



Hydrochemical characteristics and human health risk assessment of groundwater in the Shivalik region of Sutlej basin, Punjab, India

Sunil Mittal¹ · Prafulla Kumar Sahoo^{1,2} · Sunil Kumar Sahoo³ · Ravishankar Kumar¹ · Raghavendra Prasad Tiwari¹

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Abstract

Shivalik region is one of the agri-intensive regions in Punjab, India, wherein groundwater quality is a major human health concern. In this study, a total of 57 groundwater samples were collected from the Rupnagar district of this region (one sample per 36 km²) to evaluate its quality, the role of hydrogeochemical processes in its contamination, and further their potential human health hazards. The results indicate that the major water chemistry is governed by carbonate weathering followed by silicate weathering. The Fe, Mg, Mn, Se, and HCO₃⁻ concentrations exceeded the BIS drinking water standards in 86, 51, 11, 9, and 79% of the samples, respectively. Piper and Durov plots indicated the dominance of Ca-HCO₃⁻ water types, followed by Ca-Mg-Cl⁻ and Ca-Cl⁻. Furthermore, multivariate analyses indicated the geogenic origin for Fe, Mg, Mn, Se, SO₄²⁻, and anthropogenic sources (agrochemicals, cement factories, and fly ash) for NO₃⁻, Cu, and Cr. The estimated carcinogenic risk of As and Cr falls under the very low (10⁻⁶) to low (10⁻⁵) risks category. Furthermore, the cumulative risk of non-carcinogenic contaminants (F⁻, U, NO₃⁻) (HI-0.93) is at an alarming level and also close to the boundary line of USEPA limits (HI-1). There is an urgent need to undertake suitable policy measures for sustainability of groundwater quality.

Keywords Groundwater · Hydrochemistry · Health risks · Heavy metals · Punjab

Introduction

Deterioration of groundwater quality is one of the major concerns of the twenty-first century due to its huge demand for drinking and irrigation purposes (UN water report 2015; Dhawan 2017). The rapid industrialization and increased mining activities have immensely contributed to it (Li et al. 2018, 2019a). The United Nations has set targets under Sustainable Development Goals (SDG) to provide safe and affordable drinking water for all. Goal 6 of SDG focuses on to improve water quality by reducing pollution, eliminating dumping, and

minimizing the release of hazardous chemicals by 2030 (UNDP 2020).

The sustainability of groundwater quality is one of the major challenges in the current scenario (Li et al. 2021). The adverse health impacts of contaminated water on humans have been widely reported in many parts of the world (Chowdhury et al. 2016; Ji et al. 2020; He et al. 2020; Palansooriya et al. 2020; Wu et al. 2019, 2020a; Li et al. 2019b). The long-term usage of contaminated water also adversely affects the sustainability of soil and agriculture (Hou et al. 2020). The hydrogeochemical processes occurring in aquifers (dissolution, evaporation, mixing and ion exchange) also influence groundwater quality (Rajesh et al. 2012; Chung et al. 2020).

The developing countries are highly dependent on groundwater for domestic, agricultural irrigation, and industrial activities. Furthermore, groundwater mismanagement in these countries has made the situation more critical in terms of quality and quantity. The geogenic contamination of groundwater with heavy metals/metalloids (like As, U, Se, Fe, Mn) has been reported as one of the major causes of quality deterioration worldwide (Coyte et al. 2019; Martins et al. 2019a, 2019b; Solangi et al. 2019; Houria et al. 2020; Martins et al. 2020; Shaji et al. 2020; Villalba et al. 2020; Rahman et al.

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✉ Ravishankar Kumar
ravishbiochem@gmail.com

¹ Department of Environmental Science and Technology, Central University of Punjab, Mansa Road, Bathinda, Punjab 151 001, India

² Instituto Tecnológico Vale, Rua Boaventura da Silva 955, Nazare, Belém, Pará 66055-090, Brazil

³ Health Physics Division, Bhabha Atomic Research Centre, Mumbai, India

2021). Anthropogenic activities, mainly fertilizers, have also been reported as major causes of groundwater contamination in many countries (Houria et al. 2020; Kansoh et al. 2020).

Nearly, 70% of groundwater has been extracted for agricultural use. As per National Ground Water Association report (2020), India, China, the USA, Pakistan, Mexico, Iran, and Saudi Arabia collectively extract nearly 75% of the global annual groundwater extraction. India, one of the major agrarian countries of the world, extracts the highest amount of groundwater (National Ground Water Association 2020) and faces a serious crisis for groundwater sustainability in terms of quality and quantity. Groundwater fulfills nearly 50% irrigational need of India, which is much higher than the global average (40%) (Dhawan 2017). The Indian state Punjab is known as the heartland of agricultural activities and has been the nation's Green Revolution leader.

The groundwater of this state is facing a serious crisis of contamination (Hundal and Khurana 2013; Mittal et al. 2014; Kumar et al. 2018; Pacheco et al. 2018a & b; Sharma et al. 2019; Kumar et al. 2020a, 2020b; Sharma et al. 2020a, 2020b). Both geogenic and agricultural sources have reported as the sources of anions [nitrate (NO_3^-), sulfate (SO_4^{2-}), fluoride (F^-), phosphate (PO_4^{3-})] and heavy metals [(arsenic (As), uranium (U), lead (Pb))] in groundwater of Punjab (Sharma and Singh 2016; Ahada and Suthar 2018, 2019; Kaur et al. 2021; Kumar et al. 2020a, 2020b; Mittal et al. 2020). The elevated levels of these contaminants in groundwater are reported in several parts of Punjab (Shrivastava 2015; Ahada and Suthar 2018, 2019; Sharma et al. 2020a, 2020b), although some parts are still undiscovered and need serious attention. The agri-intensive Shivalik region of Sutlej basin, Punjab, (accounts 11% of the state Punjab area) is one of such region (Yadav et al. 2015). The groundwater of this region is extensively used for drinking and irrigational purposes. Although some scientists have evaluated basic groundwater quality studies in this region (Singh et al. 2011a & b; Sharma et al. 2017, 2018, 2019), detailed investigations concerning the hydrogeochemical process, source apportionment, drinking and agricultural suitability and potential health risk aspects are still lacking. The present study was focused on the Rupnagar district, wherein the increasing demand for groundwater resources for drinking and irrigation has overstressed its quality.

The main objectives of the present study were to investigate (1) hydrochemical characterization of groundwater, (2) evaluation of groundwater quality for drinking and irrigation purposes with the help of Water quality index (WQI) and Heavy metal pollution index (HPI), (3) sources of major groundwater contaminants by using multivariate analyses, and (4) degree of health risks potential for groundwater contaminants. The findings of this study have provided an insightful view of the current status of groundwater quality. This can help the policymakers implement appropriate strategies and preventive measures to manage groundwater quality and sustainability.

Material and method

Structure of the study

The groundwater samples were collected and analyzed for physicochemical parameters, anions, major cations, and heavy metals/trace metals. The suitability of groundwater for drinking purpose was assessed using the water quality index (WQI) and heavy metals pollution index (HPI). The hydrochemistry of groundwater was also evaluated by Gibbs, Piper, and Durov diagrams. Further, source analysis of groundwater contaminants was estimated using different statistical measures like PCA, HCA, and correlation analysis. The health risks of groundwater contaminants have also been predicted through carcinogenic and non-carcinogenic health risks assessment. The flowchart of the entire scheme/methodology is depicted in Fig. 1.

Description of study area

Rupnagar district (formally known as Ropar) is situated in the eastern part of the Punjab State and lies in coordinates between $76^\circ 19' 00''$ – $76^\circ 45' 00''$ N and $30^\circ 44' 00''$ – $31^\circ 25' 00''$ E. The study area falls within the Shivalik range of Sutlej basin and occupying 1440 km^2 in area (Fig. 2). State Himachal Pradesh geographically surrounds the study area in the north and northeast, Ludhiana, SBS Nagar, and Hoshiarpur districts in the west, Fatehgarh Sahib area in the southern part, and district Mohali in the southeastern part. The Rupnagar district comprises four tehsils, namely Rupnagar, Nangal, Anandpur Sahib, and Chamkaur Sahib. The main occupation of the study area is agriculture, and major crops grown are wheat, paddy, maize, sorghum (jowar), pearl millet (bajra), cotton, sugarcane, and oilseeds (Thakur et al. 2016). The study area faces extreme summer and extreme winter climate. The average annual rainfall is recorded 776 mm, and nearly 78% is received during the monsoon period. The annual temperature fluctuates between 2 and 45°C .

Geological setting and hydrogeology

The study area's geomorphology comprises four distinct geological formations, which include Shiwalik Hills, alluvial plain, alluvial fan, and Intermontane valley. These geographical units run parallel to each other. Indo-Gangetic alluvial plain separates Shiwalik Hills range from Himalayan ranges. Charnockite and sandy, silty alluvium are detected as the major rocks types of the central and western part of the Rupnagar district area. The study area's soil texture is loam to silty clay loam majorly, except some parts of River Sutlej and chaos (seasonal canals). The geological features of the study area are depicted in Map (Fig. 3 and Fig. SM1).

