fall in poor (3 samples in Phillaur, 1 in Shahkot) to very poor (1 sample of Nakodar) water classes may be attributed to the extensive agricultural and industrial activities. The dominance of Na^+ and Mg^{2+} among cations and HCO_3^- and SO_4^{2-} among anions indicates that weathering of silicate material and ion exchange process are dominant activities in the study area. Majority of the groundwater samples belong to that Ca^{2+} - Mg^{2+} - HCO_3^- hydrochemical facies with Mg^{2+} - HCO_3^- water type representing temporary hardness. The finding of Giggenbach triangle, Gibb's diagram and CAI depicts that rock-water interaction and weathering and dissolution of aquifer materials are the main processes controlling the hydrochemistry of the groundwater, which is further supported by the principal component analysis. The bivariate plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{HCO}_3^- + \text{SO}_4^{2-}$ and $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$ and $[(\text{Na}^+ + \text{K}^+) - \text{Cl}^-]$ suggests ion exchange and silicate weathering as dominant processes. Dolomite and calcite present as kankar in the study area might be a source for Ca^{2+} and Mg^{2+} in groundwater. The scatter plots of $(\text{Na}^+ + \text{K}^+)/\text{TZ}^+$ suggested that in addition to silicate weathering alkalies may be attributed from some anthropogenic sources such as agricultural, sewage, and domestic and animal waste. Results of the PCA suggest that hydrochemistry in the region is affected not only by geogenic processes (rock water interactions) but also has an impact of anthropogenic activities such as agricultural runoff, domestic and industrial discharge, leakages from septic tanks. Therefore, the chemometric technique along with geochemical signatures and bivariate plots are found to be effective for the source apportionment and hydrogeochemical characterization of the groundwater of the study area. Regular and comprehensive water quality monitoring will avoid further deterioration of the water resources in the study area. Further, it should be mandatory to adopt an integrated approach for conserving water resources in the agricultural area and industrial pockets of the region to maintain pristine for long term drinking and agricultural purposes. The soils which are irrigated with this groundwater for a long period of time should be analyzed for future studies.

Declaration of competing interest

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Appendix A. Supplementary data

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