



Hydrogeochemical assessment of groundwater quality for few habitations of Chandel District, Manipur (India)

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Abstract

A preliminary hydrogeochemical investigation of groundwater quality for spatially distributed habitations of Chandel district of Manipur was carried out with an objective to assess the suitability of groundwater for different anthropogenic uses. Altogether, eighteen (18) physico-chemical parameters including in situ parameters and major ions were analysed for classification and hydrogeochemical characterisation of groundwater resources of the study area. Some of the anions such as Cl^- and SO_4^{2-} were found in exceeding concentrations. Similarly, 23.1% samples exceed fluoride (F^-) concentration beyond the permissible limit of 1.5 mg/l. The water quality index of the groundwater samples of the habitations was found to be influenced by the elevated concentrations of water quality parameters such as F^- , EC, TDS, salinity, Cl^- and SO_4^{2-} . The geochemical analysis reveals that the majority of geochemical facies of the groundwater samples are dominated by $\text{Na}^+ - \text{Ca}^{2+} - \text{Mg}^{2+} - \text{Cl}^- - \text{HCO}_3^- - \text{SO}_4^{2-}$ type of water resulting from rock-weathering geochemical process. Bivariate and multivariate analysis indicates the influences of hydrogeochemical interactions in the aquifer on the overall water quality. The irrigational water quality indices demonstrate that the water qualities of most of the sources are within the acceptable range except for few samples with high salinity and alkali hazards.

Keywords Groundwater quality · Hydrogeochemistry · Water quality index · Fluoride · Salinity · Irrigation

Introduction

Groundwater is one of the most exploited fresh water resources across the world used for various anthropogenic purposes. Generally, groundwater quality and their uses are mainly determined by various factors such as condition of sub-surface environment, types of lithological formation, hydrogeochemical interactions within aquifer and various other anthropogenic factors (Todd 2003). The quality, accessibility and availability of groundwater play a crucial role in determining the quality of life and overall development of the people in a region (WHO 2011). Although arid and semi-arid regions across the world are extensively depended on groundwater resources, growing water scarcity scenario and quality water deficit have led to exploitation of groundwater

resources in several parts of world including India (Verma et al. 2015, Mukherjee et al. 2011; Mahanta et al. 2009). In aquifer, groundwater exists as an electrolyte solution due to release of various geogenic ions from the aquifer matrix and their presence prominently determines the quality of groundwater (McSween et al. 2003). So, in order to safely access the trapped groundwater from the aquifer of a region, it is very much essential to ensure suitability of groundwater quality for public health safety (Kumar et al. 2009; Mukherjee et al. 2011). Due to the presence of geogenic contaminants such as arsenic, fluoride, uranium, heavy and trace elements in groundwater, a range of public health issues have been reported from various parts of the world (Bhattacharya et al. 2012). Similar incidents are also reported from many parts of the Indian states, particularly Ganga–Brahmaputra–Meghna (GBM) plain of India (Verma et al. 2015; Mahanta et al. 2015; Choudhury et al. 2011). Geologically, north-east (NE) India belongs to similar origin of Himalayan orogeny and lies within the catchment of Brahmaputra and Meghna basin, where problems of geogenic contamination of groundwater are extensively reported (Alam et al. 2019; Mukherjee et al. 2015; Chakraborty et al. 2008). So,

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the presence of geogenic contaminants in the groundwater resources of the region is quite apparent, and it is already revealed by a few preliminary research findings (Alam and Yumnam 2017; Devi et al. 2012; Chakraborty et al. 2008).

Study area

The groundwater samples were collected from thirty-three (33) spatially distributed habitations of Chandel district located in the south-eastern hilly landscape of Manipur, India (Fig. 1). The district spread over an area of 3313 sq. km. having a sparsely distributed and scattered population of around 144,028 (Census 2011). The study area is situated in a peculiar physiographic location of Eastern Himalayas occupied by mostly north–south parallel hill ranges made up of consolidated and semi-consolidated rocks belonging to Pre-Mesozoic to Miocene age (CGWB 2013). The consolidated rock formations are confined towards the eastern landscape and boarder of Myanmar, while semi-consolidated formations cover almost the entire foothill and valley belonging to Disang, Barail, Surma and Tipam Group of rocks (Devi et al. 2012). Groundwater occurs in secondary porosity consisting of joints, fissures, fractures and weathered residuum of consolidated, semi-consolidated rocks and in inter-granular pore spaces. Springs are also one of the major sources of water supply in the region (CGWB 2013). The region experiences subtropical to temperate climate with temperature varying between 5 and 35 °C and receives sufficient annual average rainfall (1036 mm) mostly

contributed from SW tropical monsoon during the month of May and August (MSAPCC 2015).

Materials and methods

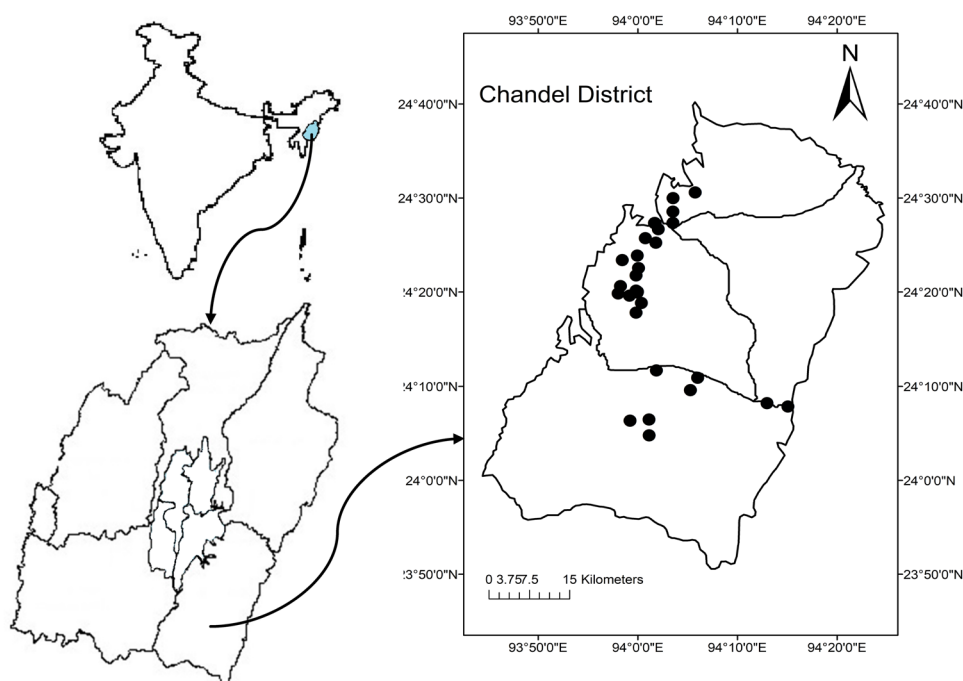
Sampling and in situ analysis

Thirty-three (33) spatially distributed groundwater samples from selected habitations of Chandel district were collected, and in situ parameters such as temperature, pH, electrical conductivity (EC), dissolved oxygen (DO), salinity, total dissolved solids (TDS) and oxidation reduction potential (ORP) were assessed using field test probes/sensors (Eutech/Hanna). The samples were collected from wells, tube wells and springs analysed as per the protocols of APHA (2005). Tube wells/wells were sufficiently flushed before collecting samples, and preservation of the samples was carried out using 1% HNO_3 to maintain pH below 2, for further laboratory analysis. Geographic coordinates of the sampling locations were recorded using Global Positioning System (GPS) (Garmin, eTrex 30) in order to mark the pinpoint locations.