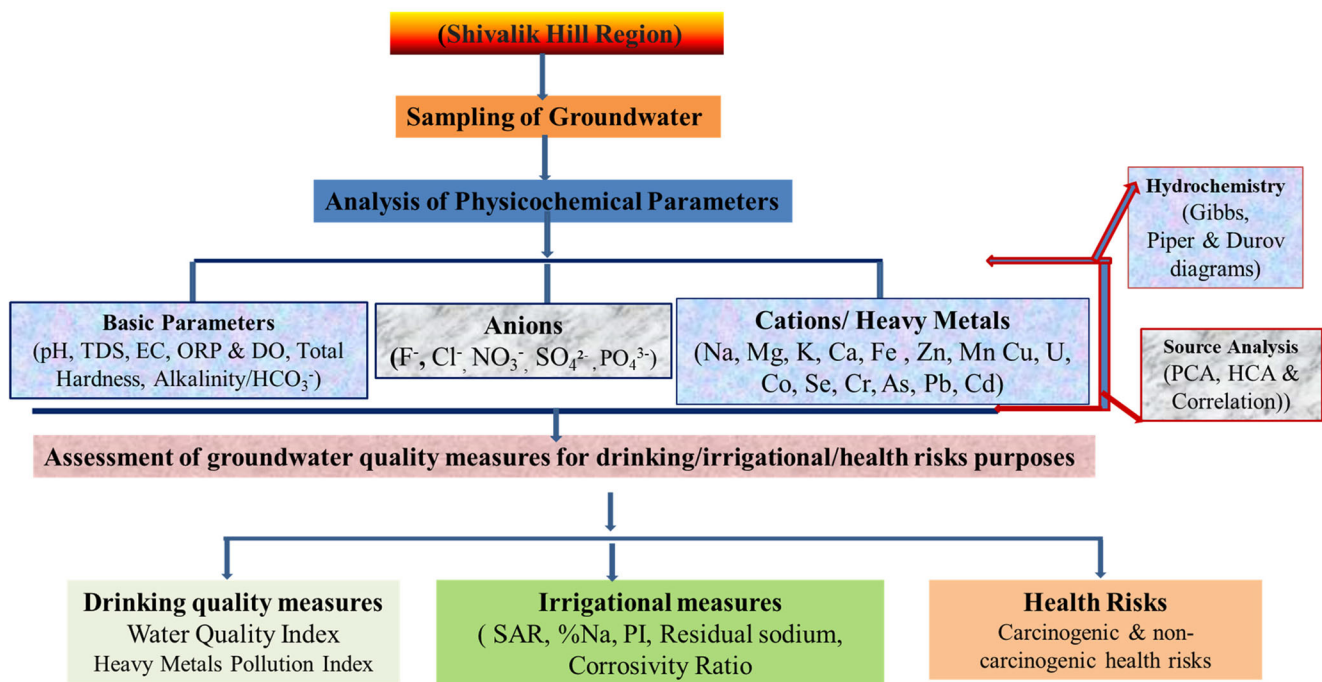


Fig. 1 Structure and methodology of the study

The sand and boulder have good groundwater potential due to their high porosity and permeability. On the other side, clay and silts are considered for poor groundwater potential due to their lesser permeability. Thus, sands and boulders relatively make good aquifers (Thakur et al. 2016). The aquifer system of the study area distributes into two parts such as southern

(Quaternary alluvial deposits) and northern parts (Shivalik formation, Intermontane Valleys and Kandi/Sirowal) (CGWB 2017). Unconfined to confined aquifer types exist in this study area. Groundwater occurs under the phreatic condition for the majority of the study area. At the northern part of the district area (intermontane valley), groundwater flow is

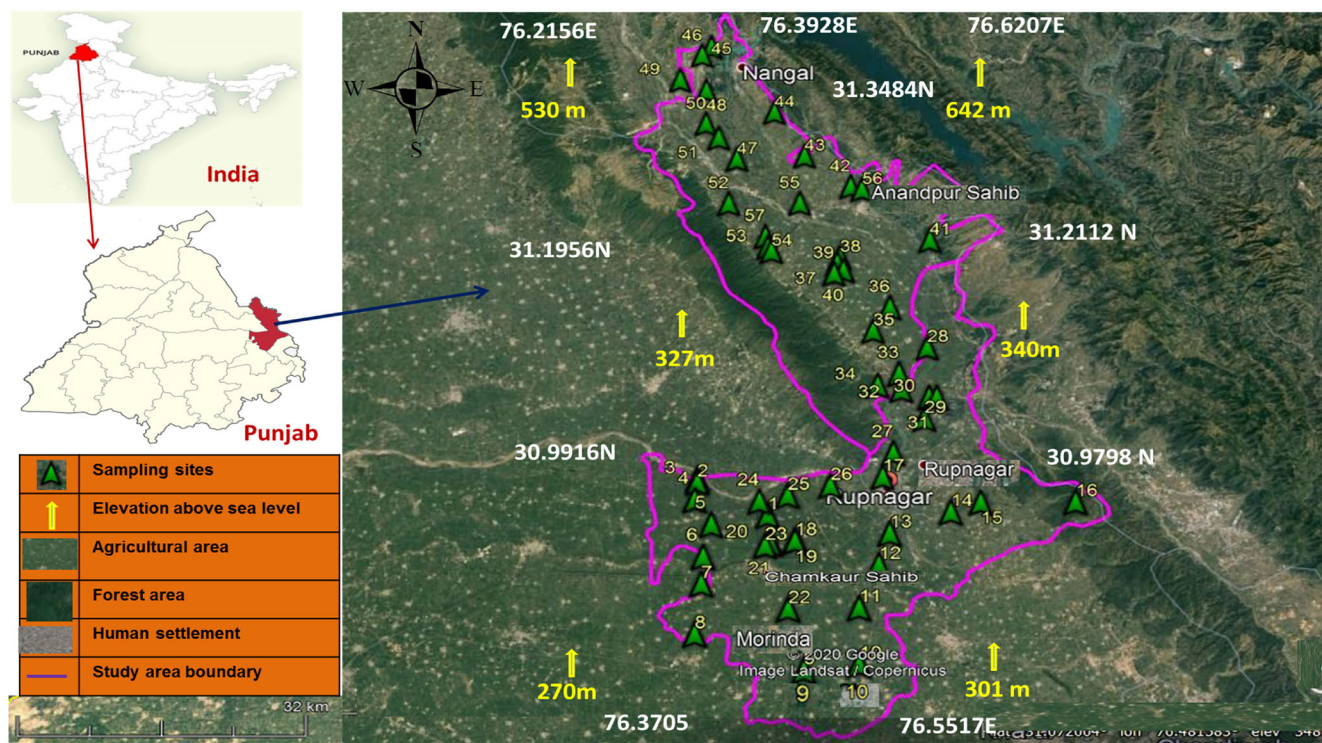
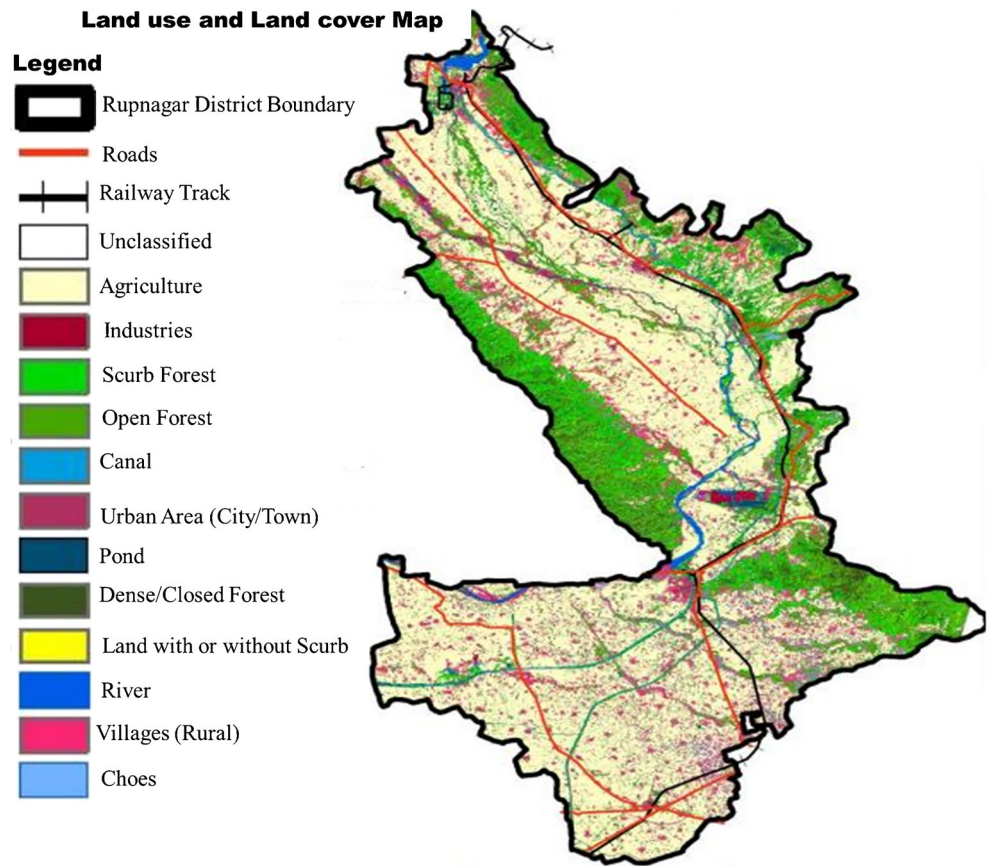


Fig. 2 Geographical locations of sampling sites of groundwater in Rupnagar district area

Fig. 3 Land use and land cover maps of Rupnagar district area, [Source: District survey report Rupnagar 2016, LISS III Data Multispectral (15th March 2016)]



towards the south and southeastern direction (Singh et al. 2011a). The depth of groundwater was observed 50 to 459 meters in this study area. The existing gross groundwater draft is 45,735 ham (hectare-meter) for all uses, whereas net annual groundwater availability is 41,947 ham. Approximately, 64232 tubewells are operated by farmers for irrigation purpose in the Rupnagar district. The groundwater discharges 731–1500 liters/min. Mostly 3 out of 5 blocks of the study area come under an overexploited region. Out of 5 blocks, 3 blocks (Chamkaur Sahib, Nurpur Bedi and Morinda) have exceeded the available recharge (> 100%) of the groundwater development stage. As per CGWB, the area suitable for artificial recharge in the district is 100 km², a sub-surface storage potential of 77 MCM (Million Cubic Meters). Around 102 MCM volume water would be required to recharge for this study area (CGWB 2017). The overall geography is summarized in Table 1.

