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RESEARCH ARTICLE



# Hydrogeochemical characterization, multi-exposure deterministic and probabilistic health hazard evaluation in groundwater in parts of Northern India

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## ABSTRACT

This work attempts to identify the latent factors controlling the hydrogeochemistry and assess the groundwater quality and associated health risks in the intermontane valley of Nalagarh in the sub-Himalayan zone in northern India. Analytical results of 64 groundwater samples, 32 each collected during pre monsoon and post monsoon seasons show contrasting results for their major chemical constituents. During pre monsoon period, only 3% of the samples exceed their permissible limits for pH, EC, TH and  $Mg^{2+}$ , while during post monsoon period, different parameters, such as TH,  $Mg^{2+}$  and  $K^+$ , exceed their limits by 9, 16, and 3%, respectively. Gibbs and Piper diagrams reveal that groundwater chemistry is mainly controlled by water-sediment (alluvial) interaction. Geochemical signatures and saturation index (*S<sub>i</sub>*) further indicate that the weathering and dissolution of silicate, calcite and dolomite minerals mainly contributed to dominance of  $Ca^{2+}$ ,  $Mg^{2+}$  and  $HCO_3^-$  ions in the aquifers. Monte Carlo simulation ascertains non-carcinogenic health risks due to  $NO_3^-$  and  $F^-$  in different sub-population groups. Deterministic and probabilistic estimates of these parameters via ingestion and dermal routes confirm their percentage hazard toxicity in the order infants (58.38; 39.62%) >children (15.62; 15.85%) >teens (6.25; 2.73%) >adults (6.25; 1.90%) for pre monsoon. The hazard toxicity for deterministic study implies only on infants (9.38%), whereas, the probabilistic simulation extracted the health risk on infants (6.57%), and children (0.58%) during post monsoon. Minor populations with their lower body weights are more vulnerable to groundwater pollution due to greater consumption of liquid diet. Therefore, treated groundwater is strongly recommended to mitigate health morbidities linked with the non-cancerous risks.

## ARTICLE HISTORY

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## KEYWORDS

Groundwater quality; geochemical signature; saturation index; health risk; Monte Carlo simulation sensitivity analysis

## 1. Introduction

Groundwater is an indispensable freshwater resource used for multiple activities supporting about two-thirds of the global population (Wang *et al.* 2020, Selvam *et al.* 2021, Gao *et al.* 2022). More than one billion people living in countries like India, China, Pakistan, Bangladesh, and Nepal heavily rely on groundwater for their needs (Gleeson *et al.* 2012, Li *et al.* 2014, Adimalla and Wu 2019). India's rapid groundwater development pace fulfills the water demand by ~50% urban and semi-urban drinking water, and ~85% rural domestic and irrigation supply (Jain and Vaid 2018, Singh *et al.* 2020b). The quality of groundwater plays a vital role in the socio-economic development, agricultural sector, and importance to

the human health perspective (Li *et al.* 2019a, Aravinthasamy *et al.* 2021). The alluvial aquifers developed along the foothills slope are more propensities to contamination due to numerous human interventions, namely urbanization, agricultural expansions, mining, and industrial activities (EPA 1993, Naik *et al.* 2008, Herojeet *et al.* 2016, Radfard *et al.* 2019). The groundwater quality of alluvial foothill zones is significant because of the strongly influenced by hydro-geological and physiographic setup, climatic and anthropogenic factors (Rajkumar *et al.* 2020). Some of the natural inputs impacting the groundwater chemistry are ion exchange, weathering and dissolution of rock minerals, litho-water interaction, and atmospheric transports (Li *et al.* 2018a, b, Karunanidhi *et al.* 2020;

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Singh *et al.* 2020a). Therefore, groundwater quality monitoring is necessary for sustainable water management to prevent over-exploitation and quality deterioration (Herojeet *et al.* 2013, Dolma *et al.* 2015, Tiwari *et al.* 2018).

In India, groundwater is often used directly for different purposes without proper treatment due to lack of awareness, and necessary economic and technological limitations (Madhav *et al.* 2018, Rao *et al.* 2021). Such practice of groundwater consumption may easily expose to various contaminants viz, inorganic, organic, heavy metals, and other pollutants are a significant threat to human health (Ghaderpoori *et al.* 2018, Aravinthasamy *et al.* 2021). The continuous exposures to fluoride ( $F^-$ ) and nitrates ( $NO_3^-$ )-containing groundwater are vulnerable to non-carcinogenic health risks on the local populace (Rao *et al.* 2021). The low content of  $F^-$  in drinking water is beneficial for the formation and development of teeth, and skeleton. Nevertheless, the concentration above the guideline limit (1.5 mg/L) is harmful to human health, causing dental fluorosis, osteoporosis, arthritis, neurotoxicity, and thyroid (WHO 2011, BIS 2012). The sources and occurrence of  $F^-$  in an alluvial aquifer are very complex and uncertain due to numerous point and non-point inputs, geochemical, and pedogenesis processes compared to aquifer developed in fractured hard rocks bearing  $F^-$  minerals (Kim *et al.* 2012, Adimalla and Venkatayogi 2017). In India, 26 States among its 29 States witness high  $F^-$  levels in groundwater, posing the risk of endemic fluorosis to ~66 million individuals (~25 million <18 years) in 250 districts (Narsimha and Rajitha 2018).

$NO_3^-$  contaminant in groundwater is a worldwide environmental concern due to its unique properties, such as high movability and solubility rate, stable oxidative state in water and associated health risks (WHO 2008, Zhai *et al.* 2017, He *et al.* 2022a). Groundwater pollution due to  $NO_3^-$  is widely reported in various countries, namely in Loess plateau, Northwest China (Li *et al.* 2019b), Matanza-Riachuelo River Basin, Argentina (Ceballos *et al.* 2021), Weining plain and Yinchuan plain, Northwest China (He *et al.* 2022a, 2022b), Donsheng district, Inner Mongolia (Feng *et al.* 2020), Gorveh-Dehgelan, Western Iran (Rahmati *et al.* 2015), Catalan Region, Spain (Carrey *et al.* 2021) and Guanzhong plain, China (Wang and Li 2022). In India, ~118 million people consume water with  $NO_3^-$  content 45–100 mg/L, and ~108 million people drink water containing  $NO_3^-$  level >100 mg/L (Rai 2003, Sangwan *et al.* 2021). Anthropogenic activities, such as application of N-chemical fertilizers (Huang *et al.*

2011), excreta from animals farm (Minet *et al.* 2017, Zhang *et al.* 2018), urban runoff (Lapworth *et al.* 2017), landfill leachate (Rao *et al.* 2021), wastewater irrigation (Elisante and Muzuka 2017) and discharge of untreated municipal, sewage and industrial effluents (Herojeet *et al.* 2016, He *et al.* 2022a), are the leading causes for  $NO_3^-$  loads. The acute toxicity of  $NO_3^-$  is often encountered even though the concentration level for drinking water is below 45 mg/L in infants (<1 year) and children by “blue baby syndrome” (Skold *et al.* 2011, BIS 2012). Long-term exposure to  $NO_3^-$  has chronic effects on human health, such as non-Hodgkin lymphoma, nitrosamines, and multiple sclerosis (Fabro *et al.* 2015, Wongsanit *et al.* 2015). Therefore, the health hazard risks of such ions are still concerns to infants and children even at low concentration due to exposure dose, sensitivity and weak tolerance limit (Adimalla and Qian 2019).

Human health risk assessment (HHRA) is an equation developed by USEPA, that deals with quantitative hazard risk appraisal on human health concerning specific chemical contents in water (Qiu and Gui 2019, Li *et al.* 2021). Most of the researchers have studied the non-carcinogenic HHRA for  $F^-$  and  $NO_3^-$  in India using deterministic method (Adimalla *et al.* 2019, Adimalla and Qian 2019, Kumar *et al.* 2019, Karunanidhi *et al.* 2020, Rao *et al.* 2021, Sangwan *et al.* 2021, Selvam *et al.* 2021). The implementation of deterministic method is conservative in risk analysis due to the fixed assigned value of input variables rather than the range of random values of each variable (Saha *et al.* 2017). The variables used in deterministic model normally vary with respect to time, places, climatic conditions (ingestion rate, bathing frequency), types of receptors (different age groups, exposure frequency and body weight) and parameter concentrations (Liu *et al.* 2022). Thus, the uncertainty associated with input variables randomness of the deterministic approach may overestimate or underestimate the risk assessment, thereby diluting the study's objective. Many researchers proposed other health risk models considering the traditional method limitation, namely gray system theory, fuzzy mathematical theory and probabilistic theory (Wang 2004). Gray system theory is a developing model with ambiguous principles due to addition of numerous concepts and methods as per the worker's discretion. Bilgil (2021) suggested that gray system theory may sometimes yield unacceptable prediction errors. Also, this model is applicable for short-term predictions with limited sample sizes and partial information of the problems (Liu *et al.* 2022). Fuzzy theory deals with the things that lacks clear boundaries of

the approach, and probabilistic statistical model is applied to study the probability approximation of events affected by input random factors (Zhou 2017). Probabilistic approach, namely, Monte Carlo Simulation (MCS), is considered the logically superior and promising stochastic method to appraise HHRA (Giri *et al.* 2020; Emenike *et al.* 2019). MCS approach caters to quantitative variability and reduces uncertainties by providing more accurate and prospective risk assessment outcomes than the conventional deterministic method.

Nalagarh represents the inter-monte valley situated in Himachal Pradesh, Northern India. During the past decades, the serene valley of Nalagarh turned into an industrial hub, thereby discharging enormous untreated effluents causing pollution on perennial and ephemeral streams and soil. Presently, groundwater is the primary source for domestic, irrigation, and industrial purposes in the study area. Due to rapid industrialization, the large-scale groundwater development witnessed a declining water level of the valley (CGWB (Central Ground Water Board) 2018). Therefore, groundwater depletion and their pollution vulnerability are the major threat in the study area. Various latent factors influence groundwater evolution, and complex processes that can be interpreted using multiple appraisal approaches, viz, interionic interpolations, geochemical characterization and thermodynamic modeling, and statistical techniques (Singh *et al.* 2020a, Sangwan *et al.* 2021). The present study is carried out to characterize the groundwater quality for drinking purposes, geochemical evolution, and non-carcinogenic HHRA of groundwater viz, ingestion, and dermal route using deterministic and probabilistic approaches in parts of Northern India.