Laboratory analysis

The collected and preserved samples were analysed in the laboratory for major parameters such as alkalinity, hardness, Na^+ , Ca^{2+} , K^+ , Mg^{2+} , Cl^- , F^- , NO_3^- , SO_4^{2-} and PO_4^{3-} using titrimetric, gravimetric and photometric methods as described in the standard procedures of APHA (2005). The concentration of fluoride (F^-) was determined

Fig. 1 Map shows the sampling locations of the study area



in the field using field test probes/sensor (Extech, FL700) and reverified using ion meter (Palintest) and spectrophotometric method (SPADNS method).

Evaluation of drinking water quality index (WQI)

Water quality index (WQI) is a collective numerical rating of water quality parameters which highlight the influences of various parameters on the overall quality of water for specific use (Hameed et al. 2010; Ramakrishnaiah et al. 2009). WQI was calculated for assessing suitability of groundwater for potable use based on WHO standards (WHO 2011). The calculation of WQI is based on assigning different weightage (W_i) to water quality parameters under consideration according to their significant influence on overall drinking water quality. Finally, the relative weightage (W_r) for each parameter are calculated using the following equation:

$$W_r = \frac{W_i}{\sum W_i}, \quad (1)$$

where i represent the number of parameter considered for the calculation of WQI. The water quality rating scale (Q_i) for each parameter were determined in accordance with their respective drinking water quality standards prescribed by WHO, using the following equation:

$$Q_i = \left(\frac{C_i}{S_i} \right) \times 100, \quad (2)$$

where C_i represents the concentration of parameters and S_i represents the drinking water quality standards for each parameter according to WHO (2011). Finally, the sub-indices (SI_i) and aggregate WQI are evaluated using the following equations:

$$SI_i = W_r \times Q_i \quad (3)$$

$$WQI = \sum SI_i \quad (4)$$

The status of the drinking water quality was assessed and classified based on the aggregate WQI, calculated as unsuitable ($WQI > 300$), very poor ($200 < WQI < 300$), poor ($100 < WQI < 200$), good ($50 < WQI < 100$) and excellent ($WQI < 50$) (Batabyal and Chakraborty 2015).

Geochemical evaluation

Hydrogeochemical classifications of groundwater samples were assessed by graphical plot between major cations and anions using Piper trilinear diagram (Piper 1953). This graphical plot distinctly categorised the major geochemical facies of groundwater and also provided an understanding on the water type. Gibbs diagrams (Gibbs 1970) represent

cationic and anionic ratio as a function of TDS that are extensively used for assessing the dominant geochemical processes. Precipitation, rock weathering and evaporation dominance are the major geochemical processes that govern the dissolution of ions into the groundwater (Drever 1997). The multivariate analysis and Pearson's correlation matrix were used to establish the covariability between parameters. Principal component analysis (PCA) was applied to determine the nature of hydrogeochemical interactions of the water with aquifers. Similarly, hierarchical cluster analysis (CA) and dendrograms were used for grouping the samples on the basis of their similar hydrogeochemical characteristics (Prusty et al. 2018).

Evaluation of irrigation water quality

Electrical conductivity (EC) is an irrigational water quality indicator that signifies the salinity hazard. Alkali hazards such as sodium absorption ratio (SAR), residual sodium carbonate (RSC) and permeability index (PI) are extensively used for the appraisal of irrigation water quality. The alkali hazards represented by the percentage of sodium (%Na) can be expressed as shown below (where concentrations of ionic species are in meq/l):

$$\%Na = \frac{(Na + K)}{(Ca + Mg + Na + K)} \times 100 \quad (5)$$

Sodium absorption ratio (SAR) is another important parameter for evaluation of sodium or alkali hazard, which is expressed as given below:

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

Similarly, residual sodium carbonates (RSCs) determine the impacts of carbonate and bicarbonate of the water on soil. High RSC value in water signifies scope for greater absorbability of sodium by soil. The RSC is mathematically expressed by the given relation:

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (7)$$

The permeability index (PI) is also another criterion for classification of irrigational water that can be defined as given below:

$$PI = \frac{(Na^+ + \sqrt{HCO_3^{-1}})}{(Ca^{2+} + Mg^{2+} + Na^+)} \times 100, \quad (8)$$

where the ionic concentrations are expressed in meq/l. The permeability index (PI) of groundwater samples is classified as per Doneen (1964) classification. Similarly, Wilcox

diagram represents plots between alkali (sodium) hazards (SAR) with EC, as an index for salinity hazards (Wilcox 1955). United States Salinity Laboratory Staff (USSLS 1954) diagram is also widely used to classify and rate the irrigation water quality into 16 classes based on plotting between sodium (alkali) hazards (SAR) with respect to salinity hazards (EC) (Richards 1954).

Results and discussion

Eighteen (18) physico-chemical parameters were analysed for 33 spatially distributed groundwater samples from the selected habitations of the Chandel district. The descriptive statistics including absolute and relative deviations, percentage of samples exceeding WHO permissible limit are presented in Table 1.