Collection of groundwater sample and chemical analysis

In this study, grid-wise sampling was performed to better represent the study area and ensure the collection of at least one sample from each grid (6 × 6 km²). The groundwater samples were collected from 57 different locations in 1L

polypropylene bottles (pre-cleaned and washed with HNO₃ and DI water) during October 2018 after 3–5 min of flushing the groundwater (hand pumps, tube wells) of varying depths range 100–350 ft. Global positioning system (GPS Model: etrex 30x) was used to record sampling site's geographical coordinates and mapped using Google Earth Pro and ArcGIS 10.8 GIS software (Fig. 1). The detailed description of all 57 sampling locations with their geographical coordinates is provided in Table SM2.

The physicochemical characteristics (pH, TDS, EC, salinity, ORP and DO) of groundwater samples were immediately measured in situ by using HANA multi-parameter (Model HI9829). The samples acidified with ultrapure HNO₃ (pH < 2) immediately after collection in the field were used for major cations (Na, Mg, K, Ca) and heavy metals/trace elements analysis, while un-acidified samples were used for the estimation of major anions (F⁻, Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻) and other basic parameters (hardness, and alkalinity). All samples were properly labelled, shifted immediately to the laboratory in ice box, and then kept in the refrigerator at 4 °C for further analysis. Total hardness (as CaCO₃), alkalinity, bicarbonate (HCO₃⁻), and chloride (Cl⁻) were estimated by using APHA (2012) titration method. The concentration of F⁻, SO₄²⁻, NO₃⁻, and PO₄³⁻ were estimated using SPADNS, barium chloride turbimetric (IS 2003), UV-visible spectrophotometer and

Table 1 Overview of Rupnagar Nagar district

Parameters	Rupnagar Nagar ^a
Population	684627
Area (km ²)	1440
Agriculture area (km ²)	1400
Major towns	Ropar, Chamkaur Sahib, Anandpur Sahib and Nangal
Major industrial activities	Steel, copper plating
Elevation (in m asl)	275
Annual total groundwater Draft (Mm ³)	3444
Major and minor rivers	Sutlej and its tributaries
Minor rivers/rivulets	Tangauri Choi
Stratigraphy	Indo-Gangatic alluvium of Quaternary age and Shiwalik Hills range
Rock formations	River terraces, gravel beds, alluvial fans, calctufa beds, conglomerates, sandstones and claystones,
Major soil types	Reddish Chestnut and Tropical arid brown soil
Depth range (m) of groundwater	50-459
Aquifer type	Unconfined to confined
Depth of unconfined aquifer (m)	20-160
Depth of confined aquifer (m)	175-300
Existing Gross Groundwater Draft for All uses (ham)	45,735
Net Annual Groundwater Availability (ham)	41,947
Groundwater development	109%

^a CGWB 2017

stannous chloride method, respectively. The major cations and heavy metals/trace elements were estimated using flame photometer (Model Systronics 2180) and inductively coupled plasma mass spectrometry (ICP-MS; Thermo Scientific Model iCAPQc), respectively.

Quality control and quality assurance

Duplicates samples and replicated analyses of certified reference materials (CRMs; GBM303-4, MRGeo08) were performed for quality assurance (QA) and quality control

(QC). Analytical grades of all the chemicals (company - Lobachemie and Sigma-Aldrich) and Millipore ultrapure water were used to prepare reagents and standards. Standardization of ICP-MS was performed by using a successive dilution of ICP multi-element standard solution (Lobachemie UN NO-3264). The precision was within ± 5% for most of the elemental analysis. Uranium concentration was crosschecked by LED fluorometer model LF-2a (Manufacturer: Quantalase Enterprises Private Limited, Indore, India), based upon the fluorescence principle of U complexes in the aqueous sample (Rathore 2013).

Table 2 Parameters and constants for calculation of WQI and HPI (according to BIS guidelines)

WQI				HPI			
Parameters	BIS (2012) Acceptable limit (mg/L)	Weigh (w _i)	Relative weight (W _i)	Heavy metals/trace elements	BIS standard Limit (LDL)	BIS Max Limit (MPL)	Unit Weightage (w _i = 1/MPL)
pH	6.5–8.5	4	0.09756	As	10	50	0.02
TDS	500	4	0.09756	Cr	50	NR	0.02
Hardness	200	2	0.04878	Pb	10	NR	0.1
Bicarbonate alkalinity	200	3	0.07317	Cd	3	NR	0.3
Cl ⁻	250	3	0.07317	Fe	300	NR	0.0033
SO ₄ ²⁻	200	4	0.09756	Cu	50	1500	0.0006
NO ₃ ⁻	45	5	0.12195	Mn	100	300	0.0033
F ⁻	1	4	0.09756	Zn	5000	15000	0.00006
Ca ²⁺	75	2	0.04878	Se	10	NR	0.1
Mg ²⁺	30	2	0.04878	U	30*	60**	0.017
Fe	0.3	4	0.09756				
Mn	0.1	4	0.09756				
		w _i = 41	W _i = 1.00				

* indicate WHO limit of U, ** represent AERB limit

Water quality index

Water quality index (WQI) is a multiparametric water quality measure, which evaluate the groundwater suitability for drinking and domestic purposes. The WQI is calculated by using the method proposed by Ramakrishnaiah et al. (2009). In this drinking quality measure, weights assigned to each parameter according to their relative influence on water quality are presented in Table 2 (Ramakrishnaiah et al. 2009). In the first step of WQI, relative weights (W_i) are determined as per Eq. (1) (value is tabulated in Table 2).

$$W_i = \frac{w_i}{\sum_{i=0}^n w_i} \quad (1)$$

where ' w_i ' is the weights of each parameter, ' W_i ' is relative weights, and n indicates the number of parameters.

In the 2nd step, the quality rating scale q_i is calculated for each parameter by using Eq. (2):

$$q_i = \frac{C_i}{S_i} \times 100 \quad (2)$$

where q_i is the quality rating scale for each parameter, C_i is the concentration of i^{th} chemical parameter of water sample (mg/l), S_i is permissible standard for BIS (2012) i^{th} parameter of water as depicted in Table 2.

In the third step, subindex (SI_i - subindex of i^{th} parameter) is calculated as per Eq. (3) for each parameter.

$$SI_i = W_i \times q_i \quad (3)$$

In the last step, WQI is calculated as following Eq. (4):

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

Heavy metal pollution index

The cumulative influence of heavy metals/trace elements contamination of groundwater was determined by using the heavy metal pollution index (HPI) (Hossain and Patra 2020). The most influencing heavy metals/trace metals in groundwater were considered for the calculation of HPI as per the context of this study area (Table 2). The HPI was calculated following Eqs. (5) to (7). Subindex (Q_i) is determined in the first step as follows:

$$Q_i = \sum_{i=0}^n \frac{C_i - L_i}{M_i - L_i} \times 100 \quad (5)$$

where, C_i is the i^{th} metal concentration in a sample and, M_i and L_i are the maximum permissible limit (MPL) and lower desirable limit (LDL) of i^{th} parameter, respectively. The MPL and LDL values were represented in Table 2. After calculation of subindex (Q_i), HPI is calculated from Eq. (6), as follows:

$$HPI = \frac{\sum_{i=0}^n W_i Q_i}{\sum_{i=0}^n W_i} \quad (6)$$

where, W_i - the unit weight of i^{th} metal, Q_i - quality rating/sub-index value of i^{th} metal

Unit weight of i^{th} metal is calculated as follows:

$$W_i = \frac{1}{MPL} \quad (7)$$

Groundwater quality for irrigation purposes

The irrigational quality of groundwater was estimated by using different indices (Eqs. (8) to (12)) such as EC classification (Wilcox 1955), sodium adsorption ratio (SAR; Richards 1954), percent sodium (%Na; Wilcox 1955), permeability index (PI; Doneen 1964), residual sodium carbonate (RSC; Richards 1954), and corrosivity ratio (Wang et al. 2020; Zhou et al. 2020).

$$SAR = \frac{Na^+}{\frac{\sqrt{Ca^{2+} + Mg^{2+}}}{2}} \quad (8)$$

$$Na\% = \frac{(Na^+ + K^+) \times 100}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \quad (9)$$

$$PI (\%) = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+} \times 100 \quad (10)$$

$$\text{Corrosivity Ratio} = \frac{Cl^- / 35.5 + 2 (SO_4^{2-} / 96)}{2 (HCO_3^- + CO_3^{2-} / 100)} \quad (11)$$

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (12)$$

The concentrations of all used variables in irrigational indices from Eqs. (8) to (12) are expressed in meq L^{-1} . The SAR and corrosivity ratio are unitless indices and denoted as a factor.

Data analysis and mapping

The descriptive statistics of groundwater data were calculated by using Excel Microsoft Office (version 2010). Piper and Durov diagrams were plotted by using Geochemist's Workbench software (version 12). Pearson's correlation matrix (PCM), principal component analysis (PCA), and hierarchical cluster analysis (HCA) were performed by using SPSS software (version 20). Pearson's correlation analysis was performed to evaluate the relationship between groundwater quality parameters. PCA and HCA were performed to examine the contamination sources of groundwater (Wu et al. 2020b). The eigenvalue value-based varimax rotation method was performed for PCA extraction. Prior to PCA and HCA, the data was pretreated and autoscaled

with log-transformation. The GIS software ArcGIS (version 10.8) was used to map of drinking water quality indices in the study area. WQI, HPI, and the health hazard potential of carcinogenic and non-carcinogenic contaminants are mapped over the study area by using Kriging technique.