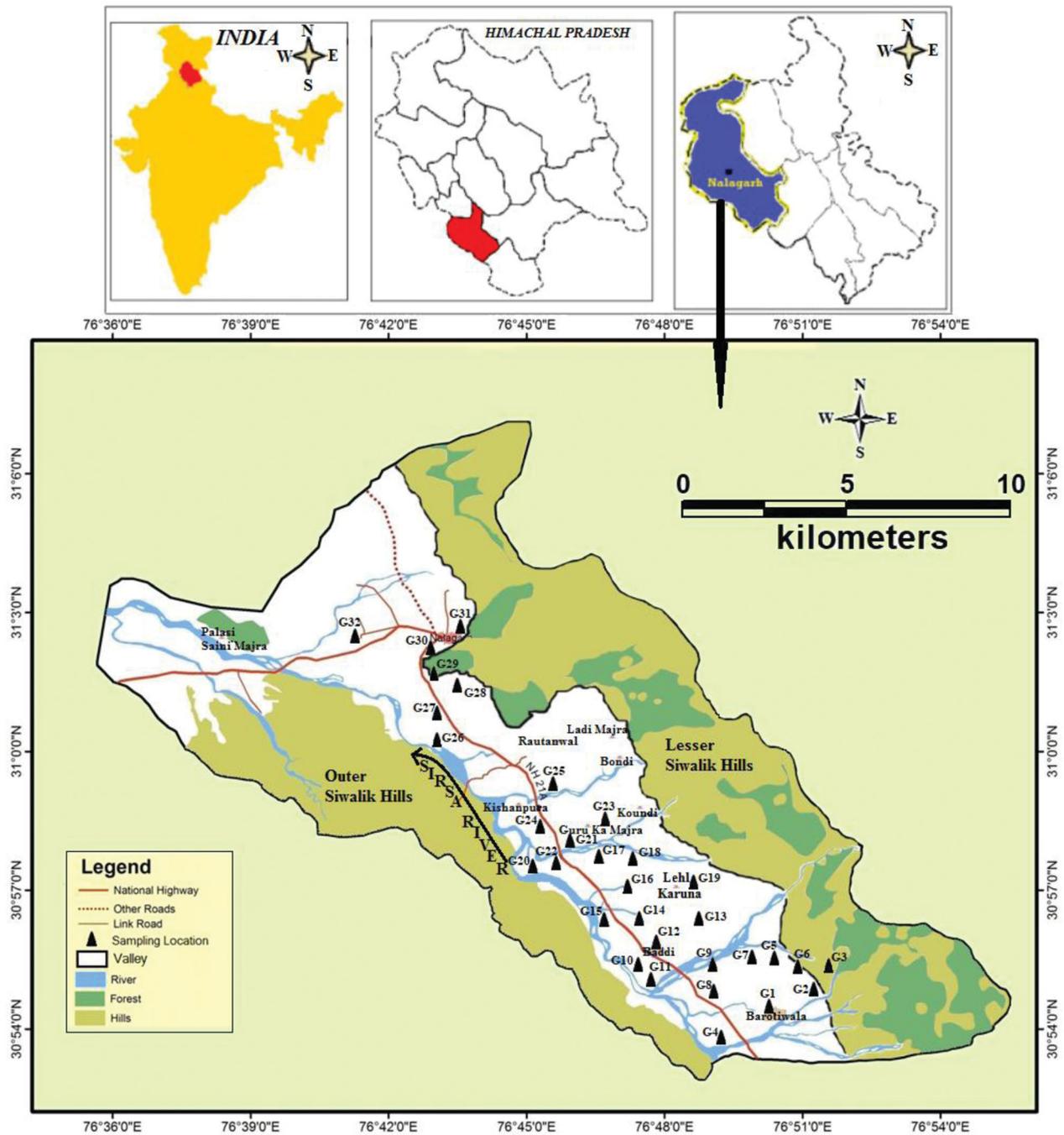
### 1.1. Study area

Nalagarh valley, a narrow stretch of low lying area carved in the tertiary formations, covering an area of about 250 km<sup>2</sup> with a population of about 254,390 people and decadal growth rate of 13.8% is selected for the present study (Figure 1). The valley is delineated by the lesser Siwalik Hills in the northeast (NE), and River Sirsa drained at the foothill of the outer Siwalik Hills in the southwest (SW). Agriculture and forest land cover classes are the dominant land use type in the study area covering about 6.67 and 36.10% of the total geographical area, respectively (Figure 2). Nearly 4.62% of the study area is covered by water bodies that include rivers and streams. Approximately 15 and 5 km<sup>2</sup> of geographical areas are

under settlement and industrial land use classes, respectively, forming around 5.4% of the study area. In the last decades, the State government has emphasized industrialization in the hilly ecosystem terrain by granting numerous special incentives (Kamaldeep *et al.* 2011). The industrial region in Nalagarh valley named as Baddi-Barotirwala-Nalagarh (BBN) witnessed 12 different industrial categories with a maximum number (~70%) of large and medium scale industrial units, which is a pollution threat to water resources (GoHP (Government of Himachal Pradesh) 2012, Rajkumar *et al.* 2020). As per a report by the BBN Authority in 2007, as many as 72% of industrial units do not install their effluent treatment plants (ETPs). These units openly discharge their untreated effluents to the open channels and agricultural lands increasing susceptibility to groundwater pollution. Numerous ephemeral and perennial streams, often loaded with untreated industrial effluents, and sewage wastewater, flow through the BBN industrial region and join the Sirsa River (CGWB (Central Ground Water Board) 2007, 2008). Therefore, Sirsa River and its tributaries cannot often fulfill the quality water demand of the study area as they are heavily contaminated due to pollutant discharges from the various sources (Rajkumar *et al.* 2019). All water requirements of the valley, including those for public water supply, industrial and irrigational supply, are met by groundwater resources only (CGWB 2013).

### 1.2. Geology and hydrogeology

Nalagarh is a northwest-southeast (NW-SE) trending intermontane valley in the lesser Himalayas in northern India (Figure 1). Flanked by the Siwaliks of Tertiary Age, it forms a relatively low lying narrow strip of about 5–7 km. Its topography and geology has been described by Rajkumar (2019, 2020). Lesser Siwalik Hills with a maximum elevation of 1150 meter above mean sea level (m amsl) form the NE flank while the outer Siwalik Hills with an elevation of about 500 m amsl form the SW flank. The formation of Nalagarh valley is linked to the last phase of upheaval of the Himalayas as it runs parallel to the main strike direction of the Siwalik formations. While pre-Holocene and Holocene deposits form the granular alluvial soils in Nalagarh valley, the common rock types encountered are sandstone, quartzite, limestone, phyllite, slate and shale. These rocks are well-jointed, fractured and crushed at places. Nalagarh and Sirsa thrusts are the two major NW-SE trending tectonic zones with the Surajpur Fault paving the path for the Sirsa River (Khan 1970).

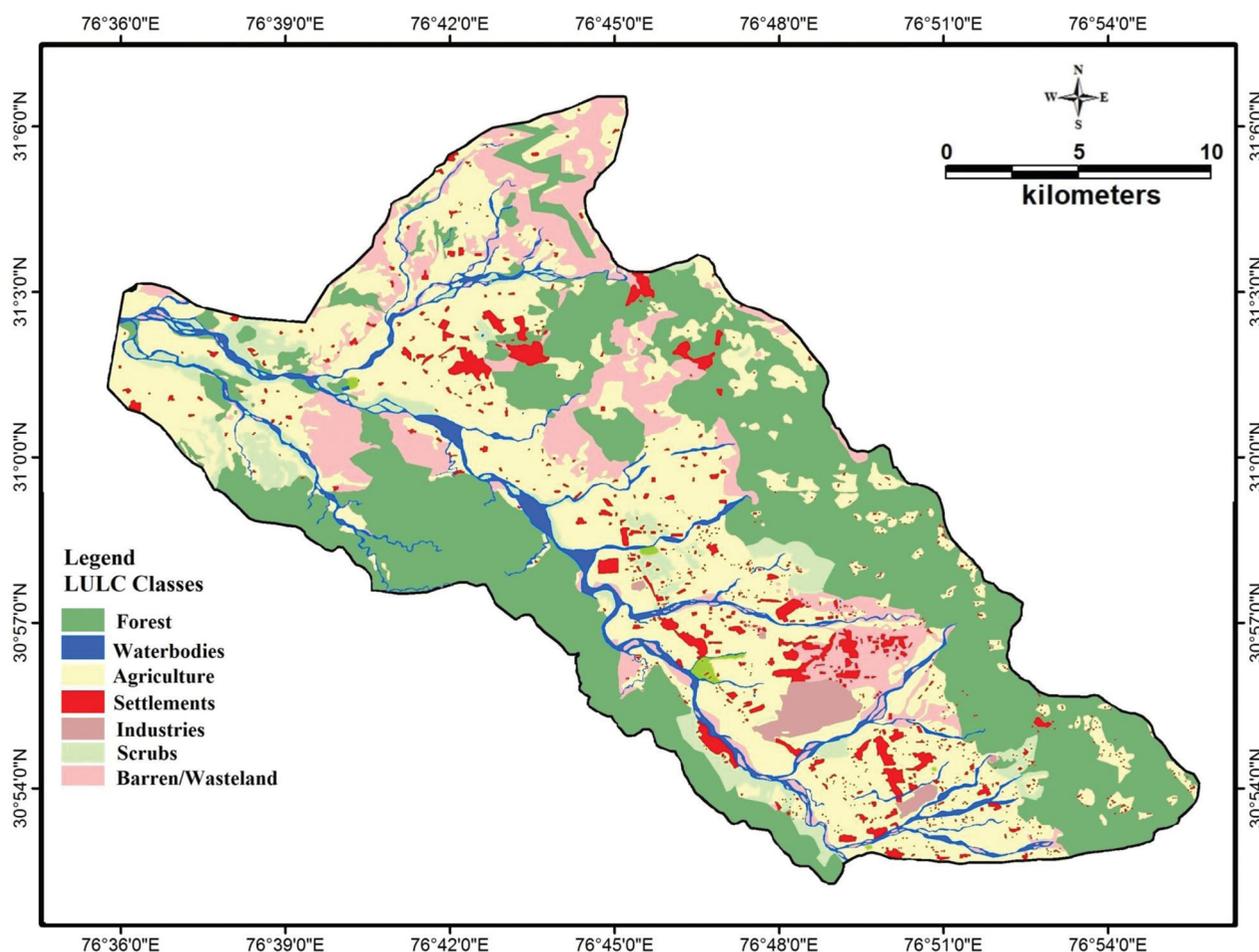


**Figure 1.** Location of the Nalagarh valley, Himachal Pradesh, India.

Groundwater in the valley occurs in pervious unconsolidated alluvial formations under both phreatic and confined conditions (CGWB (Central Ground Water Board) 2018). Groundwater levels are shallower in the main valley portions with depth to water levels (DTW) varying between near zero and 10 meter below ground level (mbgl) during premonsoon period (May 2014). As the surface slope rises toward the hills, DTW starts becoming deeper (Rajkumar *et al.* 2020). Various types of groundwater structures encountered are tubewells of varying depths, 4–60 m deep dugwells and dug-cum-

borewells. As per CGWB (Central Ground Water Board) (2008), general yields of these wells go upto 10 liters per second (lps), but wells tapping a granular zone at 25–30 m depth have yields upto 30 lps. Semi-confined aquifers are tapped by about 65–120 m deep tubewells.

The primary source of groundwater recharge in the area is South-West monsoon (July–September) that causes about 83% of rainfall with an annual average of 1129.3 mm in about 64 rainy days. Other recharge sources are the seepage from irrigation water, abandoned mine pits and influent perennial and ephemeral



**Figure 2.** Landuse Landcover (LULC) of the study area.

streams. The dendritic drainage pattern favors infiltration and percolation of a large quantity of water into the porous and highly permeable valley-fill deposits. The groundwater discharge mainly occurs naturally through evapotranspiration and effluent seepages into the major streams and artificially through groundwater extraction by dugwells, tube wells and dug-cum-borewells for various uses.

The groundwater movement follows the surface topography and is generally toward the SW direction corresponding to the orientation of the valley slope (Figure 3). The water table elevation ranges from 265 to 465 m amsl. The groundwater flow along the SW slope intersects the Sirsa riverbed and those of many other tributaries to maintain their perennial flow (CGWB (Central Ground Water Board) 2008).