Evaluation of groundwater quality parameters

In situ parameters including temperature, pH, EC, TDS, salinity, ORP, DO and fluoride (F^-) concentrations were assessed in the field condition using the field test probes/sensors. The pH values range between 5.97 and 8.67 with the average of 6.77 ± 0.01 . The concentrations of TDS of the samples range between 70 and 460 mg/l with an higher average value of 234.3 ± 17.8 mg/l, which signifies dissolution of lithophilic ions into the groundwater samples. Similarly, EC

values range between 140 and 900 $\mu\text{S}/\text{cm}$ with an average of 477.0 ± 35.5 $\mu\text{S}/\text{cm}$. Exceeding values of EC in some of the samples indicate the presence of geogenic inorganic ions, released from dissolution of rocks and mineral due rock-weathering process. This is further confirmed by high degree of correlation between TDS and EC ($R^2=0.81$), salinity and TDS ($R^2=0.61$) and salinity with EC ($R^2=0.68$). Although these parameters exhibit high degree of correlation, greater spatial variabilities were observed among the groundwater samples. Dissolved oxygen (DO) concentration was found within the desirable range (4.75–7.94 ppm) with 11.5% spatial variability. The samples exhibit positive ORP values (79–222 mV) with an average of 202.3 ± 4.94 mV, indicating oxidising potential of water and presence of redox-active salts, minerals and metal ions. Groundwater confirms the presence of bicarbonate (HCO_3^-) alkalinity with 48.7% of spatial variability. Similarly, 78.8% of groundwater samples exhibit moderately hard water, followed by 15.2% hard and 6.1% very hard water as per USGS hardness classification (Briggs and Ficke 1977) (Table 2). The hardness of groundwater results due to the presence of both carbonate and non-carbonate salts, as Cl^- concentration was found in higher range of 4.0–110 mg/l (59.2 ± 3.9 mg/l) (Table 1). Sodium (Na^+) shows elevated concentrations (96.6%) than the permissible limit of WHO, ranging between 21.64 and 472.2 mg/l (average of 119.1 ± 20.72 mg/l) with greater spatial variability. The NO_3^- and PO_4^{3-} show average of 33.4 ± 5.81 mg/l and 36.6 ± 0.01 mg/l, respectively,

Table 1 The descriptive statistics of groundwater parameters of the study area

Parameters	Units	Min	Max	Avg	SD	CV	Samples beyond WHO permissible limit (%)
Temp	$^{\circ}\text{C}$	16.90	19.70	19.35	0.57	2.94	–
pH	–	5.97	8.67	6.77	0.46	6.81	15
EC	$\mu\text{S}/\text{cm}$	140.0	900.0	477.0	204.0	42.8	75.8
Salt	ppt	0.01	0.30	0.16	0.07	46.21	54.5
ORP	mV	79.0	222.0	202.3	28.4	14.0	–
TDS	ppm	70.0	460.0	234.3	102.0	43.5	24.2
DO	ppm	4.58	7.94	7.13	0.82	11.49	3
HCO_3^-	mg/l	9.81	50.00	17.02	8.29	48.68	0
TH as CaCO_3	mg/l	60.0	225.0	106.0	34.19	32.27	0
Ca^{2+}	mg/l	20.01	74.08	45.99	13.66	29.69	3
Mg^{2+}	mg/l	0.01	42.53	11.73	9.67	82.48	6.1
Cl^-	mg/l	24.99	109.97	59.23	22.53	38.04	0
F^-	mg/l	BDL	1.65	0.68	0.49	72.62	27.3
Na^+	mg/l	21.64	472.22	189.02	119.05	62.98	96.6
K^+	mg/l	4.08	253.75	50.81	57.52	113.21	0
NO_3^-	mg/l	0.03	146.76	40.47	33.37	82.47	36.4
SO_4^{2-}	mg/l	6.65	145.22	58.13	36.61	62.99	0
PO_4^{3-}	mg/l	0.01	0.50	0.19	0.13	68.41	0

BDL below detection limit (<0.01 mg/l)

Table 2 USGS hardness classification of groundwater samples for the study area

Hardness classification	Hardness as CaCO ₃ (mg/l)	Representative samples	Samples (%)
Soft	0–60	Nil	0
Moderately hard	60–120	S-1, S-2, S-3, S-4, S-5, S-6, S-7, S-8, S-10, S-12, S-13, S-14, S-15, S-16, S-17, S-18, S-19, S-20, S-21, S-22, S-23, S-24, S-26, S-27, S-30, S-31	78.8
Hard	121–180	S-29, S-9, S-28, S-11, S-25	15.2
Very hard	> 180	S-32, S-33	6.1

with 82.5% of spatial variability in nitrate concentration of the samples. Sulphate concentration ranges between 6.65 ± 145.22 mg/l which is less than the permissible limit of 200 mg/l (WHO 2011). The authors anticipated that elevated concentration of sulphate in groundwater samples is due to sulphate mineral dissolution or oxidation of sulphur. Fluoride (F⁻) in groundwater samples ranges between BDL and 1.65 mg/l with around 27.1% samples exceeding beyond WHO permissible limit of 1.5 mg/l. The highest concentration (1.65 mg/l) of fluoride (F⁻) was recorded in the sample of Tuishimi habitation (S-8).

Water quality index (WQI)

Suitability for drinking water quality of the selected habitations was evaluated using water quality index (WQI). The WQI ranges from 32.5 to 106.1, where around 21.2% of samples fall in the category of excellent water, followed by 75.8% and 3.1% samples in the good and poor water quality, respectively (Fig. 2). Concentrations of dissolved ions such as F⁻, Cl⁻ and NO₃⁻ and higher EC value of the samples influence the WQI of samples for the habitations. Moreover, samples with higher F⁻ concentration exhibit higher WQI values, considered to be unsuitable for potable use (Table 3). The predicted spatial distribution map for WQI (Fig. 3a) and fluoride (F⁻) concentration (Fig. 3b) for the study area was prepared using inverse-distance weighting (IDW) geospatial interpolation techniques in the ArcGIS platform. The tool is extensively used for preparation of spatial distribution maps

for various water quality parameters based on interpolation techniques such as kriging and IDW (Kresic 1997). The figure highlights the probable pockets of F⁻ bearing aquifers in the region.

Correlation analysis

Correlation analysis between the physico-chemical parameters of the groundwater samples was carried out to identify the influence of the variables and also to predict the dependency of variables on each other. The linear and multiple coefficient of correlation (*r*) was estimated between the variables that range between -1 and +1 and are classified as strong ($\pm 0.7 < r < \pm 1$), moderate ($\pm 0.5 < r < \pm 0.7$) and weak ($0 < r < \pm 0.5$) correlation depending on the influences of parameters on each other and with WQI. The higher concentration of EC, TDS, Na⁺, PO₄³⁻ and SO₄²⁻ exhibits higher correlation with WQI (Table 4). The EC shows strong correlation with salinity (0.83), TDS (0.90) and SO₄²⁻ (0.87) and Na⁺ (0.87) at *p* < 0.05. The strong correlation between EC and TDS indicates that conductivity of the groundwater samples increases due to dissolutions of more dissolved inorganic ions. Similarly, strong correlation between EC and Na⁺, HCO₃⁻, NO₃⁻ and SO₄²⁻ indicates the influences of ions that have resulted from various geochemical interactions such as oxidation–reduction and ion-exchange processes. TDS also reveals strong correlation with TH (0.76), salts (0.78), Na⁺ (0.76), SO₄²⁻ (0.71) (at *p* < 0.05), indicating that TDS and hardness are two main contributing factors for