Potential health risks of groundwater contaminants

Human beings are exposed to groundwater, mainly through oral ingestion. Potential health risks of groundwater contaminants on residents are estimated quantitatively by carcinogenic and non-carcinogenic health risk assessment as per USEPA recommended equations Eqs. (13) to (16) (USEPA 1989). The present study assessed the health risks potential of carcinogenic contaminants for Cr, As, and Pb and non-carcinogenic contaminants for Fe, Cu, Zn, U, F⁻, and NO₃⁻ in term of cancer risk (CR) and hazard quotient (HQ), respectively. The ADI (average daily intake) value of water was considered mainly through ingestion mode (Eq. 13).

ADI (Groundwater Ingestion)

$$= [C \times IR \times EF \times ED] / [BW \times AT] \quad (13)$$

$$HQ = ADI / RfD \quad (14)$$

$$CR = ADI \times SF \quad (15)$$

where, C concentration of contaminants, IR ingestion rate (2 L water/day), EF exposure frequency (365 days/year), ED exposure duration (30 years), BW body weight (70 kg), and AT average time (25,550 days for carcinogenic risk and 10,950 days for non-carcinogenic risk). These values were considered in the context of the current study area (USEPA 2005; Kumar et al. 2020a, 2020b; Mittal et al. 2020).

USEPA determines the maximum permissible limits of daily oral exposure of toxic chemicals/substance/elements for human. The ADI and RfD are represented in mg/kg-day. SF stands to cancer slope factor and represented in (mg/kg-day)⁻¹. The values of RfD and SF were taken from USEPA IRIS (2020), Wongsasuluk et al. (2014), Anim-Gyampo et al. (2019), Kumar et al. (2020a, 2020b). The RfD values for carcinogenic contaminants As, Cr, and Pb are 3×10^{-4} , 3×10^{-3} , and 3.5×10^{-4} , respectively, while SF values are 1.5, 0.5, and 8.5×10^{-3} , respectively. The RfD value of non-carcinogenic contaminants such as Fe, Cu, Zn, U, F⁻, and NO₃⁻ are 0.7, 0.04, 0.3, 6×10^{-4} , 3×10^{-4} , 0.06, and 1.6, respectively. Hazard index (HI) is a cumulative influence of non-carcinogenic contaminants on human health through groundwater consumption as determined by USEPA (1989) Eq. (16).

$$HI = \sum HQ_i \quad (16)$$

where HQ_i is a non-cancer hazard quotient (HQ) for the ith contaminants

Results and discussion

Hydrochemical characteristics of groundwater

The results of chemical analysis of groundwater and their comparisons with BIS limit (2012) are summarized in Table 3. The majority of groundwater samples were slightly alkaline (mean pH 7.4) and fall within the BIS maximum allowable limit (pH 8.5) for drinking water. The alkaline nature of groundwater of this region has also been reported in previous studies of Singh et al. (2011a), Singh et al. (2014), and Sharma et al. (2019). The EC ranged from 246 to 2308 $\mu\text{S cm}^{-1}$ over study area. The TDS ranged from 172 to 1615 mg L^{-1} (mean value 515 mg L^{-1}) and was higher than the BIS acceptable limit in nearly 42% of samples. The groundwater of Rupnagar Nagar district has been classified as hard (121–180 mg L^{-1}) to very-hard water (hardness > 180 mg L^{-1}) (Kaur et al. 2017). The mean hardness was recorded 203 mg L^{-1} and 42% of samples surpassed the BIS acceptable limit (200 mg L^{-1}). The elevated concentration of total hardness indicates the intense leaching of lime containing agricultural chemicals and detergents to the district's groundwater table (Sharma et al. 2019). The alkalinity level exceeded the BIS drinking water acceptable limit (200 mg L^{-1}) in nearly 80% of the study area. The dominance of bicarbonate in groundwater is mainly influencing alkalinity level for this region.

The mean concentration of anions followed in the order of HCO₃⁻ (304 mg L^{-1}) > SO₄²⁻ (62.5 mg L^{-1}) > Cl⁻ (38.2 mg L^{-1}) > NO₃⁻ (13.2 mg L^{-1}) > F⁻ (0.78 mg L^{-1}) > PO₄³⁻ (0.18 mg L^{-1}). Except for HCO₃⁻, nearly 95% of groundwater samples were within the BIS/WHO acceptable limits of anions. Thakur et al. (2016) have also reported a similar range of anions concentration for this district. The order of mean concentrations (mg L^{-1}) of major cations was Na (44.2) > Mg (35) > Ca (22.5) > K (14). The concentration of Mg exceeded the BIS limit (30 mg L^{-1}) in 51% of sites among those cations. Thakur et al. (2016) have also made a similar observation of Mg (average Mg 36.4 mg L^{-1}) and Ca level (average Ca 47.4 mg L^{-1}) in this district. The high level of Mg and Ca reflects their major contribution to total hardness.

Assessment of heavy metals/trace elements concentrations

The mean concentration ($\mu\text{g L}^{-1}$) of heavy metals in groundwater varied in the order of Fe (615) > Zn (133) > Mn (31.4) > Cu (16.4) > U (6.25) > Se (3.23) > Cr (1.87) > Co (1.76) > As (1.48) > Pb (0.19) > Cd (0.07) (Table 3). The Fe content is predominant in groundwater with nearly 86% sites exceeded BIS acceptable limit (300 mg L^{-1}). Sharma et al. (2017) have also reported that Fe and Mn concentrations exceeded the BIS limit in 92% and 9% samples, respectively. Sharma et al. (2018) further reported elevated concentration of Fe in pre- (mean 860 $\mu\text{g L}^{-1}$) and post-monsoon (mean 2660 $\mu\text{g L}^{-1}$) at 11 sites of Rupnagar district. The concentration of Se exceeded the BIS/WHO limit (10 μg

Table 3 Hydrochemical characteristics of groundwater quality in Rupnagar district

Parameters	Units	(n- 57)			Limit		% of sample exceeding BIS permissible limit
		Range	Mean	SD	BIS 2012	WHO 2011	
pH		6.87–8.27	7.4	0.29	6.5–8.5	–	–
TDS	mg L ⁻¹	172–1615	515	256	500	–	42
EC	μS cm ⁻¹	246–2308	730	369	–	–	–
ORP	mV	126–184	162	14	–	–	–
DO	mg L ⁻¹	2.54–5.44	4.42	0.67	–	–	–
F ⁻	mg L ⁻¹	0.17–3.15	0.78	0.35	1	1.5	5
Cl ⁻	mg L ⁻¹	7.50–220	38.2	31	250	–	–
NO ₃ ⁻	mg L ⁻¹	0.5–251	13.2	34.4	45	–	5
SO ₄ ²⁻	mg L ⁻¹	3.32–263	62.5	54	200	–	3
PO ₄ ³⁻	mg L ⁻¹	BDL-1	0.18	0.21	-	–	-
Total hardness	mg L ⁻¹	65–400	203	77	200	–	42
Alkalinity/HCO ₃ ⁻	mg L ⁻¹	45–750	304	125	200	–	79
Na	mg L ⁻¹	2–108	44.2	30	–	–	–
Mg	mg L ⁻¹	3.2–82.8	35	18.7	30	–	51
K	mg L ⁻¹	0.18–180	14	27.7	–	–	–
Ca	mg L ⁻¹	12–36	22.5	5.4	75	–	–
Cr	μg L ⁻¹	0.21–11.94	1.87	1.88	50	50	–
Mn	μg L ⁻¹	0.21–201	31.4	46.5	100	–	11
Fe	μg L ⁻¹	121–1637	615	308	300	–	86
Co	μg L ⁻¹	0.03–45	1.76	8.17	–	–	–
Cu	μg L ⁻¹	0.6–123	16.4	22.2	50	2000	5
Zn	μg L ⁻¹	0.91–510	133	134	5000	–	–
As	μg L ⁻¹	0.07–10.8	1.48	1.95	10	10	2
Se	μg L ⁻¹	BDL-22.4	3.23	5.11	10	10	9
Cd	μg L ⁻¹	BDL -0.94	0.07	0.18	3	3	–
Pb	μg L ⁻¹	BDL-5.73	0.19	0.80	10	10	–
U	μg L ⁻¹	0.18–51	6.25	8.88	–	30*	2

Where *n* indicates the number of analyzed samples. * indicate WHO standard used for comparison in case of uranium. – indicates either data not available or 0%. *BDL* below detectable limit

L⁻¹) at 9% of sites. The concentration range of Se was BDL - 22.4 μg L⁻¹ in this district. The results are consistent with previous studies of Bajaj et al. (2011) and Dhillon and Dhillon (2016). The concentration of Cr (range 0.21–11.94 μg L⁻¹), Pb (BDL-5.73 μg L⁻¹), As (0.07–10.8 μg L⁻¹) Cd (BDL-0.94 μg L⁻¹), and U (0.18–51 μg L⁻¹) were less than their respective BIS/WHO limits in most of the samples. Sharma et al. (2017) reported groundwater As concentration in the range of 2.31–15.9 μg L⁻¹ at 11 sites of the district. Recently, Tiwari et al. (2020) also reported a similar level of As (6.64 μg L⁻¹) and Cr (1.81 μg L⁻¹) in the Rupnagar district.