## 2. Materials and methods

### 2.1. Sampling and laboratory investigation

Groundwater samples were collected from 32 different locations including 18 sites from the phreatic aquifers and 14 sites from semi-confined aquifers in the study

area (Figure 1) during both pre and post monsoon seasons (May and October, 2012) using the Global Position System. Thus, a total of 64 groundwater samples were collected for chemical analysis. Plastic bottles (HDPE) of 1000 ml capacity were prewashed with 10% nitric acid ( $\text{HNO}_3$ ) and soaked with double deionized water. To obtain fresh samples, flushing the groundwater source for about 10–15 min will remove the stagnant water stored in pipes. Bottles were again rinsed 2–3 times with the water to be collected to preserve and maintain the original water characteristics. Parameters, namely pH, and electrical conductivity (EC) were examined at the sampling sites itself using portable multiparameter (Hanna HI98194) and total dissolved solids (TDS) were calculated using the formula ( $\text{TDS} = \text{EC} * 0.64$ ) immediately on the spot. Each sampling site has collected one pair of groundwater samples using Whatman filter paper ( $0.45 \mu\text{m}$ ) to remove suspended particulate matter. Samples were preserved by acidifying ( $\text{pH} \sim 2$  with  $\text{HNO}_3$ ) and kept at a temperature of  $4^\circ\text{C}$  for the analysis of major cations. The standard protocol (APHA 2005) was followed for the investigation of major cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,

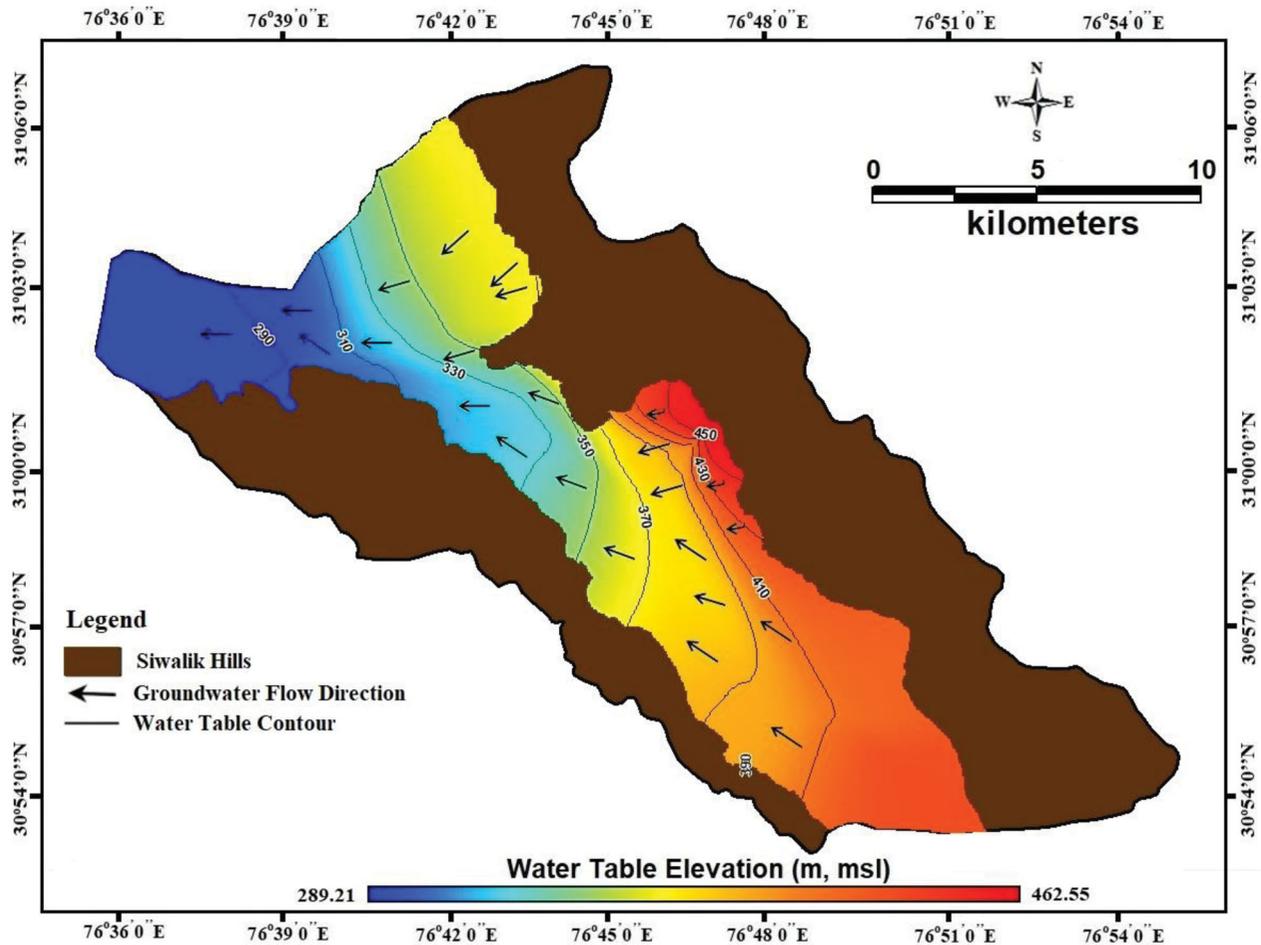


Figure 3. Groundwater flow direction in the Nalagarh valley, Himachal Pradesh.

Na<sup>+</sup>, and K<sup>+</sup>) and major anions (HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>). Merck-GR grade chemicals and reagents were used to prepare the chemical solutions using double deionized water. All the glassware and apparatus were soaked with 10% hydrochloric acid (HCl) for one day and cleaned with double deionized water. Blank samples were prepared from the stock solutions of each parameter for instrumental calibration. The accuracy of analyze datasets was computed using the charge balance error (CBE) equation (Equation 1), and each sample value was less than their acceptable limit ( $\pm 5\%$ ) (Hounslow 2018).

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

Mapinfo Professional 6.5 is used for the map digitization, and Originpro 18 and MS Office 2010 are used for various graphical interpolations and statistical calculations. RockWorks15 and PHREEQC Version 3 are used for geochemical modeling in groundwater.

## 2.2. Deterministic and probabilistic human health risk analysis

Risk analysis is an essential mathematical model to evaluate the negative effect on human health due to harmful contaminants in water sources over a specific time period (USEPA (US Environmental Protection Agency) 1989, 1992). Human health risk assessment (HHRA) guidelines give four necessary steps: (i) hazard identification, (ii) exposure assessment, (iii) dose-response assessment, and (iv) risk characterization (Luo *et al.* 2012, Ma *et al.* 2016).

- i. *Hazard identification*: The hazard level is evaluated for chemical contaminants due to their high mobility and adverse toxic effects when exposed to humans over a specific time (USEPA (US Environmental Protection Agency) 2004, Guleria and Chakma 2021). Interaction with local people in the study area confirmed their sole dependence on groundwater for drinking, domestic and agricultural purposes. The potential human health risk associated with a low concentration of

contaminants in groundwater through various pathways may be negligible. Although, the degree of adverse health effects on different age groups may be concerned even at low concentrations because of the physiological variation, organs developmental process, age factor, and specific chemical tolerance on the human body. Therefore, the adverse toxicity health risk may be relatively intensified with increased contaminants in water.

- ii. *Exposure assessment*: The exposure of HHRA is estimated through three different pathways, namely, direct oral ingestion as drinking water, inhalation of water droplets or aerosol through mouth and nose, and dermal contact to exposed skin (USEPA (US Environmental Protection Agency) 1989). Among the three exposure pathways, direct oral ingestion and dermal contact are the significant and shared pathways for chemical exposure to the human body (Singh and Kumar 2017, Emenike *et al.* 2019). In the present study,  $F^-$  and  $NO_3^-$  are the target parameters, and their average daily dose (ADD) is used to determine the non-carcinogenic HHRA via, direct ingestion ( $ADD_{ingestion}$ ) and dermal contact ( $ADD_{dermal}$ ) through bathing and other domestic activities using the Equations 2 and 3 (USEPA (US Environmental Protection Agency) 2011). The assessment of ADD is computed on four different subpopulation groups, namely; infants (<1 year), children (1–11 years), teens (11–18 years), and adults (>18 years), respectively, due to their behavioral and physiological attributes.

$$ADD_{ingestion} = \frac{C_M \times IR_w \times EF_r \times ED}{BW \times AT_r} \quad (2)$$

$$ADD_{dermal} = \frac{C_M \times SA \times K_p \times EF_r \times ED \times ET \times CF}{BW \times AT_r} \quad (3)$$

- iii. *Dose-response assessment*: The quantification of exposure hazard level of any potentially toxic non-carcinogenic chemical on human health is examined by dose-response assessment (Lee *et al.* 2006, Guleria and Chakma 2021). Reference dose (RfD) is defined as the permissible guideline limit set by USEPA, above which the designated population is susceptible to toxic substances (Ma *et al.* 2016). The reference dose of dermal skin adsorption ( $RfD_d$ ) for many contaminants is not available in IRIS database (<https://www.epa.gov/iris>). However, USEPA (US Environmental Protection Agency) (2002a) suggested a formula to derive the dermal reference dose ( $RfD_d$ ) from

the oral reference dose ( $RfD_i$ ) using the following Equation 4.

$$RfD_d = RfD_i \times ABS_i \quad (4)$$

Where  $ABS_i$  is the gastrointestinal absorption factor (unitless) of the  $i^{\text{th}}$  chemical parameter. The  $ABS_i$  value of  $NO_3^-$  and  $F^-$  is 1 (USDHAHS 2017, USEPA (US Environmental Protection Agency) 2002b). Therefore, RfD of  $NO_3^-$  and  $F^-$  for ingestion and dermal route are 1.6 mg/kg per day and 0.06 mg/kg per day, respectively (USEPA (US Environmental Protection Agency) 2002a, 2012;

- iv. *Risk characterization*: Risk characterization of non-carcinogenic chemical parameter is assessed through hazard quotient (HQ) and hazard index (HI). HQ is the ratio of exposure assessment of health risk (ADD) for different age groups and their respective reference dose (RfD) of target parameter at each pathway (USDHAHS 2017, USEPA (US Environmental Protection Agency) 2004) and is computed by using Equations 5 and 6. HQ is unitless value. If HQ value exceeds the threshold limit 1, the potential adverse health effect is associated with a particular exposure pathway.

$$HQ_{ingestion} = \frac{ADD_{ingestion}}{RfD_i} \quad (5)$$

$$HQ_{dermal} = \frac{ADD_{dermal}}{RfD_d} \quad (6)$$

Furthermore, HI is the combined non-carcinogenic risk, i.e. the summation of HQ of each assessment subpopulation group for different chemical parameters and exposure pathways (Saha *et al.* 2017). HI is unitless and calculated using Equations 7 and 8.

$$HI_{ingestion} = \sum_{i=1}^n HQ(F^-)_{ingestion} + \sum_{i=1}^n HQ(NO_3^-)_{ingestion} \quad (7)$$

$$HI_{dermal} = \sum_{i=1}^n HQ(F^-)_{dermal} + \sum_{i=1}^n HQ(NO_3^-)_{dermal} \quad (8)$$

$$THI = \sum_{i=1}^n HI_{ingestion} + \sum_{i=1}^n HI_{dermal} \quad (9)$$

Where THI is the total hazard index, and  $i$  indicate the exposure pathway considered in the study (Equation 9).  $HI > 1$  indicates the potential non-carcinogenic toxicity in the specified age group (USEPA (US Environmental Protection Agency) 2004).