Fig. 2 Categorisation of groundwater samples based on WQI w.r.t WHO standards

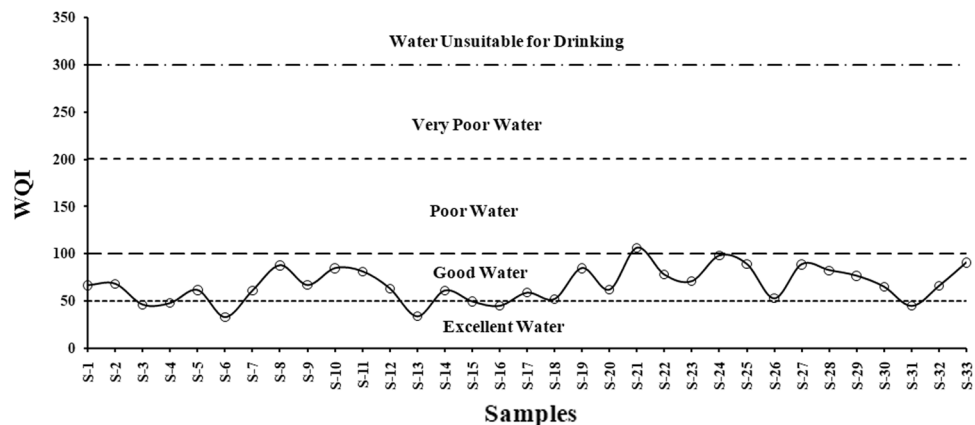


Table 3 Standards (S_i), assigned weight (W_i) and relative weight (W_r) for evaluation of WQI

Sl. no.	Chemical parameter	WHO (S_i)	Weight (W_i)	Relative weight (W_r)
1	pH	6.5–8.5	4	0.0833
2	Fluoride (F^-)	1.5 mg/l	5	0.1042
3	Chloride (Cl^-)	250–1000 mg/l	4	0.0833
4	Electrical conductivity (EC)	500 μ S/cm	3	0.0625
5	Alkalinity (HCO_3^-)	244–732 mg/l	3	0.0625
6	TH as $CaCO_3$	300–600 mg/l	3	0.0625
7	Dissolved oxygen (DO)	4–6 mg/l	4	0.0833
8	Total dissolved solids (TDS)	500–2000 mg/l	3	0.0625
9	Calcium (Ca^{2+})	75–200 mg/l	2	0.0417
10	Magnesium (Mg^{2+})	30–100 mg/l	2	0.0417
11	Sodium (Na^+)	200 mg/l	2	0.0417
12	Potassium (K^+)	300 mg/l	2	0.0417
13	Nitrate (NO_3^-)	45–100 mg/l	5	0.1042
14	Sulphate (SO_4^{2-})	200–400 mg/l	3	0.0625
15	Phosphate (PO_4^{3-})	0.1 mg/l	3	0.0625
			$\Sigma = 48$	$\Sigma = 1$

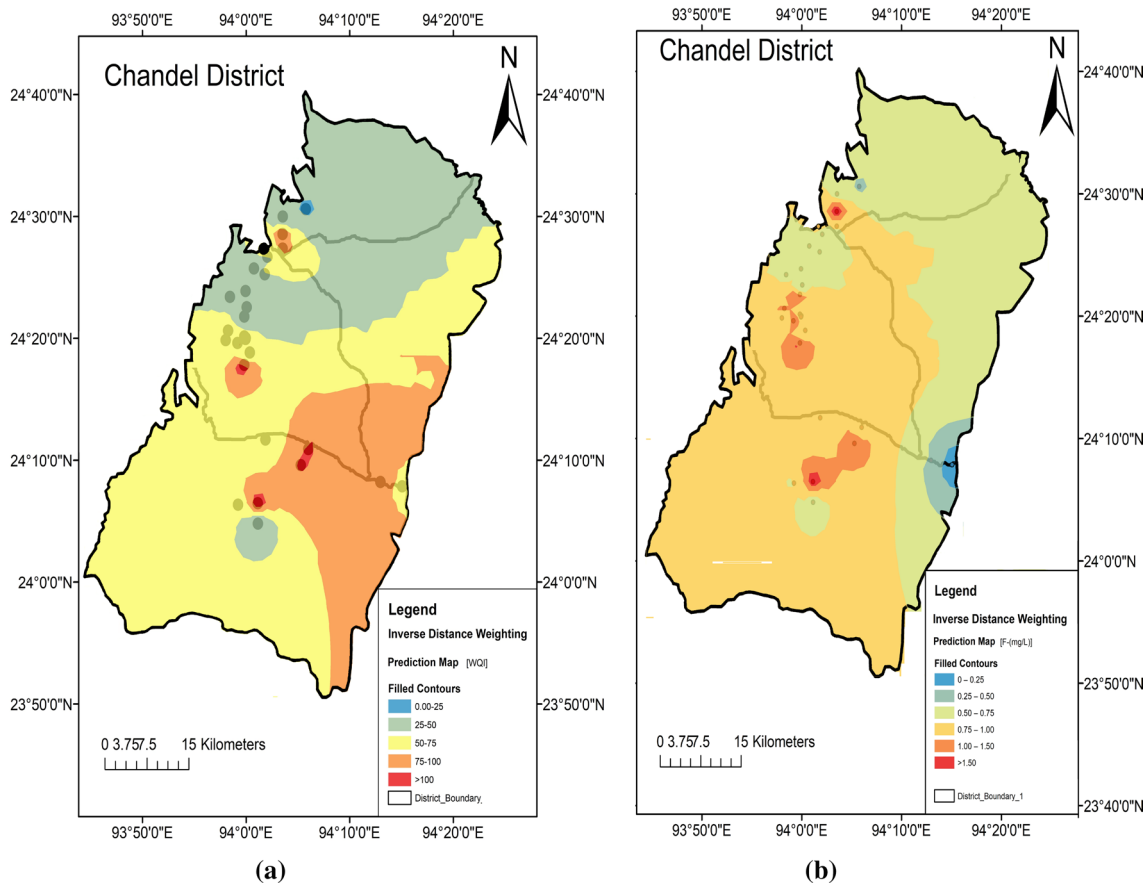


Fig. 3 Predicted geospatial distribution map for **a** water quality index (WQI) and **b** fluoride (F^-) concentration, for the study area

Table 4 Correlation matrix of physico-chemical parameters of the groundwater samples of the study area