Drinking water quality assessment based on WQI and HPI

WQI and HPI are the two very important measures to assess drinking water quality. The WQI ranges 1–50, 51–100, 101–

200, 201–300, and > 300 are categorized as excellent, good water, poor water, very poor water, and unsuitable water (Ramakrishnaiah et al. 2009). As shown in the spatial distribution map of WQI, most of the study area is under the ‘good water’ category (51–100) (Fig. 4(a)). Nearly similar range of WQI (51–100) was also reported by Singh et al. (2011a) and Chaudhry and Sachdeva (2020) for this study area. The HPI represents the cumulative influence of heavy metals on the overall quality of water. The HPI ranges represent 1–25 for excellent, 26–50 for good, 51–75 for poor, and 76–100 for very poor and > 100 for unsuitable water types (Vetrimurugan et al. 2017). The entire study area can be nearly classified as excellent HPI category (1–25) (Fig. 4(b)), indicating heavy metal contamination in groundwater is not a major concern for this study area. However, Fe concentration in groundwater of the district was mostly high, but, it was not so high to affect its overall quality. Presently, trace

amounts of As, Cr, and U in groundwater are not a threat, but need to be monitored regularly for the future.

Irrigation quality of groundwater

The EC classification depicted that nearly all groundwater samples were under good ($< 750 \mu\text{S cm}^{-1}$) to permissible category ($< 2000 \mu\text{S cm}^{-1}$), and only 2% of the samples fall under the doubtful category (Table 4). The SAR classification revealed that all the groundwater samples were in excellent category (< 10) for irrigation, indicating no alkali hazard to the crops. The SAR values also suggest no adverse impacts through exchangeable sodium in the entire study area (Thakur et al. 2016). According to Wilcox classification (Na%), most groundwater samples (95%) were found safe for irrigation purposes. The PI value was above 25% permeability at nearly all sites, indicating groundwater suitability for irrigational usages. However, 65% of sites under class II quality (25–75% permeability) reflect that most groundwater samples are marginally suitable for agriculture purposes. Based on the RSC classification of groundwater, 54%, 28%, and 18% of samples fallen under good, doubtful, and unsuitable categories, respectively. The corrosivity ratio of 88% groundwater samples was less than 1, reflecting safe transportation through pipes. However, nearly 12% of groundwater samples were not safe (corrosivity ratio > 1) for transportation purposes through pipes.

Groundwater hydrochemistry

Gibbs, Piper, and Durov diagrams were used to understand the groundwater hydrochemistry (Figs. 5 and 6; Sahoo et al. 2019). The results of these diagrams are well corroborated to each other. Gibbs diagram (Gibbs 1970) (Fig. 5) illustrates that rock-water interaction is the main factor influencing major ions chemistry. Carbonate, silicate, weathered lime, dolomitic limestone, Charnockite, sandy, and silty alluvium are reported as the major rocks types of this region (Singh et al. 2014; Thakur et al. 2016). Weathering of these rocks releases chemical ions species in groundwater. The study of Thakur et al. (2016) also suggests the role of carbonate weathering in groundwater chemistry for this district. Rupnagar district is a hilly region with the dominance of carbonate rocks (dolomitic limestone and weathered lime). Weathering of carbonate rocks during the rainy season may cause groundwater's alkaline character (Singh et al. 2011b). Weathering of carbonate minerals is responsible for an elevated level of HCO_3^- ions in groundwater (above than BIS limit) of the study area (Rao et al. 2017).

Further, both Piper and Durov diagrams also give information about the geochemical evolution and origin of groundwater with classifications of different water types (He and Li 2020). The Piper plot demonstrated that most groundwater

samples fell under Ca-HCO_3^- field, followed by Ca-Mg-Cl^- and Ca-Cl^- types (Fig. 6(a)). Similar findings for this study area were also reported by Thakur et al. (2016). Further, most samples are located under Mg^{2+} and HCO_3^- field in Piper plot, thus recognized as the major cation and anion, respectively. After HCO_3^- , SO_4^{2-} are recognized as the 2nd abundant ions in groundwater. Durov diagram also shows similar findings as observed Mg^{2+} and HCO_3^- are major cation and anions, respectively (Fig. 6(b)). Durov diagram also reveals that most groundwater samples have a TDS less than 1000 mg L^{-1} in which HCO_3^- was the main anion. Both Piper and Durov plots indicate the dominance of Ca, Mg, and HCO_3^- in groundwater. The Ca/Mg ratio of the majority of the samples was < 1 . This indicates the contribution of calcite weathering to the existence of Ca and Mg in groundwater. Furthermore, the molar ratio of Na/Cl was > 1 , indicates dominancy of silicate weathering (Singh et al. 2011b). The molar ratio of $\text{Ca/SO}_4^{2-} > 1$ in 52% samples and $\text{Ca/SO}_4^{2-} < 1$ in 48% samples indicate dissolution of dolomite and precipitation of calcite, respectively. Hence, these minerals are the major sources of Ca in the study area (Singh et al. 2014). These findings suggest that major ions dissolution has existed in this region's groundwater through the natural geogenic process (Thakur et al. 2016). The detailed impacts of natural lithology and the influence of anthropogenic practices have been assessed by multivariate analysis in the next section for the major existing contaminants in groundwater.

Source analysis of heavy metals/trace element and anions

The sources apportionment pattern of groundwater contaminants was analyzed using multivariate analyses (PCA, HCA and PCM). The PCA components were extracted based on eigenvalue > 1 (Li et al. 2019a). In the PCA analysis, four principal components (PC) were extracted for groundwater characteristics with 50% of the total variance (Table SM3). Subsequently, cluster (dendrogram) and PCM analysis (Table 5) were performed for the reliability of PCA and more specific detection of sources/origins along with their association for groundwater contaminants (Fig. 7).

The PC1 shows high loading of Na, Mg, Cl, F, HCO_3^- , PO_4^{3-} , and SO_4^{2-} with 17.45% variance and their occurrence in the same cluster, suggests their common origin and co-existence. The PC1 components showed partial to moderate correlation between them ($r = 0.13$ to 0.48). The major sources of all PC1 components are suggested to be geogenic. The positive association of SO_4^{2-} with EC, TDS, and Cl ($r = 0.24$ to 0.48) indicates that geogenic activities such as weathering of gypsum and silicate bearing rocks may release SO_4^{2-} to groundwater (Sharma et al. 2017). The dissolution of

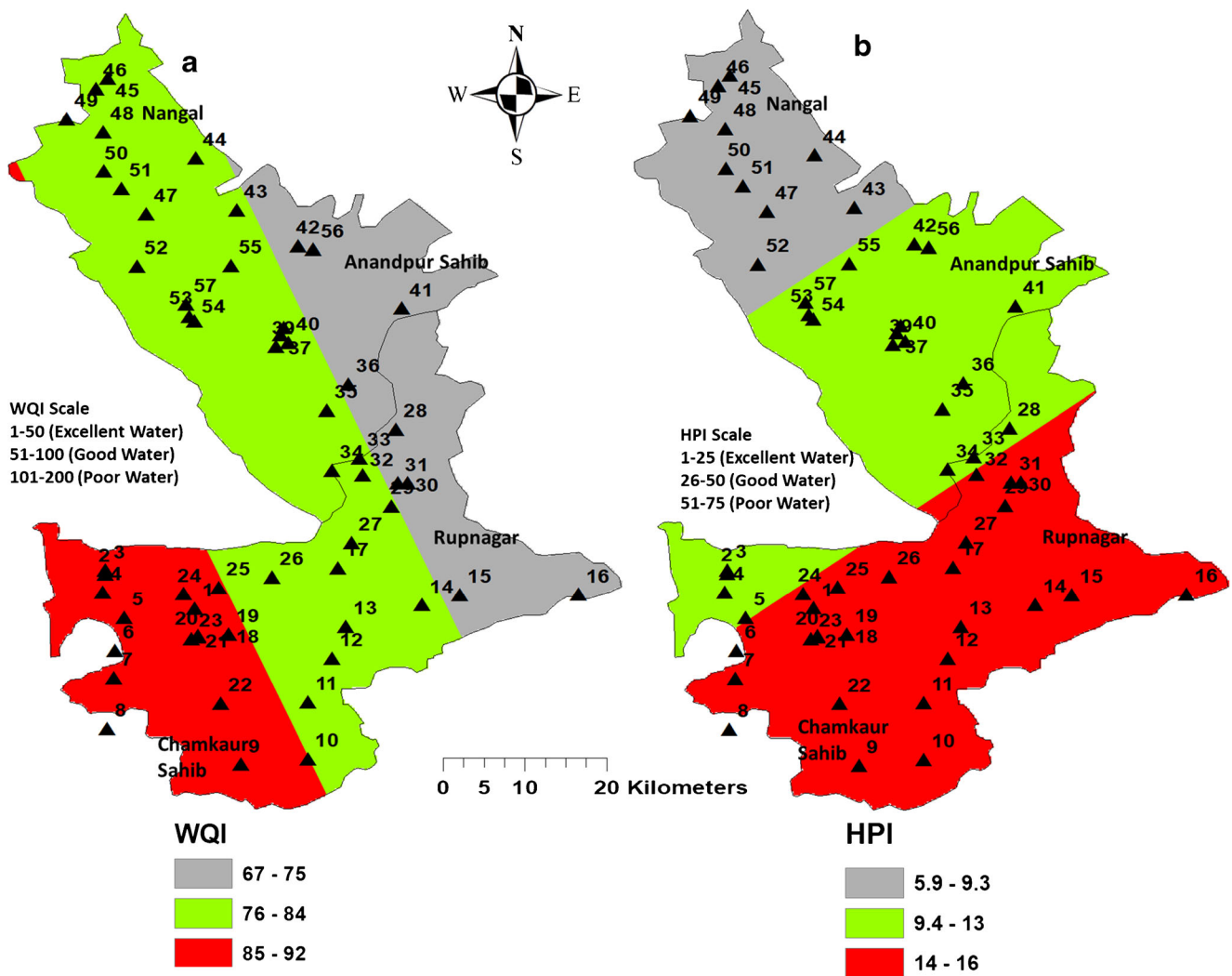


Fig. 4 Spatial distribution maps of groundwater quality measures (a) WQI, (b) HPI, over the study area

F^- bearing minerals in an alkaline environment (biotites, fluorite, granite, mica, topaz) is probable source for the existence of F^- in groundwater (Singh et al. 2011b; Rasool et al. 2018; Li et al. 2014, 2019b). The interactions of underground rocks like schists, quartzites, and granites with water in an alkali environment are major sources suggested being the season for Na enrichment in groundwater (Singh et al. 2014). The ratio of $SO_4^{2-}/Cl^- > 1$ indicates fertilizers and effluents are additional sources of SO_4^{2-} in this region (Lee and Song 2007; Egbi et al. 2020).