In this study, deterministic and probabilistic risk analysis methods are employed to ascertain the uncertainty and sensitivity of health risk assessment. The deterministic approach used the simple mathematical

formula recommended by USEPA, where the input variables are fixed values for different exposure routes (Lin *et al.* 2016). The output risk results generated from this method are only point or single value that neglects the quantitative variability and uncertainty in the applied model's input variables (USEPA (US Environmental Protection Agency) 1997, Rajasekhar *et al.* 2018). Therefore, the deterministic approach of HHRA cannot cater to the absolute or holistic scenario of risk assessment for the inclusive member of population interest due to differences in person-to-person characteristics and dynamism prevailing in the environment. USEPA (US Environmental Protection Agency) (1997) suggested probabilistic techniques as an alternative and viable statistical application offering a sound methodology and new research dimension that provides more credible information and authentic scientific output for the risk analysis.

Probabilistic techniques, namely, MCS are purposely applied to analyze the input variables that reduce the associated uncertainty of various pathways in risk assessment. MCS is a computer software application configuring a statistical distribution array in the form of probabilistic approximation of a mathematical equation to generate more corroborates reproducibility results. MCS is performed using Oracle Crystal Ball software version (11.1.2.4.850). Each input parameter is arranged according to their corresponding minimum, maximum, mean, and standard deviation (SD) values to assign the best-fitted statistics distribution types and establish their probability distribution functions (PDFs) (USEPA (US Environmental Protection Agency) 1997). The input parameters such as ingestion rate ( $IR_{vw}$ ), exposure frequency ( $EF$ ), expose skin surface area ( $SA$ ), exposure time ( $ET$ ), and body weight ( $BW$ ) are employed 10,000 repetitions of oral ingestion and dermal contact route for each subpopulation category. Thus, the numerical stability of MCS is obtained at 10,000 permutations for  $HQ$ ,  $HI$ , and  $THI$  (Ganyaglo *et al.* 2019, Jamal *et al.* 2019). The sensitivity analysis is

also employed to extract the significant input variables impacting the outcome of risk simulation model. The target parameters, i.e.  $F^-$  and  $NO_3^-$ , are defined by the auto-select to best-fitted probability distribution pattern based on their concentration values, and their goodness of fit (GoF) statistics outcome are presented in Table 1. The values and types of distribution of various variables for ingestion and dermal pathways for the deterministic and probabilistic risk assessment are provided in supplementary Table S1.

### 3. Results and discussions

#### 3.1. General groundwater characteristics

The basic statistical information that includes minimum, maximum, mean  $\pm$  SD values of analyzed groundwater parameters and compliance with drinking water standards of WHO (2011) and BIS (2012) is presented in Table 2. The analytical results of pH indicate the alkaline nature of groundwater and ranges from 7.2 to 8.7 (mean  $\pm$  SD value  $7.6 \pm 0.4$ ) and 7.0 – 8.1 (mean  $\pm$  SD value  $7.4 \pm 0.2$ ) during the investigational period i.e. pre and post monsoon seasons. All the groundwater samples have pH values within their recommended limit (6.5 – 8.5) of BIS (2012) and WHO (2011), except for one sample (S8) during pre monsoon season (Table 2). EC values vary between 500 and 1513  $\mu S/cm$  and 443 and 1348  $\mu S/cm$  during pre and post monsoon seasons, respectively, and well within the guideline value (1500  $\mu S/cm$ ) of WHO (2011); except for one sample (S31) during pre monsoon season (Table 2). TDS values varies between 324 and 992 mg/L (pre monsoon) and 284 and 875 mg/L (post monsoon), whereas, TH concentration ranges from 206 to 622 mg/L and 186 to 772 mg/L during the investigational period. The mean concentrations of EC and TDS are slightly more in pre monsoon season (909  $\mu S/cm$  and 589 mg/L) than during the post monsoon period (808  $\mu S/cm$  and 522 mg/L). This may be due to groundwater draft before the onset of

**Table 1.** Best fitted probability distribution for nitrate and fluoride parameters and goodness of fit (GoF) outcomes.

Parameters	Distribution types and their parameter values	Anderson-Darling Test	Anderson-Darling Test ( $p$ value)	Kolmogorov-Smirnov Test	Kolmogorov-Smirnov Test ( $p$ value)	Chi-Square Test	Chi-Square Test ( $p$ value)
Premonsoon Fluoride	Lognormal (Location = 0.00, Mean = 0.22, Std. Dev = 0.16)	0.5585	0.068	0.1215	0.152	7.00	0.030
Nitrate	Beta (Minimum = 0.87, Maximum = 66.03, Alpha = 1.58292)	0.2620	–	0.0852	–	2.1250	0.145
Postmonsoon Fluoride	Gamma (Location = 0.05, Scale = 0.10, Shape = 1.53618)	0.2977	0.824	0.0874	0.944	2.8750	0.238
Nitrate	Exponential (Rate = 0.26)	0.6470	0.314	0.1387	0.312	5.8750	0.209

Table 2. Statistical analyses of groundwater samples in Nalagarh valley, Himachal Pradesh, India.

Parameter	BIS (2012) Standards		Pre monsoon						Post monsoon						
	AL	PL	Range	Mean $\pm$ SD	AL	PL	% of samples (numbers) above BIS (2012) Standards	Range	Mean $\pm$ SD	AL	PL	% of samples (numbers) above BIS (2012) Standards	AL	PL	Analytical method
<b>Physical parameters</b>															
pH	6.5-8.5		7.2-8.7	7.6 $\pm$ 0.4		3.0 (1)		7.0-8.1	7.41 $\pm$ 0.23		NIL			NIL	pH/EC/TDS meter
EC	1500*		500-1513	909 $\pm$ 248		3.0 (1)		443-1348	808 $\pm$ 271		NIL			NIL	pH/EC/TDS meter
TDS	500	2000	324-992	589 $\pm$ 185	65.6 (21)		NIL	284-875	522 $\pm$ 175	46.9 (15)			46.9 (15)		TDS = EC* 0.64
TH	200	600	206-622	306 $\pm$ 87	96.9 (31)	3.0 (1)	3.0 (1)	186-772	381 $\pm$ 155	84.4 (27)		9.4 (3)	84.4 (27)		Titration with EDTA using Eriochrome Black T as indicator
<b>Major cations</b>															
Mg <sup>2+</sup>	30	100	20.6-137.2	56.7 $\pm$ 21.7	90.6 (29)	3.0 (1)	3.0 (1)	31.7-172.8	73.4 $\pm$ 36.7	84.4 (27)		15.6 (5)	84.4 (27)		Titration with EDTA as titrant and eriochrome black T as indicator
Ca <sup>2+</sup>	75	200	35.3-157.3	74.0 $\pm$ 28.2	40.6 (13)	NIL	NIL	27.6-138.6	79.8 $\pm$ 31.1	53.1 (17)		NIL	53.1 (17)		Titration with EDTA using Murexide as indicator
Na <sup>+</sup>	200*		12.0-99.9	35.0 $\pm$ 22.0		NIL	NIL	9.1-62.5	29.5 $\pm$ 12.1			NIL		NIL	Flame photometric
K <sup>+</sup>	12*		0.9-8.8	2.4 $\pm$ 1.5		NIL	NIL	0.4-19.0	2.1 $\pm$ 3.2			3.0 (1)		3.0 (1)	Flame photometric
<b>Major anions</b>															
HCO <sub>3</sub> <sup>-</sup>	500*		60.0-196.0	118.9 $\pm$ 28.7		NIL	NIL	62.0-204.0	129.6 $\pm$ 28.4			NIL		NIL	Titrimetric method using standard H <sub>2</sub> SO <sub>4</sub> with phenolphthalein and methyl orange as an indicator
Cl <sup>-</sup>	250	1000	2.8-36.2	15.2 $\pm$ 9.0	NIL	NIL	NIL	3.9-39.8	15.8 $\pm$ 9.6	NIL		NIL	NIL		Titration with AgNO <sub>3</sub> using potassium dichromate as indicator
SO <sub>4</sub> <sup>2-</sup>	200	400	10.0-27.0	13.2 $\pm$ 3.3	NIL	NIL	NIL	9.7-26.5	13.3 $\pm$ 4.0	NIL		NIL	NIL		Spectrophotometer (using BaCl <sub>2</sub> as conditioning agent)
F <sup>-</sup>	1	1.5	0.06-1.20	0.22 $\pm$ 0.21	3.0 (1)	NIL	NIL	0.05-0.50	0.20 $\pm$ 0.11	NIL		NIL	NIL		Spectrophotometer (SPADNS Method)
NO <sub>3</sub> <sup>-</sup>	45		2.6-38.8	14.6 $\pm$ 9.2		NIL	NIL	BDL-18.9	3.9 $\pm$ 4.3			NIL		NIL	Spectrophotometer (using phenol disulfonic acid)

Note: Unit in mg/L. Except EC ( $\mu$ S/cm) and pH and BDL means below detectable limit. AL and PL specifies the acceptable limit and the permissible limit.

\*Since BIS (2012) does not specify any guideline value, WHO (2011) guideline value has been considered.

**Table 3.** Groundwater classification based on TDS, TH, F<sup>-</sup> and NO<sub>3</sub><sup>-</sup>.

Parameters	Range	Classification	No of samples exceeding allowable limits	
			Pre monsoon	Post monsoon
TDS (mg/L) (Freeze and Cherry 1979)	<1000	Fresh	32	32
	1000–10,000	Brackish	Nil	Nil
	10,000–100,000	Saline	Nil	Nil
	>100,000	Brine	Nil	Nil
TH (mg/L) (Sawyer and McCarty 1967)	<75	Soft	Nil	Nil
	75–150	Moderately hard	Nil	Nil
	150–300	Hard	18	16
	>300	Very hard	14	16
NO <sub>3</sub> <sup>-</sup> (mg/L) (Adimalla <i>et al.</i> 2019 and Singh <i>et al.</i> 2020b)	<45	Low risk (suitable for drinking)	32	32
	46 – 100	High risk (not suitable for drinking)	Nil	Nil
	>100	Very high risk (not suitable for drinking)	Nil	Nil
F <sup>-</sup> (mg/L) (Adimalla <i>et al.</i> 2019; Singh <i>et al.</i> 2020b)	<0.5	Class 1 (dental Caries)	31	32
	0.6 – 1.5	Class 2 (required levels for human health)	1	Nil
	1.6 – 2.0	Class 3 (dental fluorosis)	Nil	Nil
	2.1 – 3.0	Class 4 (dental & skeletal fluorosis)	Nil	Nil
	>3.0	Class 5 (leads to skeletal fluorosis)	Nil	Nil

monsoon season, and enhancement of ion exchange processes for mineralization and salinity in the aquifers (Herojeet *et al.* 2016). The groundwater quality of the study area is classified into freshwater category i.e. TDS values <1000 mg/L as per Freeze and Cherry 1979 classification (Table 3). Sawyer and McCarty 1967 (Sawyer and McCarty 1967) classification based on TH values, all groundwater samples are categorized into hard to very hard water classes for both the seasons (Table 3). Further, the plot between TDS vs. TH infers that the groundwater is hard to very hard in nature during the investigational period (Figure S1). Continuous consumption of such water types may link to various cardiovascular diseases viz, urolithiasis, anencephaly, neurological problems, and muscle slackening (Kumar and Augustine 2021, Sangwan *et al.* 2021). TH mean value is more during post monsoon (381 mg/L) than pre monsoon (306 mg/L), as carbonate minerals (calcite, dolomite, sandstone) are readily dissolved in percolating slightly acidic rainwater during monsoon period and reverse ion exchange process (Zhou *et al.* 2020). Similarly, the average content of Mg<sup>2+</sup> and Ca<sup>2+</sup> ions are more in post monsoon than pre monsoon in the groundwater (Table 2). Thus, the high degree of hardness is often associated with the elevated concentration of Mg<sup>2+</sup> and Ca<sup>2+</sup> in the aquifer system (Herojeet *et al.* 2016). The relative abundance order of major ions in the groundwater of the study area are as follows; Mg<sup>2+</sup>>Ca<sup>2+</sup>>Na<sup>+</sup>>K<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>>Cl<sup>-</sup>>SO<sub>4</sub><sup>2-</sup>>NO<sub>3</sub><sup>-</sup>>F<sup>-</sup> [Figure 4(a)].