	Tem	pH	EC	Salt	ORP	TDS	DO	HCO ₃ ⁻	TH	Ca ²⁺	Mg ²⁺	Cl ⁻	F ⁻	Na ⁺	K ⁺	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	WQI	
Tem	1.00	-0.28	0.18	0.48	0.44	0.13	0.48	0.24	-0.68	-0.05	-0.74	0.26	0.18	0.30	0.21	-0.74	0.30	0.12	-0.21	
pH		1.00	0.28	-0.01	-0.57	0.27	-0.10	-0.02	0.42	0.53	0.35	0.02	0.20	0.04	-0.05	0.35	0.04	0.32	0.50	
EC			1.00	0.83*	0.06	0.90*	-0.30	0.63	0.34	0.50	-0.04	0.53	0.24	0.87*	0.35	-0.04	0.87*	0.55	0.75*	
Salt				1.00	0.40	0.78*	-0.03	0.08	-0.06	0.32	-0.36	0.48	0.31	0.88*	0.24	-0.36	0.88*	0.46	0.50	
ORP					1.00	0.04	0.13	-0.16	-0.54	0.00	-0.50	0.08	0.23	0.32	-0.13	-0.50	0.32	0.10	-0.11	
TDS						1.00	-0.34	0.09	0.76*	0.62	0.06	0.40	0.08	0.70*	0.45	0.06	0.71*	0.45	0.77*	
DO							1.00	0.07	-0.50	-0.29	-0.40	0.00	0.00	-0.21	-0.17	-0.40	-0.21	-0.16	-0.47	
HCO ₃ ⁻								1.00	-0.08	-0.01	-0.04	-0.03	-0.10	-0.07	0.39	-0.04	-0.07	-0.04	-0.05	
TH									1.00	0.28	0.85	-0.04	-0.31	0.05	0.00	0.85	0.05	-0.11	0.45	
Ca ²⁺										1.00	0.14	0.16	0.26	0.24	0.21	0.14	0.24	0.39	0.57	
Mg ²⁺											1.00	-0.54	-0.37	-0.31	-0.25	1.00	-0.31	-0.25	0.25	
Cl ⁻												1.00	0.14	0.71*	0.50	-0.54	0.59	0.26	0.17	
F ⁻													1.00	0.40	-0.07	-0.37	0.40	0.75*	0.65	
Na ⁺														1.00	0.28	-0.31	1.00	0.63	0.76*	
K ⁺															1.00	-0.25	0.28	0.12	0.13	
NO ₃ ⁻																1.00	-0.31	-0.25	0.25	
SO ₄ ²⁻																	1.00	-0.31	0.25	
PO ₄ ³⁻																		1.00	0.63	
WQI																			1.00	0.80*

*Correlation is significant at $p < 0.05$

alkali hazard and non-carbonate hardness (Cl^- and SO_4^{2-}) in the majority of the samples. Moreover, SO_4^{2-} exhibits strong correlation with salinity (0.88) and PO_4^{3-} exhibits strong correlation with F^- (0.75), indicating dissolution of phosphorite minerals such as apatite (hydroxyapatite, fluorapatite) in the aquifer.

Geochemical classification

Geochemical classification and characterisation of groundwater samples for the study area were carried out using a geochemical diagnostic tool for better visual interpretation. The Piper trilinear diagram (Fig. 4) exhibits general trend of dominance of major cations and anions in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ type and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$ type, respectively. The figure also reveals that the majority of geochemical facies of groundwater samples are dominated by $\text{Na}^+ - \text{Ca}^{2+} - \text{Mg}^{2+} - \text{Cl}^- - \text{HCO}_3^- - \text{SO}_4^{2-}$ -type of water, followed by $\text{Na}^+ - \text{Ca}^{2+} - \text{K}^+ - \text{Cl}^- - \text{HCO}_3^-$ type of water. Classification of dominant geochemical process was carried out using Gibbs diagram (Fig. 5), which is extensively used for assessing the major geochemical processes that governs

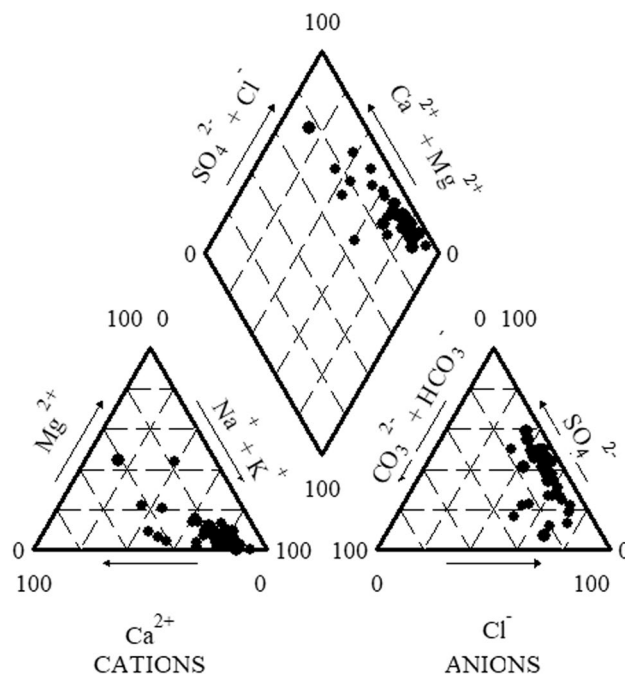


Fig. 4 Piper diagram representing the major geochemical facies of groundwater resources for the habitations in the study area