The PC2 shows high loading of As, Cr, Co, Cu, and K (variance - 13%), clustered together. The moderate positive correlation between these elements ($r = 0.31$ to 0.62) indicates a similar origin. The anthropogenic activities such as excessive use of agrochemicals, cement factories, coal fly ash from the thermal power plant are likely the major sources of these heavy metals/trace elements in groundwater (Sharma et al. 2019). The study area has plants of agrochemicals, cement factories, coal, and thermal power.

The presence of PC3 (Ca, Mn, and Zn) with 10% variance is mainly attributed as their natural origins. These elements also clustered together and show partial to the moderate association ($r = 0.14$ to 0.66). The strong association between Mn and Zn ($r = 0.66$) indicates a common source. The geogenic processes such as weathering of manganese-bearing rocks in deeper layers of earth and partial influence of anthropogenic sources (leaching of fly ash released by a thermal power plant) may be the major source of Mn in groundwater (Sharma et al. 2017). The gypsum dissolution and precipitation of calcite are suggested to the major sources of Ca (Singh et al. 2014). The alkaline and calcareous nature of soils can be attributed to a low concentration of Zn in groundwater for this study area (Sharma et al. 2018).

The PC4 has a high loading of Fe and Se (variance 9.3%) with partial to moderate correlation ($r = 0.18$ to 0.48), which indicates their common origin and existence. Selenium sources are strongly regarded as geogenic, and no anthropogenic sources are suggested (Bajaj et al. 2011). The rainwater

Table 4 Classification of groundwater samples of Rupnagar district for suitability of irrigation

Irrigation groundwater quality Parameters	Groundwater classification	Classification range	% of samples in post-monsoon
EC ($\mu\text{S cm}^{-1}$) Wilcox 1955	Excellent	< 250	5
	Good	250–750	74
	Permissible	750–2000	19
	Doubtful	2000–3000	2
	Unsuitable	> 3000	0
Alkalinity hazard (SAR) (Richards 1954)	Excellent	< 10	100
	Good	10–18	0
	Doubtful	18–26	0
	Unsuitable	> 26	0
Percent sodium (%Na) (Wilcox 1955)	Excellent	< 20	23
	Good	20–40	47
	Permissible	40–60	25
	Doubtful	60–80	5
	Unsuitable	> 80	0
Permeability Index (PI) (Doneen 1964)	Suitable for Irrigation	Class I: > 75% permeability	35
	Marginally suitable for irrigation	Class II: 25-75% permeability	65
	Unsuitable for irrigation	Class III: < 25% permeability	0
Residual sodium carbonate (Richards 1954)	Suitable for Irrigation	< 1.25	54
	Marginally suitable for irrigation	1.25-2.5	28
	Unsuitable for irrigation	> 2.5	18
Corrosivity Ratio (Raman 1985)	Safe	< 1	88
	Unsafe	> 1	12

dilution and movement of Se-bearing rocks and sediments in the Shivalik Hills region are possible sources for Se in groundwater for this region (Dhillon and Dhillon 2014, 2016). Dhillon and Dhillon (2014) have reported Se content in rock

samples of lower ($1864\text{--}2754 \mu\text{g kg}^{-1}$) and upper Siwalik sub-Himalayan ranges ($11\text{--}847 \mu\text{g kg}^{-1}$). The majority of soils in this district are alkaline, promoting Se-species' mobility (Eiche et al. 2015). The major source of Fe has been reported

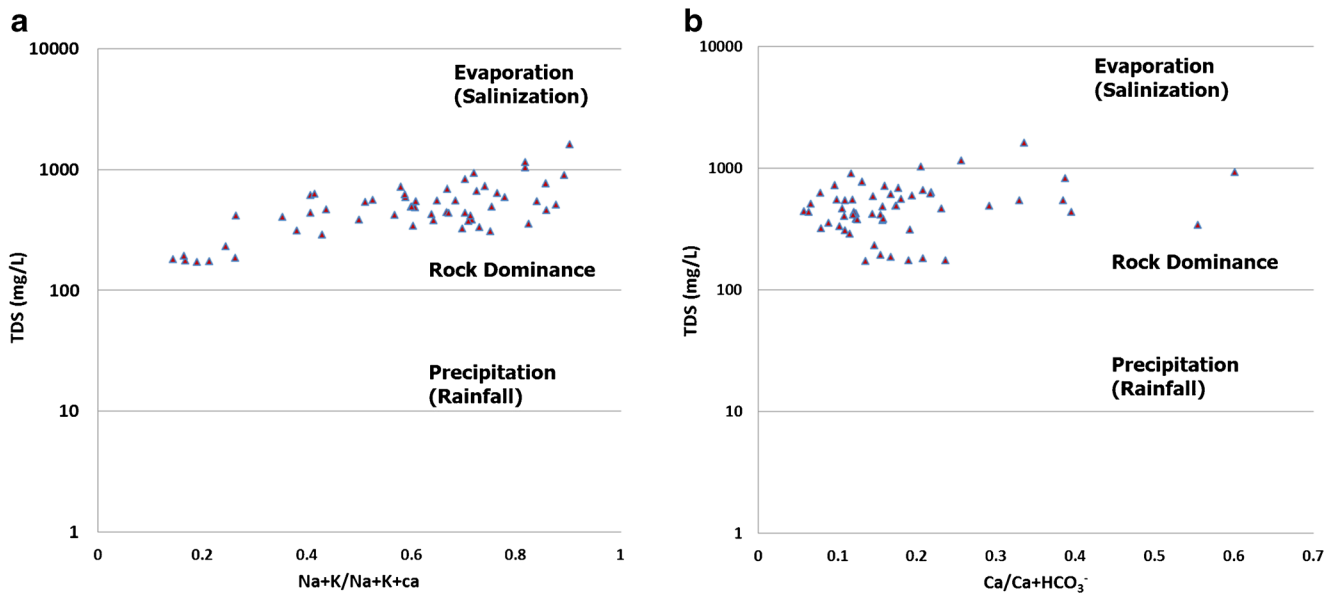


Fig. 5 Gibbs diagram for groundwater hydrochemistry of Rupnagar district: (a) TDS vs. $\text{Na}+\text{K}/(\text{Na} + \text{K} + \text{Ca})$ for cations, (b) TDS vs. $\text{Cl}/(\text{Cl}+\text{HCO}_3^-)$ for anions

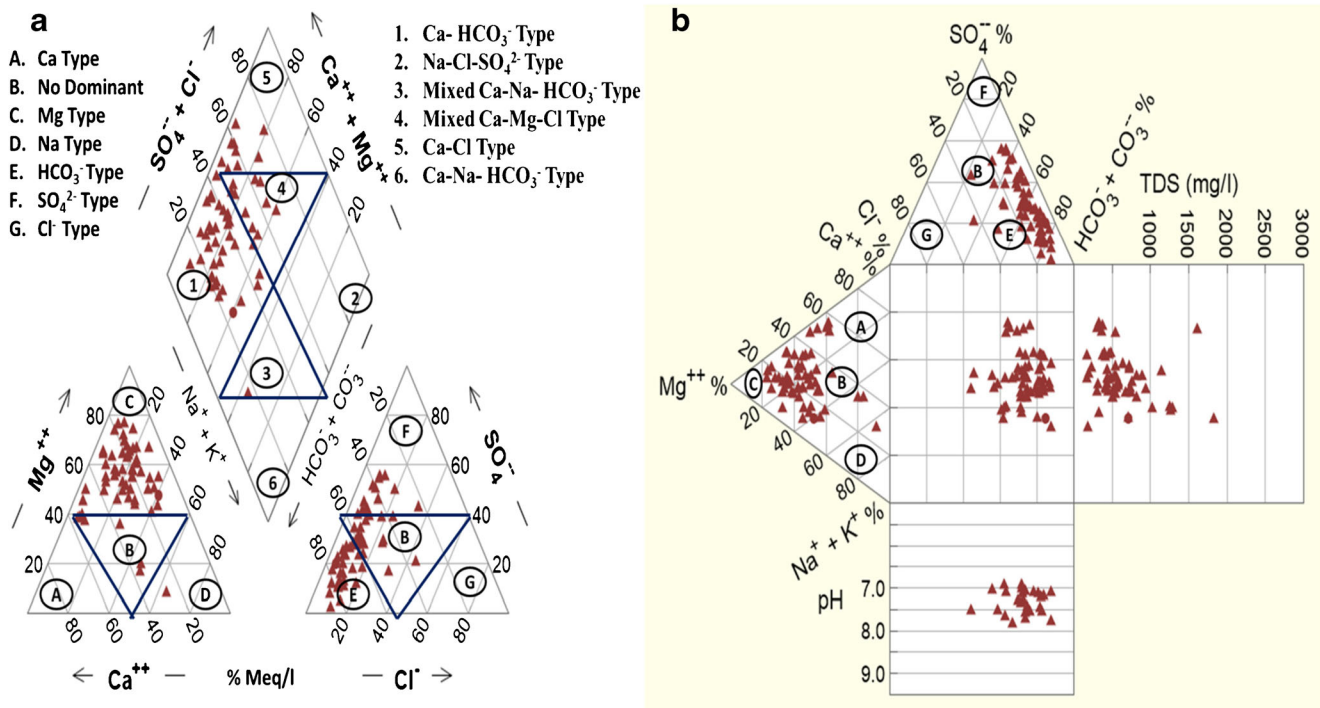


Fig. 6 Assessment of groundwater hydrochemistry plots (a) Piper plot, (b) Durov diagram

as Fe-bearing minerals like ferruginous quartzite, pyrites, and goetheite (Singh et al. 2011b; Sharma et al. 2018) for this region. Cd and Pb's location in the same cluster indicates their concurrent existence and may release through coal fly ash, as suggested by Sharma et al. (2019).