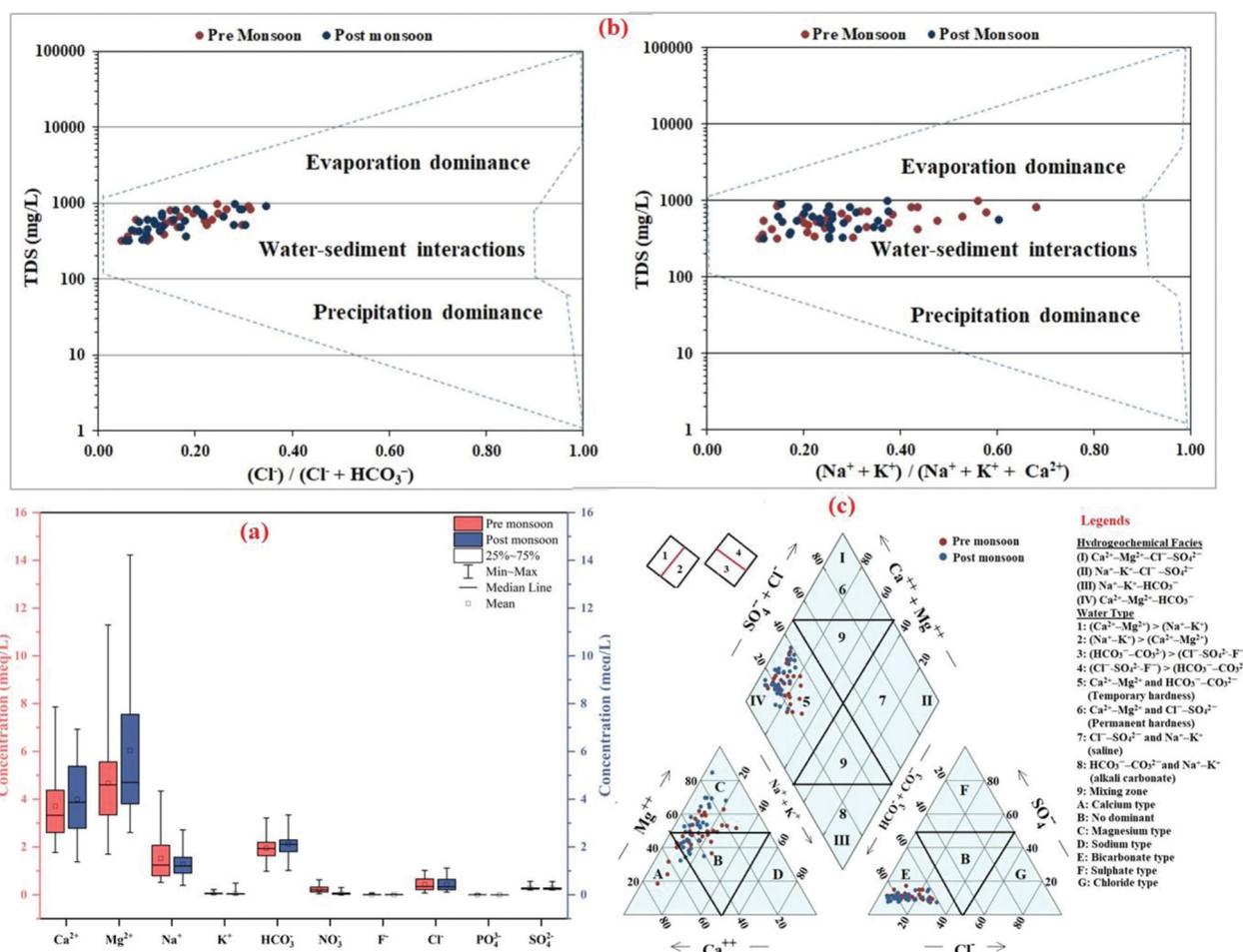
### 3.2. Major ions chemistry

In groundwater, Mg<sup>2+</sup> content ranges from 20.6 to 137.2 mg/L with 56.7 ± 21.7 and 31.7 – 172.8 mg/L with 73.4 ± 36.7, respectively, during pre and post

monsoon. 3% (pre monsoon) and 16% (post monsoon) samples are above the Mg<sup>2+</sup> permissible limit (100 mg/L) of BIS (2012) (Table 2). Ca<sup>2+</sup> concentration varies from 35.3 to 157.2 mg/L and 27.6 to 138.6 mg/L during pre and post monsoon, respectively. About 41% of groundwater samples in pre monsoon and 53% in post monsoon have Ca<sup>2+</sup> levels above the acceptable limit (75 mg/L) for drinking purposes (BIS 2012) (Table 2). Several geochemical processes like weathering of silicate minerals (plagioclase, amphiboles, pyroxenes) and magnesium bearing minerals (dolomite, sandstone) along with reverse ion exchange, and fertilizers applications may be the possible sources of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in the groundwater of the study area (Zhou *et al.* 2020, Singh *et al.* 2020b, Liu *et al.* 2021).

Na<sup>+</sup> concentration ranges from 12.0 to 99.9 mg/L in pre monsoon and 9.1 to 62.5 mg/L in post monsoon seasons. Higher mean value of 35.0 mg/L in pre monsoon season (Table 2) indicates ion exchange and silicate weathering processes (Gao *et al.* 2021). K<sup>+</sup> (the least dominant cation) content varies between 0.9 and 8.80 mg/L (pre monsoon) and 0.4 and 19.0 mg/L (post monsoon) in the study area. Only 3% of post monsoon samples have surpassed the K<sup>+</sup> guideline limit of 12 mg/L for drinking purposes (WHO 2011) with no significant variation in mean concentrations in both the seasons (Table 2).

HCO<sub>3</sub><sup>-</sup> is the most dominant ion among the anions and ranges from 60.0 to 196.0 mg/L (118.9 ± 28.7) and 62.0 to 204.0 mg/L (129.6 ± 28.4) during pre monsoon and post monsoon seasons, respectively. The mean concentration of HCO<sub>3</sub><sup>-</sup> ion in groundwater is slightly higher during post monsoon season (129.6 mg/L) compared to that of pre monsoon period (118.9 mg/L) indicating dissolution of silicate and carbonate



**Figure 4.** (a) Relative abundance order of major ions in groundwater samples, (b) Gibbs diagram representing the factor controlling groundwater chemistry, and (c) Piper diagram illustrating hydrochemical facies and water type.

minerals with the percolating rainwater during the monsoon. Cl<sup>-</sup> concentration varies from 2.8 to 36.2 mg/L and 3.9 to 39.8 mg/L during pre monsoon and post monsoon seasons, respectively. SO<sub>4</sub><sup>2-</sup> concentration ranges between 10.0 and 27.0 mg/L and 9.7 and 26.5 mg/L, respectively, during these seasons. The mean values of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions in groundwater show no significant variation for both the seasons (Table 2). The parameters HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are within the respective guideline limits prescribed by the BIS (2012) and WHO (2011) (Table 2).

### 3.3. Health concern parameters

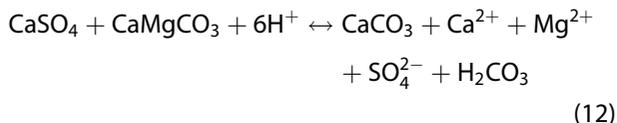
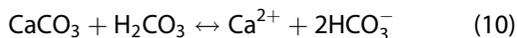
F<sup>-</sup> concentration varies from 0.06 to 1.20 mg/L with mean (0.22 mg/L) (pre monsoon), and 0.05 to 0.50 mg/L with mean (0.20 mg/L) (post monsoon) and within the permissible limit for human intake i.e. 1.5 mg/L (BIS 2012) (Table 2). Only 3% sample during pre

monsoon is above the F<sup>-</sup> acceptable limit (1.0 mg/L) of BIS (2012). The groundwater classification based upon F<sup>-</sup> content by Adimalla *et al.* (2019) and Singh *et al.* (2020b) is summarized in Table 3. All groundwater samples for both seasons are categorized in class-I (<0.5 mg/L; conducive to dental caries), except one sample (S13 in the central part of the study area) during pre monsoon. NO<sub>3</sub><sup>-</sup> content in pre and post monsoon seasons ranges from 2.6 to 38.8 mg/L and below detection limit (BDL) to 18.9 mg/L respectively (Table 2) and within the guideline limit (45 mg/L) of BIS (2012). Table 3 shows that all groundwater samples are categorized into low risk NO<sub>3</sub><sup>-</sup> content class as per Adimalla *et al.* (2019) and Singh *et al.* (2020b). Analytical results revealed that few groundwater sampling locations mostly confined to the Baddi industrial region showed an elevated level of NO<sub>3</sub><sup>-</sup>. Anthropogenic factors like municipal and industrial discharges, seepage from the septic tanks, and

drainage channels are the contributing factors for  $\text{NO}_3^-$  in the study area (Rao *et al.* 2012, Singh *et al.* 2019, Wang *et al.* 2021).

### 3.4. Hydrogeochemical processes

For a better understanding of the key mechanisms controlling aquifer chemistry, Gibbs diagrams (Gibbs 1970) are prepared to represent the relationship between the TDS and cation ratio i.e.  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  or anion ratio i.e.  $\text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-)$ . Figure 4(b) shows that all the groundwater samples are clustered on water-sediment interaction zone. Such interactive phenomena of water-alluvial sediment are mainly due to the dissolution and weathering of rock-forming minerals along with the cation exchange (direct and reverse) processes (Herojeet *et al.* 2013, Sidhu *et al.* 2013). The alluvial deposits are rich in silicate minerals along with secondary carbonate minerals like calcite [ $\text{CaCO}_3$ ] and dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] in the study area (CGWB (Central Ground Water Board) 2018). The weathering of these minerals determines the groundwater characteristic and the possible ions constituents in the groundwater (Rao 2017, Rao *et al.* 2021). Further, the Piper diagram (Piper 1944) is prepared to identify the hydrochemical facies and water types through the mixing effects between groundwater and aquifer minerals. All the groundwater samples belong to Zone IV during the investigational period, i.e.  $\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$  hydrochemical facies [Figure 4(c)]. The diamond field of Piper's diagram indicates that alkaline earth elements ( $\text{Ca}^{2+}\text{-Mg}^{2+}$ ) exceed the alkalis elements ( $\text{Na}^+\text{-K}^+$ ) and weak acids ( $\text{CO}_3^{2-}\text{-HCO}_3^-$ ) exceed the strong acids ( $\text{SO}_4^{2-}\text{-Cl}^-$ ), indicating thereby that the groundwater is dominated by  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$  ions [Figure 2(c)]. Such water types are mainly attributed to carbonate-rich material dissolution within the aquifers as expressed in Equations 10–12 (Singh *et al.* 2019, Zhang *et al.* 2020, Keesari *et al.* 2021).