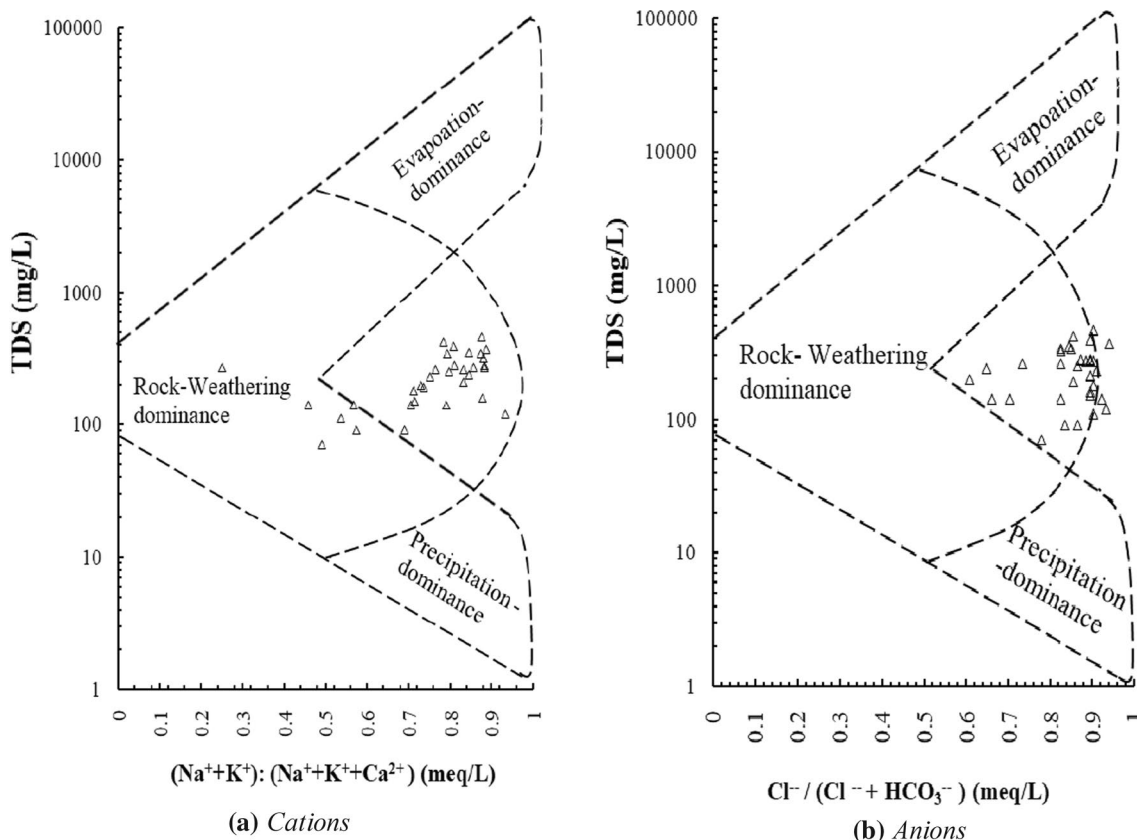


Fig. 5 Gibbs diagram showing rock weathering as a dominant geochemical process for dissolution of **a** cations and **b** anions in the groundwater samples for the study area

the water type and ion chemistry in the aquifers. The figure exhibits that the rock weathering is a major dominant geochemical process that governs the release of ions into the groundwater of the study area.

Principal component analysis (PCA)

The principal component analysis (PCA) was applied to determine the nature of variations in hydrogeochemical interactions of the water quality parameters (Prusty et al. 2018). The five principal components (PCs) are presented in Table 5 (with eigenvalue > 1), which accounts for 83.0% of variances in the hydrogeochemical variables. The PC-1 accounts for 34.4%, PC-2 accounts for 59.0%, PC-3 accounts for 69.0%, PC-4 accounts for 77.2%, and PC-5 accounts for 83.0% of variances within the variables, respectively. The PCs identify the underlying hydrogeochemical processes, and it is fairly distinct that about 34.4% of variances of the data are highly correlated with EC, salinity, TDS, Cl^- , Na^+ , SO_4^{2-} and PO_4^{3-} . But it can also be seen that variances of the variables are inversely correlated with NO_3^- , Mg^{2+} , DO and TH. Similarly, PC-2 indicates 24.6% of variances in the variables are correlated with TH, Mg^{2+} and NO_3^- and inversely correlated with temperature, ORP, DO, HCO_3^- and F^- , respectively. Occurrences of these variances among the variables are expected due to intrusion of surface water from heavy precipitation in the region (> 1036 mm/year) and dissolution of ions in the aquifer. Moreover, shallowness of the aquifers (10–20 m bgl) (CGWB 2013) in the region may be another attributing factor.

Cluster analysis (CA)

The hierarchical cluster analysis (CA) was applied to determine and group the samples on the basis of their spatial similar characteristics. The cluster analysis indicates four major clusters or groups of water types, i.e. groups I, II, III and IV (Fig. 6; Table 5). The groups show the considerable spatial variability of water quality parameters due to variability of the aquifer types and their formations. Most of the samples are collected from wells, tube wells and springs that occur under unconfined aquifer condition and are mostly shallow in nature. EC value varies from 470 to 540 $\mu\text{S}/\text{cm}$ (group I), 140–210 $\mu\text{S}/\text{cm}$ (group II), 270–390 $\mu\text{S}/\text{cm}$ (group III) and 630–900 $\mu\text{S}/\text{cm}$ (group IV). Thus, group IV samples are categorised together for the samples with higher concentrations of Cl^- , Ca^{2+} , Na^+ , EC, TDS, salinity, TH, indicating mostly non-carbonate hardness of water characterised by NaCl , CaCl_2 type of water. Also, group IV shows higher concentration of Na^+ (247.4–472.2 mg/l) and Cl^- (44.9–110.0 mg/l), indicating NaCl type of water resulting from dissolution of halite, as the region is having evidence of the presence of saline springs (Singh et al. 2013;

Table 5 Varimax rotated factor loadings with eigenvalues and % of variances for the groundwater quality parameters

Parameters	Component				
	PC-1	PC-2	PC-3	PC-4	PC-5
Tem	0.53	−0.63	0.19	0.12	0.30
pH	0.03	0.61	−0.24	0.61	−0.06
EC	0.82	0.51	0.09	−0.09	0.06
Salt	0.89	0.09	0.05	−0.19	0.24
ORP	0.40	−0.51	−0.23	−0.49	0.31
TDS	0.75	0.56	0.22	−0.04	0.19
DO	−0.06	−0.62	0.01	0.27	0.12
HCO_3^-	0.04	−0.06	0.58	0.41	0.47
TH	−0.21	0.91	0.13	−0.17	−0.09
Ca^{2+}	0.38	0.52	−0.13	0.33	0.23
Mg^{2+}	−0.57	0.77	−0.03	−0.15	0.20
Cl^-	0.73	−0.03	0.30	0.04	−0.57
F^-	0.50	−0.10	−0.65	0.35	−0.01
Na^+	0.91	0.21	−0.06	−0.24	−0.05
K^+	0.41	0.08	0.69	0.25	−0.18
NO_3^-	−0.57	0.77	−0.03	−0.15	0.20
SO_4^{2-}	0.91	0.21	−0.06	−0.24	−0.05
PO_4^{3-}	0.78	0.19	−0.46	0.29	0.00
Eigenvalues	6.20	4.42	1.79	1.49	1.03
Variability (%)	34.43	24.58	9.97	8.26	5.71
Cumulative (%)	34.43	59.02	68.98	77.24	82.95

Values in bold indicates significant factor loadings

CGWB 2013). Similarly, salinity of groups I and IV was found to be higher (0.2–0.3 ppt), indicating halite-dominated aquifer formations. As per the hardness classification, groups I, II and IV represent more non-carbonate types of hardness as HCO_3^- concentrations are comparatively lower in each group. Moreover, $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{HCO}_3^- + \text{SO}_4^{2-}$ ratio is slightly lesser than unity, whereas Na^+/Cl^- is greater than unity, indicating ion-exchange silicate weathering.