Health risk potential of groundwater contaminants

The health risks of drinking groundwater (carcinogenic and non-carcinogenic) on Rupnagar district residents have been presented in Table 6. The mean ADI value of contaminants via ingestion of groundwater was in order of $\text{NO}_3^- > \text{F}^- > \text{Fe} > \text{Zn} > \text{Cu} > \text{U} > \text{Cr} > \text{As} > \text{Pb}$. The mean carcinogenic risk potential of groundwater contaminants followed in the order of $\text{Cr} > \text{As} > \text{Pb}$. The majority of the area is under very low (10^{-6}) to low (10^{-5}) carcinogenic risks potential of As and Cr (Fig. 8). Sharma et al. (2017) have also reported the probability of 438 cancer cases/lakh in the district due to As ingestion through drinking water in a study of 11 sites of this study area, which is significantly higher than the USEPA limit (1cases for every 1,000,000). The study further described that local people has also been exposed to low risks of As through rice grain ingestion. The high-risk potential of Cr through groundwater consumption (mean $\sim 1\text{E}-03$) has also been reported by Sharma et al. (2019) at a few Ropar wetland sites. Sharma et al. (2018) has reported Cr presence in wheat grains, rice grains, mustard seeds, and maize grains for

this area. The health risk of Pb was not observed at any site in the entire district.

Further, the mean risk potential of non-carcinogenic contaminants (mean HQ) via oral groundwater ingestion was estimated in the order as $\text{F}^- (0.37) > \text{U} (\sim 0.28) > \text{NO}_3^- (0.23) > \text{Fe} (0.025) > \text{Cu} (0.011) > \text{Zn} (0.01)$. The non-cancerous contaminants were within the health risk limit ($\text{HQ} > 1$) in the majority of sites of this district (Table 6). The HI value of non-carcinogenic chemicals was < 1 (i.e., 0.93), indicating that cumulative health impacts through drinking of all non-carcinogenic chemicals are alarming, and currently do not pose any significant health risks to residents. Distribution maps (Fig. 8) show the majority of the area is at very low carcinogenic risk. In the case of non-carcinogenic risks, the majority of the area is below USEPA health risks limit (HI-1). However, a high risk of non-carcinogenic chemicals was observed near Nangal block, while carcinogenic risks were observed higher in some areas of Chamkaur Sahib Block.

Comparison of groundwater quality of Shivalik and other regions of Punjab

The groundwater quality of this district is relatively safe compared to many other parts of Punjab. Recently, we examined the groundwater quality in different geographical regions of Punjab such as Sutlej basin (Kumar et al. 2020a, 2020b), Shivalik Hill range (Mittal et al. 2020) and associated parts of Tosham hill region (Kumar et al. 2020a). The U concentration followed a decreasing trend as it passes through the

Table 5 Pearson correlation matrix among groundwater quality parameters of Ruppangar district

	pH	TDS	EC	ORP	HCO ₃ ⁻	Hardness	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	PO ₄ ³⁻	Na	Mg	K	Ca	Cr	Mn	Fe	Co	Cu	Zn	As	Se	Cd	Pb	U	
pH	1.00																										
TDS	-0.55	1.00																									
EC	-0.54	0.98	1.00																								
ORP	-0.52	0.43	0.41	1.00																							
HCO ₃ ⁻	-0.13	0.51	0.49	0.21	1.00																						
Hardness	-0.40	0.63	0.60	0.54	0.32	1.00																					
F ⁻	0.00	0.22	0.22	0.01	0.13	0.11	1.00																				
Cl ⁻	-0.20	0.68	0.68	0.14	0.25	0.53	0.21	1.00																			
NO ₃ ⁻	-0.18	0.05	0.02	0.07	0.18	0.10	-0.24	0.01	1.00																		
SO ₄ ²⁻	-0.30	0.48	0.46	0.01	0.24	0.37	0.30	0.43	0.15	1.00																	
PO ₄ ³⁻	0.07	0.25	0.21	0.19	0.30	0.20	0.12	0.43	-0.02	0.28	1.00																
Na	-0.30	0.76	0.75	0.23	0.49	0.34	0.19	0.47	0.03	0.15	0.13	1.00															
Mg	-0.42	0.61	0.60	0.62	0.31	0.97	0.11	0.48	0.08	0.30	0.17	0.37	1.00														
K	-0.35	0.45	0.47	0.10	0.40	0.11	0.08	0.34	0.15	0.42	0.20	0.32	0.13	1.00													
Ca	0.03	-0.13	-0.18	-0.19	-0.21	0.02	-0.04	-0.01	0.03	0.09	-0.08	-0.35	-0.16	-0.21	1.00												
Cr	-0.25	0.29	0.34	0.25	0.11	0.14	0.19	0.29	0.01	0.25	0.23	0.22	0.14	0.35	0.05	1.00											
Mn	-0.18	0.19	0.17	-0.01	-0.02	0.08	-0.01	0.00	-0.09	0.22	-0.11	0.06	0.03	0.21	0.15	-0.03	1.00										
Fe	-0.11	-0.09	-0.09	-0.03	0.06	-0.10	0.00	-0.10	-0.03	0.01	0.15	-0.16	-0.06	0.19	0.04	0.12	0.30	1.00									
Co	-0.33	0.17	0.17	-0.08	0.08	-0.07	0.08	0.06	0.07	0.24	0.02	0.24	-0.08	0.43	0.02	0.38	0.48	0.45	1.00								
Cu	-0.17	0.05	0.07	-0.07	-0.09	-0.11	-0.04	0.00	0.10	-0.04	-0.09	0.24	-0.11	0.31	-0.05	0.35	0.24	0.16	0.62	1.00							
Zn	0.09	-0.02	-0.02	-0.20	-0.06	-0.04	-0.06	0.01	-0.05	0.05	-0.08	-0.01	-0.13	-0.18	0.32	0.03	0.66	0.04	0.27	0.26	1.00						
As	-0.08	0.02	0.06	-0.10	0.02	-0.21	-0.06	0.15	0.15	-0.01	0.15	0.21	-0.15	0.32	-0.20	0.35	-0.27	0.14	0.38	0.38	-0.33	1.00					
Se	-0.17	0.05	0.04	0.12	-0.03	-0.09	0.13	-0.03	-0.04	0.06	0.16	0.16	-0.01	0.09	-0.43	-0.07	0.06	0.22	0.36	0.04	-0.07	0.05	1.00				
Cd	0.06	-0.01	0.01	-0.15	0.08	0.00	-0.05	-0.02	0.18	-0.13	-0.21	0.17	-0.06	-0.19	0.24	0.10	0.09	-0.02	0.18	0.23	0.36	0.03	-0.24	1.00			
Pb	0.01	-0.14	-0.10	-0.16	-0.08	-0.03	-0.11	0.02	0.01	-0.06	0.00	-0.25	-0.11	-0.09	0.36	0.04	-0.04	0.17	0.13	0.13	-0.03	0.06	0.00	0.13	1.00		
U	-0.01	0.18	0.18	-0.13	0.13	0.23	0.13	0.10	0.09	0.10	-0.33	0.28	0.21	0.21	0.07	0.02	-0.08	-0.27	0.00	0.23	-0.13	0.08	-0.28	0.20	-0.18	1.00	