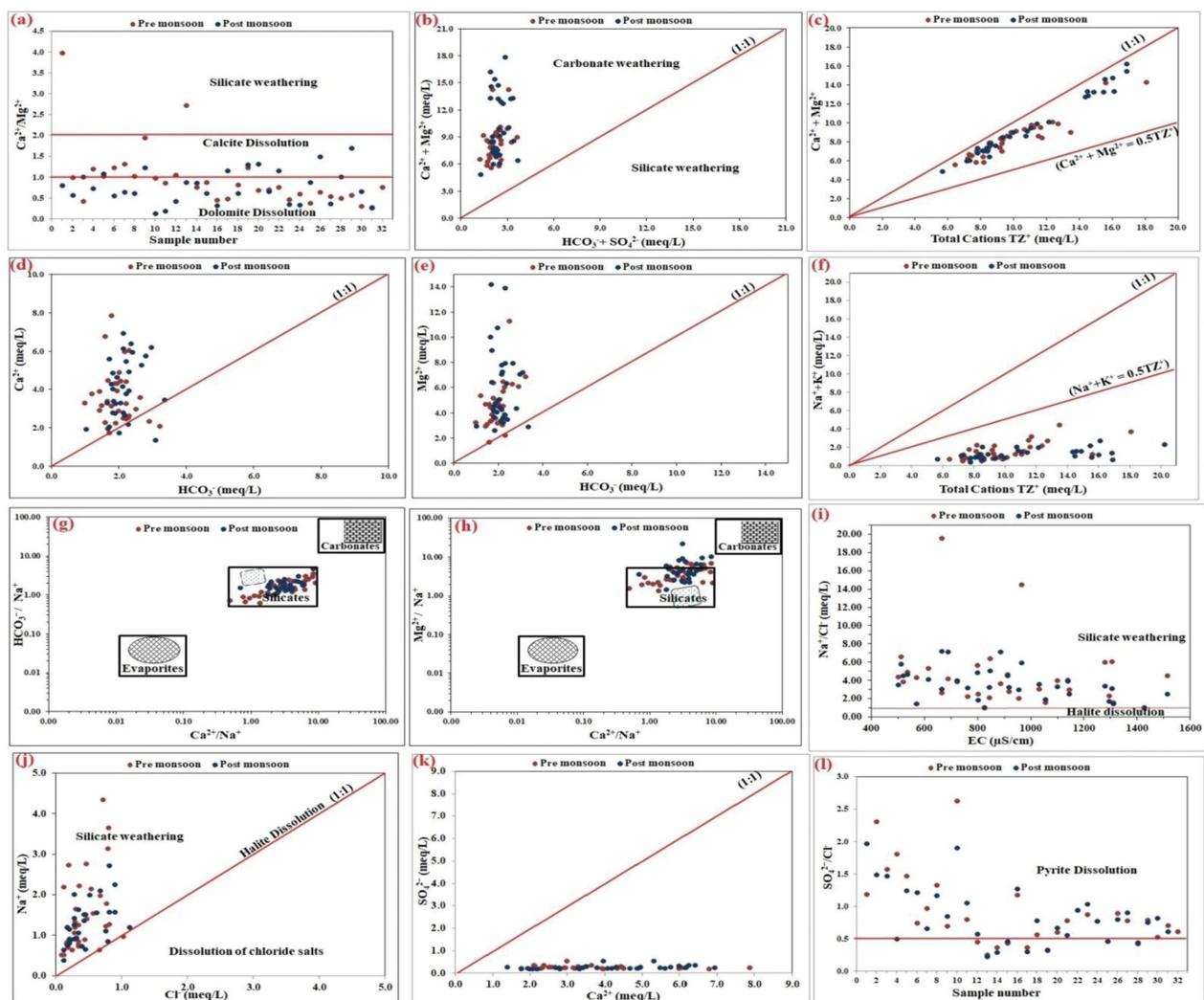
### 3.5. Geogenic weathering and ion exchange

Various interionic plots were prepared to understand the hydrogeochemical and chemical weathering processes in the aquifers.  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio was computed to determine the possible sources of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$

in the aquifer systems (Gao *et al.* 2022). In Figure 5(a), ~66% of groundwater samples during the investigational period are fall in  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio below 1, which indicates the dominance of dolomite dissolution over calcite dissolution in the study area (Mayo and Loucks 1995). Few samples (28% pre monsoon and 34% post monsoon) lie on or above  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio line 1 but less than 2, specifies the dissolution of both dolomite and calcite minerals. The remaining 6% samples during pre monsoon fall above  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio line 2, suggesting the effect of silicate minerals (Figure 5(a)). The plot between  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs.  $\text{HCO}_3^- + \text{SO}_4^{2-}$  shows all the groundwater samples are falling above the equiline (1:1), reflecting the carbonate weathering (calcite and dolomite) is largely affecting the aquifer chemistry (Figure 5(b)). The dominance of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  over  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  may also be attributed to the reverse ion exchange process (as expressed in Equations (17) and (18) and carbonate weathering (Luo *et al.* 2021, Karunanidhi *et al.* 2021b). The bivariate plot of  $\text{Ca}^{2+} + \text{Mg}^{2+}$  vs. Total Cations ( $\text{TZ}^+$ ) shows all the samples are scattered between the equiline (1:1) and  $\text{Ca}^{2+} + \text{Mg}^{2+} = 0.5 \text{TZ}^+$  line (Figure 5(c)). It depicts the weathering of calc-silicate minerals (plagioclase, amphiboles) and carbonates (dolomite and calcite) is contributing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in the aquifer (Li *et al.* 2020). In the bivariate plot of  $\text{Ca}^{2+}$  vs.  $\text{HCO}_3^-$  (Figure 5(d)), very few samples (6% and 9%) fall below the equimolar line (1:1), whereas a large scatter of samples (93% and 91%) are falling above the equimolar line (1:1) during the investigational period. The plot  $\text{Mg}^{2+}$  vs.  $\text{HCO}_3^-$  (Figure 5(e)) indicates that 97 and 3% of samples fall above and below the equiline (1:1) for both seasons. These trends show the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are dominantly contributed from calcite and dolomite weathering and reverse ion exchange processes in the aquifer chemistry of the study area (Marghade *et al.* 2021, Selvam *et al.* 2021).

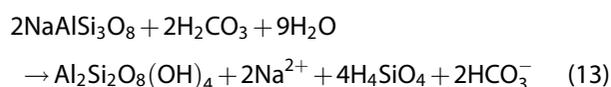
### 3.6. Mixed factors (geogenic and anthropogenic)

The bivariate plot between  $\text{Na}^+ + \text{K}^+$  and  $\text{TZ}^+$  (Figure 5(f)) infers that all the water samples are scattered below the equiline ( $\text{Na}^+ + \text{K}^+ = 0.5\text{TZ}^+$ ). It implies the weathering of potash and silicate-containing minerals and anthropogenic inputs like the application of potash fertilizers and sewage wastewater which contributes mainly  $\text{Na}^+$  and  $\text{K}^+$  ions to the groundwater (Srinivasamoorthy *et al.* 2014, Rao *et al.* 2021). The dissolution of sodium bearing silicate minerals like albite (as expressed in Equation (13) and other soda plagioclase feldspars in the presence of  $\text{H}_2\text{CO}_3$  acid (formed

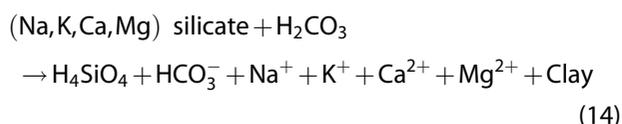


**Figure 5.** Inter-ionic relationship between major ions in groundwater: (a)  $\text{Ca}^{2+}/\text{Mg}^{2+}$ , (b)  $(\text{Ca}^{2+} + \text{Mg}^{2+} \text{ vs. } \text{HCO}_3^- + \text{SO}_4^{2-})$ , (c)  $(\text{Ca}^{2+} + \text{Mg}^{2+} \text{ vs. total cations } \text{TZ}^+)$ , (d)  $(\text{Ca}^{2+} \text{ vs. } \text{HCO}_3^-)$ , (e)  $(\text{Mg}^{2+} \text{ vs. } \text{HCO}_3^-)$ , (f)  $(\text{Na}^+ + \text{K}^+ \text{ vs. total cations } \text{TZ}^+)$ , (g)  $(\text{Ca}^{2+}/\text{Na}^+ \text{ vs. } \text{HCO}_3^-/\text{Na}^+)$ , (h)  $(\text{Ca}^{2+}/\text{Na}^+ \text{ vs. } \text{Mg}^{2+}/\text{Na}^+)$ , (i)  $(\text{Na}^+/\text{Cl}^- \text{ vs. EC})$ , (j)  $(\text{Na}^+ \text{ vs. Cl}^-)$ , (k)  $(\text{SO}_4^{2-} \text{ vs. } \text{Ca}^{2+})$ , and (l)  $(\text{SO}_4^{2-}/\text{Cl}^-)$  of the study area.

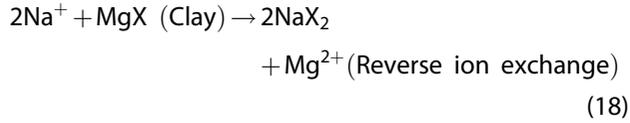
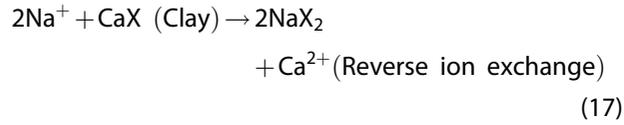
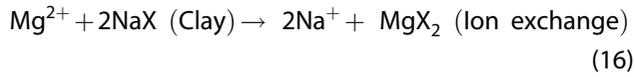
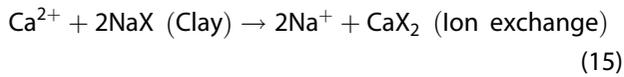
in above mentioned Equations (11) and (12) may enhance the  $\text{Na}^+$  content in the groundwater of the study area (Keesari *et al.* 2021, Singh *et al.* 2020b).



Further, the end-member plot  $\text{HCO}_3^-/\text{Na}^+ \text{ vs. } \text{Ca}^{2+}/\text{Na}^+$  (Figure 5(g)) clearly indicates that the silicate weathering processes predominantly drive the aquifer chemistry (Gaillardet *et al.* 1997, Gao *et al.* 2021). The general silicate weathering reaction with carbonic acid is as follow:



On the other hand, the plot  $\text{Mg}^{2+}/\text{Na}^+ \text{ vs. } \text{Ca}^{2+}/\text{Na}^+$  (Figure 5(h)) depicts majority of the groundwater samples are clustered within the silicate zone, and very few samples are scattered in the silicate-carbonate mixing region during the investigational period. This plot clearly shows that silicate mineral is not only the prime source of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  in the study area. The dissolution of carbonate minerals and reverse ion exchange elevates the contents of alkaline earth elements in groundwater (as expressed in Equations (10–12), (17), and (18)). Gao *et al.* (2022) reported that clay minerals, when rich in alluvial sediment, enhance cation exchange processes that affect the cation concentrations in groundwater. The following reactions explain the cation exchange for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with  $\text{Na}^+$  in the clay sediments as expressed in Equations (15–18) (Li *et al.* 2018a, 2018b, Zhou *et al.* 2020).