Irrigation water quality

Suitability of irrigation water quality was evaluated using water quality parameters such as EC, TDS and irrigational water quality indices such as sodium percentage (%Na), sodium absorption ratio (SAR), residual sodium carbonate (RSC), permeability index (PI), USSLS and Wilcox diagram. The irrigational water quality is greatly influenced by EC and TDS as these two parameters represent the measure of salinity hazards which have profound effects on soil osmotic pressure (O'Geen 2015). The EC of the groundwater samples varies within 140–900 $\mu\text{S}/\text{cm}$ with average value of 477.0 ± 35.5 $\mu\text{S}/\text{cm}$ (Table 6). Approximately 12.1% of samples exhibit EC concentrations beyond 750 $\mu\text{S}/\text{cm}$, considered as harmful for irrigational uses (Richards 1954).

Fig. 6 Dendrogram based on hierarchical cluster analysis, highlighting on spatio-similarity of the samples for the study area

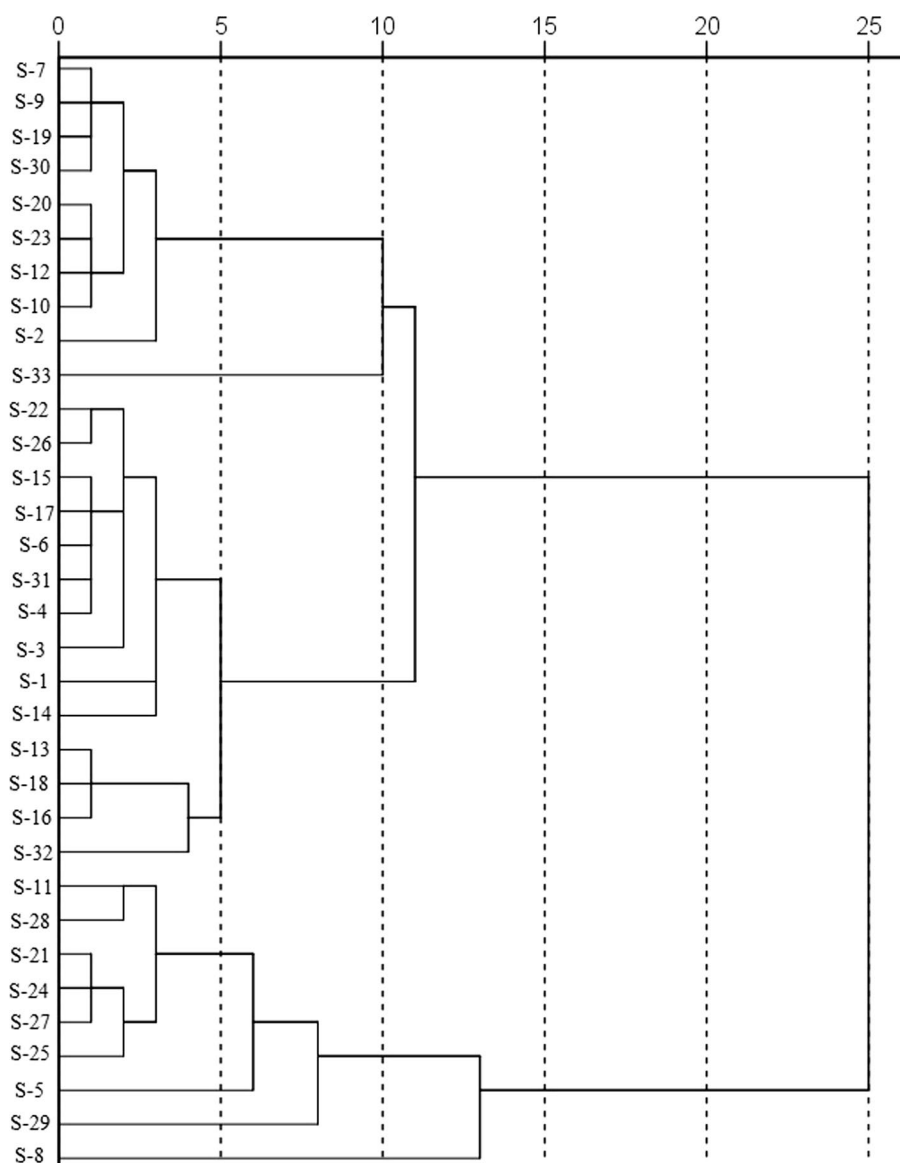


Table 6 Groups showing similar types of groundwater quality in the study area

Group	Sampling stations
Group I	S-7, S-9, S-19, S-30, S-20, S-23, S-12, S-10, S-2, S-33
Group II	S-22, S-26, S-15, S-17, S-6, S-31, S-4, S-3, S-1, S-14
Group III	S-13, S-18, S-16, S-32
Group IV	S-11, S-28, S-21, S-24, S-27, S-25, S-5, S-29, S-8

TDS concentrations (70–460 mg/l) indicate that most of groundwater belongs to freshwater category and suitable for irrigational use (Table 7). According to sodium percentage, groundwater samples lie within excellent to permissible category. Approximately 78.8% samples fall in the category of low alkali hazard (SAR), whereas 18.2% and

3% of samples fall in the category of increasing problem and severe problem of alkali hazards, respectively. Similarly, PI values indicate that approx. 21.2% samples show suitability and 78.8% samples show unsuitability for irrigational uses. Likewise, RSC values (Table 7) reveal that about 9.1% of samples have possibility of impact on soil due to the presence of carbonates and bicarbonates in water and remaining 90.9% samples are safe for irrigation due to low value of RSC (< 1.25). Elevated RSC value in water signifies scope for greater absorption of sodium by soil (Eaton 1950). The Wilcox diagram displays plots between Na % and EC (Fig. 7). The figure demonstrates approximately 15.2% of samples in the category of good to permissible range and 84.8% of samples are in the category of excellent to good range for irrigational water. The USSLS (1954) diagram classifies the irrigation water on the basis of salinity (EC)

Table 7 Classification of groundwater for irrigational use based on irrigational indices

Parameters	Range	Groundwater class	Number of samples	% of samples
EC ($\mu\text{S}/\text{cm}$) (Richards 1954)	< 250	Excellent	4	12.1
	250–750	Good	25	75.8
	750–2000	Permissible	4	12.1
	2000–3000	Doubtful	0	0
	> 3000	Unsuitable	0	0
TDS (mg/l) (Freeze and Cherry 1979)	< 1000	Freshwater	33	100
	1000–3000	Slightly saline	0	0
	3000–10,000	Moderately saline	0	0
	10,000–35,000	Highly saline	0	0
	> 35,000	Brine	0	0
%Na (Wilcox 1955)	< 20	Excellent	23	69.7
	20–40	Good	7	21.2
	40–60	Permissible	3	9.1
	60–80	Doubtful	0	0
	> 80	Unsuitable	0	0
SAR (Bouwer 1978)	< 6	No problem	26	78.8
	6–9	Increasing problem	6	18.2
	> 9	Severe problem	1	3.00
PI (Doneen 1964)	< 60	Suitable for irrigation	7	21.2
	> 60	Unsuitable for irrigation	26	78.8
RSC (Eaton 1950)	> 1.25	Unsuitable for irrigation	3	9.1
	< 1.25	Safe for irrigation	30	90.9

and alkali (sodium) hazards (Fig. 8). Approximately 57.6% of the samples exhibit medium salinity and low alkali hazards, followed by 18.1% samples in the category of high salinity and low alkali hazards (C2–S1). Similarly, approximately 12.1% samples fall in the category of low salinity and low alkali hazard (C1–S1), 6.1% samples fall in the category

of medium salinity and medium alkali hazard (C2–S2), and 6.1% samples fall in the high salinity and medium alkali hazard (C3–S2) category, respectively.