Bold at significance level $p \leq 0.05$

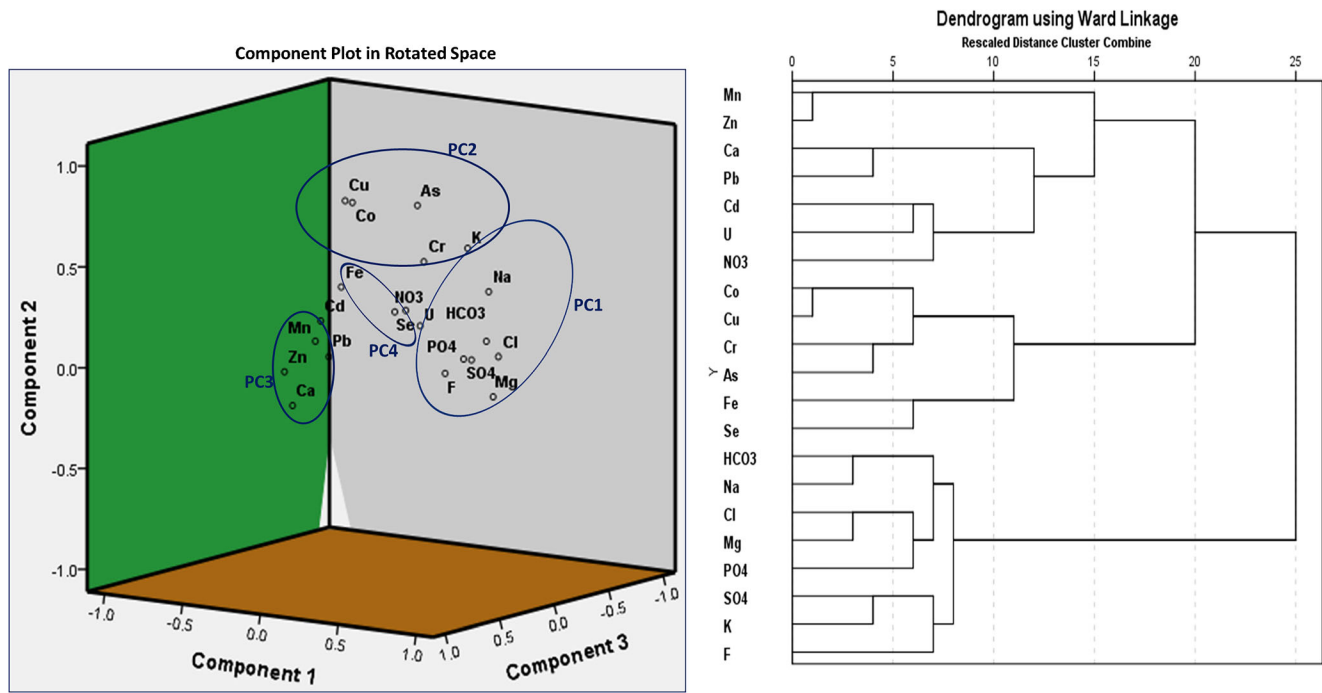


Fig. 7 Principal component and cluster analysis of selected water quality parameters in groundwater samples of Rupnagar district

southward to northward part of Punjab. A similar observation was also reported by Shrivastava (2015). Comparison with Tosham hill region that associated with parts of Bathinda and Barnala district (Hundal and Khurana 2013; Bajwa et al. 2017; Kumar et al. 2020a), the Shivalik region is less affected by other toxic contaminants As, U, F⁻, and NO₃⁻ (Thakur et al. 2016; Sharma et al. 2019; Mittal et al. 2020). The other studies in Shivalik region (Hoshiarpur, Kapurthala, Jalandhar, Rupnagar, and SBS Nagar districts) have also been reported concentration of F⁻, SO₄²⁻, As, Fe, Cu, Zn, Cr, Pb, and U in groundwater is within the BIS/WHO drinking water limit (Singh et al. 2011b; Krishan et al. 2014; Lapworth et al. 2017). The similar inference was made from in Shivalik region of state Himachal Pradesh (Dev and Bali 2019) and Uttarakhand (Kumar et al. 2017). However, industrial and agricultural activities in a few locations may have altered groundwater quality in some areas of Shivalik region (Singh et al. 2010; Bhutiani et al. 2017). Moreover, a higher Se level has been reported in the northern Shivalik hill region than

other Punjab parts due to Se enriched rocks in the district (Bajaj et al. 2011; Dhillon and Dhillon 2016).

Conclusions

The groundwater of the Shivalik region in Sutlej basin is alkaline in nature and water type Ca-HCO₃⁻ exists predominantly. The level of Fe, Mn, and Se in groundwater exceeded the BIS standard on 86, 11, and 9% sites, respectively. The groundwater quality is found to be suitable for both drinking and agricultural purposes. The carcinogenic contaminants As and Cr may pose low category risks (1 in 1,00,000 person) to the residents. The cumulative exposure of non-carcinogenic contaminants (HI-0.93) is alarming and is at the boundary line of USEPA limits (HI-1). Both natural and anthropogenic sources contribute anions and heavy metals/trace elements in groundwater. Multivariate analyses indicate that Fe, Mg, Mn Se, and SO₄²⁻ are of geogenic origin majorly and

Table 6 Risks assessment of carcinogenic and non-carcinogenic contaminants through groundwater ingestion in Rupnagar district

	Carcinogenic chemicals			Non-carcinogenic chemicals					
	Cr	As	Pb	Fe	Cu	Zn	U	F ⁻	NO ₃ ⁻
Mean ADI	2.2E-05	1.8E-05	1E-06	0.017	5E-04	0.004	2E-04	0.022	0.38
Range ADI	2.5E-06-1E-04	8E-07-1E-04	0-2.6E-05	0.003-0.046	2E-05-0.003	3E-05-0.014	1E-05-0.001	0.005-0.09	0-7.17
Mean health risk	1E-05	2.7E-05	9E-09	0.025	0.011	0.01	0.28	0.37	0.23
Range health risk	1.2E-06-7.3E-05	1.2E-06-2E-04	1E-10-2E-07	0.005- 0.067	4E-04-0.09	9E-05-0.05	0.008-2.43	0.07-1.5	0-4.48

HI (hazard index) value for non-carcinogenic chemicals – 0.93; ADI - Average Daily Intake

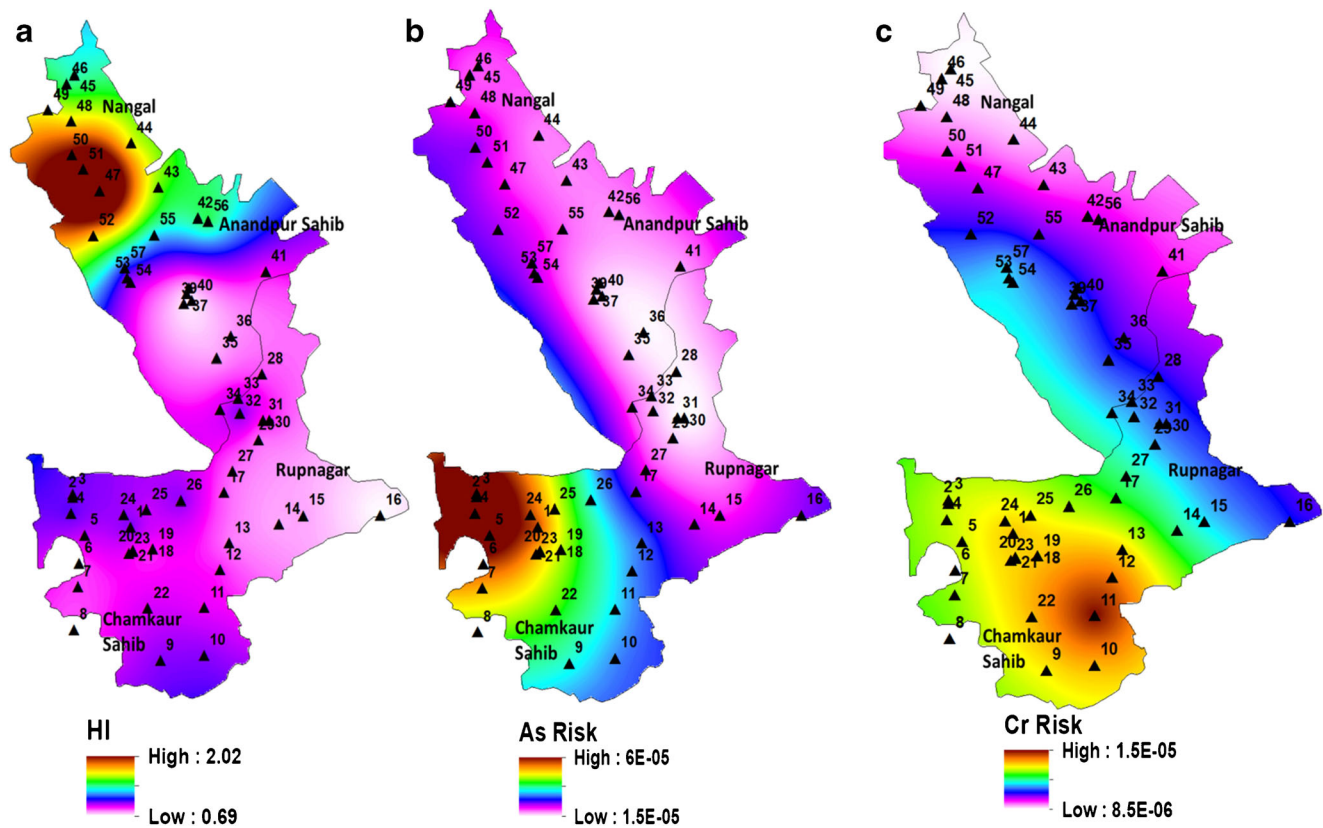


Fig. 8 Maps illustrating the potential carcinogenic risks of non-carcinogenic risks (cumulative) (a) HI, and carcinogenic risks of, (b) As, (c) Cr, through ingestion of groundwater in Rupnagar district

anthropogenic sources contribute NO_3^- , Cu, and Cr to groundwater. The overall assessment suggests the groundwater quality in the Shivalik region is relatively safe, as compared with other parts of Punjab. However, existence of trace amount of As, Cr, and U in groundwater is like an alarm for future.

Thus, continuous groundwater quality monitoring along with proper management of groundwater with strict regulations is essential for maintaining groundwater sustainability for Shivalik region. The findings of the current study can be used to fulfill the United Nations target of sustainable development goals 2030 agenda (SDG 2030). In future work, source analysis of major toxic contaminants of groundwater should be well established.

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Author contribution Sunil Mittal and Ravishankar Kumar have designed and performed the experimental/research work, as well as written the manuscript. Prafulla Kumar Sahoo and Sunil Kumar Sahoo were involved in the interpretation of data and statistical analysis and also helped to review and edit the manuscript. Raghavendra Prasad Tiwari was involved in data analysis, and manuscript editing works.

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Data availability All data set used in the current manuscript is original. The corresponding author has all raw data of the manuscript and related experiments; it can be provided as a reasonable request.

Code availability Not applicable.

Declarations

Ethics approval Not applicable to this research work.

Consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The authors declare no competing interests.

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