The molar  $\text{Na}^+/\text{Cl}^-$  ratio and bivariate plot  $\text{Na}^+/\text{Cl}^-$  vs. EC (Figure 5(i)) are prepared to understand the plausible sources of salinity and saline incursions in the study area (Luo *et al.* 2021). The  $\text{Na}^+/\text{Cl}^-$  ratio varies between 1.0 and 19.6 and 1.1 and 7.2 during pre and post monsoon. All the water samples have molar ratio of  $\text{Na}^+/\text{Cl}^- > 1$  and  $\text{Na}^+/\text{Cl}^-$  vs. EC  $> 1$  for both season. Therefore,  $\text{Na}^+$  ions has other sources than silicate weathering process (weathering of sodic plagioclase mineral as expressed in Equation (13); such as, ion exchange and anthropogenic activities enhance the  $\text{Na}^+$  and  $\text{Cl}^-$  ions relative mobility in groundwater (Marghade 2020). The ratio of  $\text{Na}^+$  vs.  $\text{Na}^+ + \text{Cl}^-$  is  $\geq 0.5$  in all the samples during pre monsoon (0.50–0.95) and post monsoon (0.52–0.88), divulges silicate weathering and ion exchange (as expressed in Equations (14–16)). Further, the plot between  $\text{Na}^+$  vs.  $\text{Cl}^-$  (Figure 5(j)) enables identifying the  $\text{Na}^+$  enrichment in the groundwater of the study area. Majority of the water samples (94 and 100%) during the investigational period fall above the equiline (1:1), elucidating the dominance of  $\text{Na}^+$  over  $\text{Cl}^-$  may be derived from silicate weathering and cation exchange processes along with some anthropogenic inputs (Gao *et al.* 2021, Marghade *et al.* 2021). Few samples (6%) during pre monsoon fall below the equiline 1:1 line suggests the halite dissolution (as expressed in Equation (19) is very limited, thus supports the impact of anthropogenic inputs (Liu *et al.* 2021, Wang *et al.* 2021). Hence, the presence of  $\text{Cl}^-$  in groundwater may be due to industrial discharges, seepage from the septic tanks, and chemical fertilizers application.



The plot of  $\text{SO}_4^{2-}$  vs.  $\text{Ca}^{2+}$  indicates the groundwater samples are scattered below the equiline (1:1) for both seasons (Figure 5(k)). The dominance of  $\text{Ca}^{2+}$  over  $\text{SO}_4^{2-}$  depicts anhydrite ( $\text{CaSO}_4$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) minerals are not the principal source of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in the aquifers (Mu *et al.* 2021,

Karunanidhi *et al.* 2021b). Therefore,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  contents in groundwater are originated from different sources in the study area. Moreover, the molar ratio  $\text{SO}_4^{2-}/\text{Cl}^-$  is computed to identify the contribution of inorganic sulfide and pyrite ( $\text{FeS}_2$ ) dissolution in the groundwater (Chirenje *et al.* 2007). During the investigational period, majority of the samples (81 and 78%) have  $\text{SO}_4^{2-}/\text{Cl}^- > 0.5$  (Figure 5(l)), reflecting the oxidation of pyrite minerals and leaching of inorganic sulfide in soil may be the primary source of  $\text{SO}_4^{2-}$  in the groundwater (Okiongbo and Douglas 2015, Singh *et al.* 2020a). The remaining samples (19 and 22%) during pre and post monsoon have  $\text{SO}_4^{2-}/\text{Cl}^- < 0.5$  indicates the influence of anthropogenic inputs on groundwater namely, fertilizers applications, irrigation water seepage, and wastewater discharge (Suthar *et al.* 2009). From the above discussion, it can be inferred that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  are mainly derived from the carbonate and silicate weathering and reverse ion exchange process occurring in the aquifer. On the other hand, the parameters  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are majorly controlled by mixed factors with cation exchange process.

#### 4. Pearson correlation matrix (PCM) analysis

Pearson correlation matrix analysis of major ions (Table S2) is employed to understand the inter-ion relationships and extract meaningful information about the various geochemical processes prevailing in the study area aquifer system. The absolute correlation values 0.50–0.75 and  $> 0.75$  represent moderate and strong correlation among the ions, respectively (Hossain *et al.* 2020). During pre monsoon,  $\text{Mg}^{2+}$  have strong positive correlation with  $\text{Na}^+$  ( $r=0.67$ ) and moderately with  $\text{SO}_4^{2-}$  ( $r=0.88$ ), and for post monsoon,  $\text{Ca}^{2+}$  show moderately correlation with  $\text{Cl}^-$  ( $r=0.67$ ) and weak correlation with  $\text{Na}^+$  ( $r=0.40$ ) indicates the dissolution of carbonate minerals and reverse ion exchange process impacting the aquifer chemistry (Herojeet *et al.* 2017).  $\text{Na}^+$  have strong positive correlation with  $\text{HCO}_3^-$  (0.76 in pre monsoon and 0.78 in post monsoon),  $\text{SO}_4^{2-}$  (0.81 in pre monsoon and 0.76 in post monsoon), and moderate positive correlation with  $\text{Cl}^-$  (0.51 in post monsoon). It divulges and supports the role of silicate weathering, limited halite dissolution, ion exchange processes, and anthropogenic inputs, as discussed in above section 3.2.  $\text{HCO}_3^-$  have moderate positive correlation with  $\text{SO}_4^{2-}$  ( $r=0.65$ ) and  $\text{Cl}^-$  ( $r=0.57$ ) during pre monsoon depicts the presence of sulfate, carbonate, and chloride in the top soil aids the organic matter

decomposition process at different levels (El-Shinnawi *et al.* 1974). This process increases the  $\text{CO}_2(\text{g})$  in the upper layer of soil. The percolating water in the soil reacts with  $\text{CO}_2(\text{g})$  forming carbonic acid ( $\text{H}_2\text{CO}_3$ ) and further breakdown into  $\text{HCO}_3^-$  in the aquifer system (Raju and Singh 2017).  $\text{Cl}^-$  exhibits strong positive correlation with  $\text{NO}_3^-$  (0.86 in pre monsoon) and moderate correlation with  $\text{SO}_4^{2-}$  (0.55 in pre monsoon and 0.50 in post monsoon) indicates that these ions are originated from similar anthropogenic sources (Khan *et al.* 2021, Liu *et al.* 2021). The relationship of these ions reflects the impact of human activities such as fertilizer use, animal wastes, and farming activity that enrich  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$  in the groundwater of the study area (Rao *et al.* 2012, Marghade *et al.* 2021). Further,  $\text{SO}_4^{2-}$  shows an insignificant correlation with  $\text{Ca}^{2+}$  (Table S2), indicates that pyrite dissolution and anthropogenic inputs may also be responsible for  $\text{SO}_4^{2-}$  content in groundwater (Singh *et al.* 2020b, Marghade *et al.* 2021). From the PCM results, it can be concluded that the reverse ion exchange and weathering of aquifer minerals largely controlled  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  ions concentrations in groundwater. On the other hand, the enrichment of these ions, namely,  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are influenced by mixed factors and  $\text{NO}_3^-$  alone by anthropogenic inputs.

## 5. Dissolution and saturation state of minerals

The results of geochemical profiling (Piper plot, Gibb's diagram, and interionic plots) and PCM clearly indicated that the aquifer chemistry of the study area is mainly influenced by interactions of aquifer materials (minerals-water phases) and cation exchange, except for some ions. Saturation index (*SI*) is computed to ascertain the thermodynamic equilibrium about the dissolution and precipitation state of minerals vis-à-vis the types of water-alluvial interaction (Khan *et al.* 2021, Liu *et al.* 2021). *SI* is the logarithm (base 10) of the ratio of ionic activity product (*IAP*) to mineral solubility product constant ( $K_{sp}$ ) and is evaluated by using Equation (20)

$$SI = \log IAP/K_{sp} \quad (20)$$

The *SI* value  $<0$  indicates the mineral in solution is unsaturated,  $SI=0$  (saturation), and *SI* value  $>0$  (over saturation) with respect to a particular mineral (Zhang *et al.* 2020, Singh *et al.* 2020b). The *SI* values for seven minerals namely: anhydrite ( $\text{CaSO}_4$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), halite ( $\text{NaCl}$ ), sylvite ( $\text{KCl}$ ), calcite ( $\text{CaCO}_3$ ), dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ], and aragonite ( $\text{CaCO}_3$ ) are extracted and presented in Table S3. The

scatter plots of *SI* vs. EC for the groundwater samples are presented in supplementary Figure S2(a–g).

All the groundwater samples have *SI*  $<0$  i.e. negative (-) values for anhydrite (-3.16 to -2.62 and -3.39 to -2.50), gypsum (-2.95 to -2.34 and -3.06 to -2.17), halite (-9.02 to -7.25 and -9.0 to -7.33) and sylvite (-9.52 to -7.94 and -9.55 to -7.68) for pre and post monsoon seasons (Table S3). The negative *SI* values for anhydrite and gypsum also corroborate the results of geochemical signatures discussed in section 3.2; thus, dissolution will continue to release  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions in the aquifer system. Further, the *SI* values (-) for halite mineral supports the role of restricted dissolution in the contribution of  $\text{Na}^+$  and  $\text{Cl}^-$  ions (as discussed in above section 3.2) in the groundwater of the study area. The plots between *SI* vs. EC indicate that anhydrite and gypsum minerals are more influenced in the hydrochemistry due to the faster dissolution process than halite and sylvite [Figure S2(a–d)]. Also, the increasing trend of *SI* values of anhydrite, gypsum, halite, and sylvite along with EC divulges that the dissolution of these minerals in the aquifer system with time may directly lead to groundwater salinity.

Further, the mutual independence between EC and *SI* values infers that the groundwater chemistry has already been affected by the fast dissolution of calcite, dolomite, and aragonite [Figure S2(e–g)]. Calcite *SI* values (-0.45 to 0.95 and -0.85 to 0.5) indicate ~43 and ~41% samples are positive (saturated and over saturated) in the total samples for both seasons. Similarly, the *SI* values for dolomite (-0.45 to 2.04 and -1.09 to 1.11) infer ~60 and ~72% samples are positive, and aragonite (-0.6 to 0.8 and -1.99 to 0.36) show a positive in ~38 and ~13% in the groundwater samples during the investigational period. It appears that the aquifer system has manifested the equilibrium between the aqueous groundwater phase and the carbonate minerals phase, subsequently over saturated leading to precipitation of these minerals. The precipitation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  makes  $\text{HCO}_3^-$  the dominant anion and the effective increment of  $\text{Na}^+$  concentration in the groundwater (Li *et al.* 2018a, b). Moreover, anhydrite, gypsum, halite, and sylvite dissolution may lead to dolomite, calcite, and aragonite sequestration and increase aquifer salinity in the study area (Marghade *et al.* 2021, Karunanidhi *et al.* 2021a).

## 6. Human health risk assessment

### 6.1. Average daily dose (ADD)

The estimated ADD values (mean, median, SD, 5th, and 95th percentile) using deterministic and

probabilistic methods for the target subpopulation category through ingestion and dermal route are presented in Tables S4 and S5. In the present study, deterministic and probabilistic risk analysis used the 5th and 95th percentile as their lower and upper values estimated for different models. The calculated mean, 5th and 95th percentile  $ADD_{ingestion}$  values of  $F^-$  and  $NO_3^-$  using deterministic and probabilistic methods for the pre and post monsoon seasons are pretty the same for all population groups (Table S4).