Fig. 7 Wilcox diagram demonstrating suitability of water quality for irrigational use

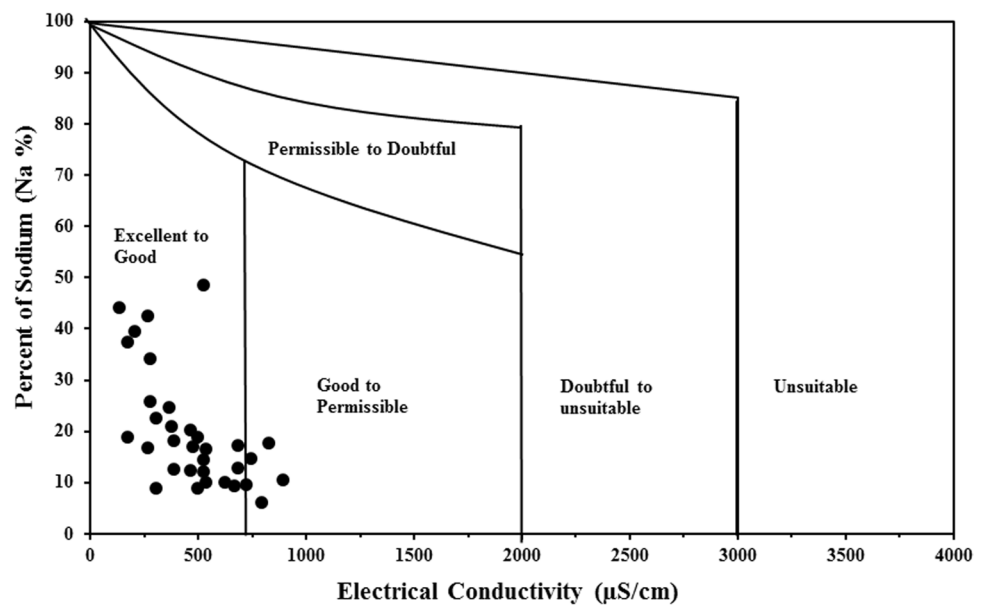
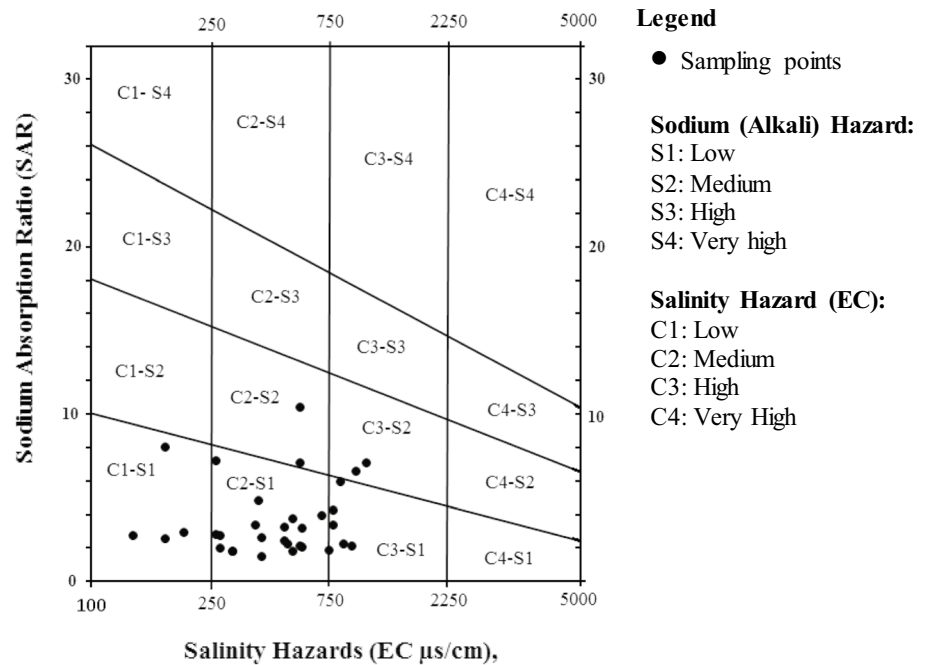


Fig. 8 The USSLS diagram for classification of irrigation water of the study area based on alkali (SAR) and salinity (EC) hazards



Conclusion

The present assessment reveals the spatial variability of groundwater quality parameters and hydrogeochemistry of the aquifer formation in the study area. The studies also unveil the presence of geogenic contaminants such as F^- , Cl^- and SO_4^{2-} in some of the groundwater samples in exceeding concentration. Groundwater quality is significantly influenced by elevated concentrations of EC, TDS, salinity, Na^+ , Cl^- and SO_4^{2-} that further impact the overall groundwater quality indices for a few habitations. WQI of the study area was found to be excellent to good except for few habitations where WQI exhibits poor value due to elevated concentrations of F^- , Cl^- , EC, salinity, TDS, SO_4^{2-} and PO_4^{3-} . The fluoride concentration in few samples exceeds permissible limit of WHO, which highlights the possibility of public health impacts. The predicted geospatial distribution maps of WQI and fluoride concentration indicate the presence of possible pockets of F^- contaminated aquifer in the habitations. The major hydrogeochemical classification indicates $Na^+Ca^{2+}Mg^{2+}Cl^-HCO_3^-SO_4^{2-}$ type of water, and the major ion chemistry is dominated by rock weathering and silicate weathering process. The five principal components account for 83.0% variances in the hydrogeochemical variables of the study area. The PCA identifies the nature of variations in hydrogeochemical interactions and underlying geochemical processes that are highly correlated with EC, salinity, TDS, Cl^- , Na^+ , SO_4^{2-} and PO_4^{3-} . The irrigational water quality of majority of groundwater samples was found to be in acceptable range except for few samples where high salinity (EC) and alkali

(sodium) hazards were witnessed due to elevated concentration of alkali metal ions and halite-dominated salts.

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Compliance with ethical statements

Conflict of interest The authors declare that they have no conflict of interest.

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