The range of variation for  $ADD_{dermal}$  values estimated by the deterministic method is higher than the probabilistic technique for both seasons (Table S5). For instance, the deterministically calculated mean, 5th and 95th percentile  $ADD_{dermal}$  values for  $F^-$  are  $\sim 7$ ,  $\sim 9$ , and  $\sim 5$  higher than the probabilistic method for both seasons. The  $ADD_{dermal}$  point estimate for  $NO_3^-$  indicates a similar range of mean and 95th percentile, i.e.  $\sim 7$  and  $\sim 6$  times higher than the probabilistic approach for both seasons. The 5th percentile  $ADD_{dermal}$  of  $NO_3^-$  divulges deterministic variation  $\sim 8$  (pre monsoon) and  $\sim 18$  (post monsoon) times higher than the probabilistic approach. Further, the comparative study within deterministic (pre monsoon vs. post monsoon) and probabilistic (pre monsoon vs. post monsoon) values reveal that 5th percentile and 95th percentile  $ADD_{ingestion}$  and  $ADD_{dermal}$  for  $F^-$  parameter for both seasons indicate no significant variation. On the contrary, the probabilistically (pre monsoon vs. post monsoon) and deterministically (pre monsoon vs. post monsoon) estimated 95th percentile  $ADD_{ingestion}$  and  $ADD_{dermal}$  for  $NO_3^-$  during pre monsoon show  $\sim 3$  and  $\sim 2$  times and 5th percentile values as  $\sim 14$  and  $\sim 6$  times higher than the post monsoon values for all subpopulation groups. This may be due to pre monsoon  $NO_3^-$  concentration levels  $\sim 4$  times higher than post monsoon, thus crediting the  $ADD$  ingestion and dermal contact values more than  $F^-$  in both risk estimate models.

## 6.2. Hazard quotient

Deterministic and probabilistic  $HQ$  estimation for  $F^-$  and  $NO_3^-$  through ingestion and dermal contact of groundwater is shown in Tables S6 and S7. The mean  $HQ$  values of  $F^-$  and  $NO_3^-$  for ingestion and dermal exposure route are below the acceptable limit, i.e.  $HQs < 1$  for each subpopulation group. Risk certainty level ( $RCL$ ) is assessed to generate the likelihood percentage scenarios of hazard risk above the threshold value ( $HQs > 1$ ) from all the datasets of particular pathway on the target subpopulations. It is another advantage to determine the  $RCL$  value in health risk assessment for any exposure

pathway even if their mean, 5th, and 95th percentile are below their threshold limit. During pre monsoon, the deterministic estimate through  $F^-$  ingestion indicates 3.13%  $RCL$  in infants and children, respectively. Probabilistic  $RCL$  related to groundwater ingestion of  $F^-$ , only infants (2.58%) have a higher risk of non-carcinogenic effect ( $HQs > 1$ ) as compared to other groups like children (0.44%), teens (0.07%), and adults (0.04%) show minimal health impact (Table S6). For post monsoon, deterministic  $RCL$  confirm no adverse health on the subpopulation groups, whereas probabilistic  $RCL$  depict the non-carcinogenic health effect on infants (1.51%) and children (0.04%) through  $F^-$  ingestion of groundwater.

The  $HQ_{ingestion}$  of  $NO_3^-$  signify non-cancer health impact at different  $RCLs$  on target groups from deterministic results (infants: 31.25%; children: 15.63%; teens: 6.25% and adults: 6.25%) more than probabilistic estimates (infants: 23.72%; children: 7.66%; teens: 0.77% and adults: 0.48%) for pre monsoon (Table S6). During post monsoon, deterministic  $RCL$  shows the only potential threat to infants (3.13%), whereas probabilistic  $RCL$  refers to infants (1.65%) and children (0.18%) groups that pose a health risk due to groundwater ingestion containing  $NO_3^-$  (Table S6). The  $HQ$   $RCLs$  dermal pathway of chemical parameters ( $F^-$  and  $NO_3^-$ ) indicate no possible health risk on the specified subpopulation groups from both approaches (Table S7). Among the analyzed human exposure routes, the ingestion pathway is more profound in health risk from  $RCL$  results, and the  $NO_3^-$  parameter is the key risk indicator for infants and children. For example, the  $RCL$  ratio of deterministic ( $NO_3^-$ ) vs. deterministic ( $F^-$ ) and probabilistic ( $NO_3^-$ ) vs. probabilistic ( $F^-$ ), their magnitude values range from 1–9.98 and 1–9.21, respectively, thus confirm that  $NO_3^-$  is the prominent ion inducing the plausible risk factor.

Further, the ratios of deterministic vs. probabilistic mean  $HQ_{ingestion}$  values ( $F^-$  and  $NO_3^-$ ) for infants, children, teens, and adults vary from 1.12 to 1.23, 1.13 to 1.16, 1.17 to 1.22, and 1.34 to 1.38, respectively, during the investigational period. Also, the range of deterministic vs. probabilistic ratio of 5th and 95th percentile  $HQ_{ingestion}$  values ( $F^-$  and  $NO_3^-$ ) for infants (1.57–3.90 and 0.76–1.16), children (1.27–3.03 and 0.86–1.27), teens (1.27–3.28 and 0.93–1.33), and adults (1.42–3.63 and 1.07–1.53) for both seasons. This range variability of  $HQ$  values indicates that deterministically estimated values are higher than probabilistically assessed values for the entire subpopulation groups. The above analysis divulges that the deterministic method estimate is based on the extreme value

of the input variables, leading to overestimating the output results.

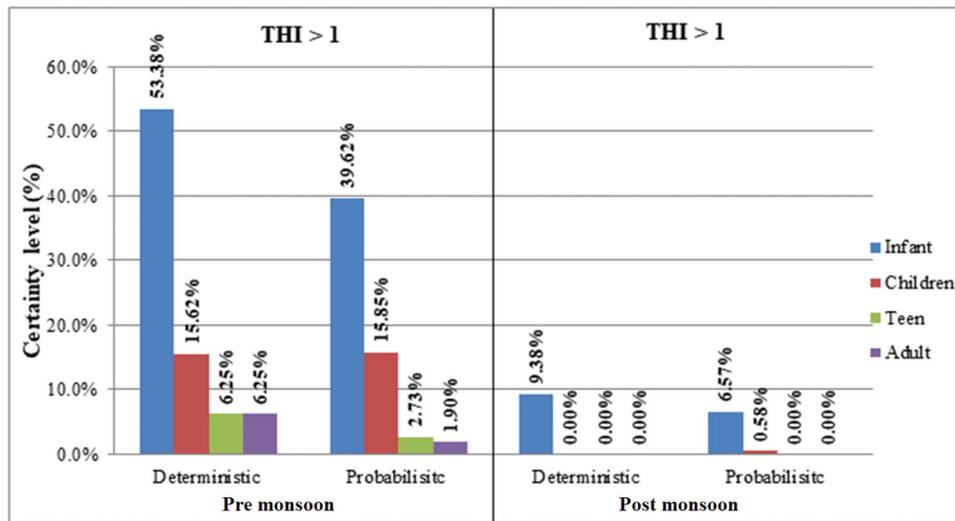
### 6.3. Hazard index and total hazard index

The non-carcinogenic  $HI$  associated with groundwater ingestion and dermal contact are presented in Table S8. The pre monsoon mean  $HI_{ingestion}$  value exceeds the safety reference level ( $HI > 1$ ) only on the infants' group indicating minor population is more vulnerable in the target subpopulation groups (Figure S3a). In contrast, the post monsoon  $HI_{ingestion}$  mean values of all different groups are below the threshold limit (Figure S3a). However, the  $RCLs$  of deterministic and probabilistic estimates above the acceptable value ( $HI_{ingestion} > 1$ ) for pre monsoon season are as follows: infants (59.38 and 39.60%), children (15.63 and 15.84%), teens (6.25 and 2.72%), and adults (6.25 and 1.87%) (Table S8). For post monsoon season, the significant  $RCL$  for the deterministic study is only reflected on infants (9.38%), whereas the probabilistic  $RCL$  results reflect on infants (6.57%) and children (0.58%) as more susceptible groups to health risk than the remaining populations (Table S8). The  $HI_{dermal}$  mean, 5th, and 95th percentile values are less than unity and is observed as no threat to the target population groups due to insignificant  $RCL$  (Table S8 and Figure S3b). Ji *et al.* (2020) from their study in Guanzhong plain, China, also reported that the non-carcinogenic  $HI_{oral}$  ( $F^-$  and  $NO_3^-$ ) from the chlorinated water and terminal tap water are higher on children than that of adults during dry and wet seasons. The present study conclude that  $HQ$  and  $HI$  ingestion pathways have more potential human health risks than that of dermal contacts. Liu *et al.* (2022) got similar findings of non-cancerous health risks from the groundwater of Weining plain, China.

Total hazard index (THI) is the combination of non-carcinogenic hazard risk factors of  $F^-$  and  $NO_3^-$  through multi-exposure pathways (ingestion and dermal) of groundwater, as shown in Table 4. For pre monsoon, the deterministic  $RCL$  values indicate that infants are 3.8 – 9.5 times more susceptible to risk than remaining groups, and children show 2.5 times more risk threat than teens and adults. The probabilistic  $RCL$  estimates specify that infants are 2.5 – 20.9 times higher non-cancer risk than children, teens, and adults, children (5.8 – 8.3 times) than teens and adults and teens (1.4 times) than adults. During post monsoon, only infants are marked highest  $RCL$  i.e. 9.38 times than the remaining population groups from deterministic results. On the contrary, probabilistic  $RCL$  results show

**Table 4.** Statistical description of deterministically and probabilistically calculated total hazard index (THI) for ingestion and dermal pathways at different age groups.

Age group	THI	Deterministic value					Probabilistic value					Risk certainty level (%)	
		Mean	Median	Stdev.	5%	95%	Mean	Median	Stdev.	5%	95%	THI > 1	THI > 1
Pre monsoon	Infant	1.16E+00	1.15E+00	7.12E-01	3.14E-01	2.16E+00	1.03E+00	8.41E-01	1.73E+00	2.75E-01	2.39E+00	59.38%	39.62
	Children	7.51E-01	7.44E-01	4.61E-01	2.04E-01	1.40E+00	6.57E-01	5.82E-01	1.03E+00	2.07E-01	1.36E+00	15.62%	15.85
	Teen	5.42E-01	5.37E-01	3.33E-01	1.47E-01	1.01E+00	4.49E-01	4.08E-01	6.87E-01	1.44E-01	9.10E-01	6.25%	2.73
Post monsoon	Adult	5.83E-01	5.78E-01	3.59E-01	1.58E-01	1.09E+00	4.24E-01	3.81E-01	6.45E-01	1.41E-01	8.44E-01	6.25%	1.90
	Infant	5.18E-01	4.26E-01	3.01E-01	2.19E-01	1.16E+00	4.64E-01	3.75E-01	8.15E-01	1.17E-01	1.11E+00	9.38%	6.57
	Children	3.36E-01	2.76E-01	1.95E-01	1.42E-01	7.54E-01	2.92E-01	2.55E-01	4.69E-01	8.74E-02	6.30E-01	0.00%	0.58
Adult	Teen	2.42E-01	1.99E-01	1.41E-01	1.03E-01	5.44E-01	2.04E-01	1.77E-01	3.23E-01	6.50E-02	4.32E-01	0.00%	0.00
	Adult	2.61E-01	2.15E-01	1.52E-01	1.10E-01	5.86E-01	1.89E-01	1.67E-01	2.96E-01	6.08E-02	3.94E-01	0.00%	0.00



**Figure 6.** Deterministic and probabilistic results of risk certainty level for different population group.

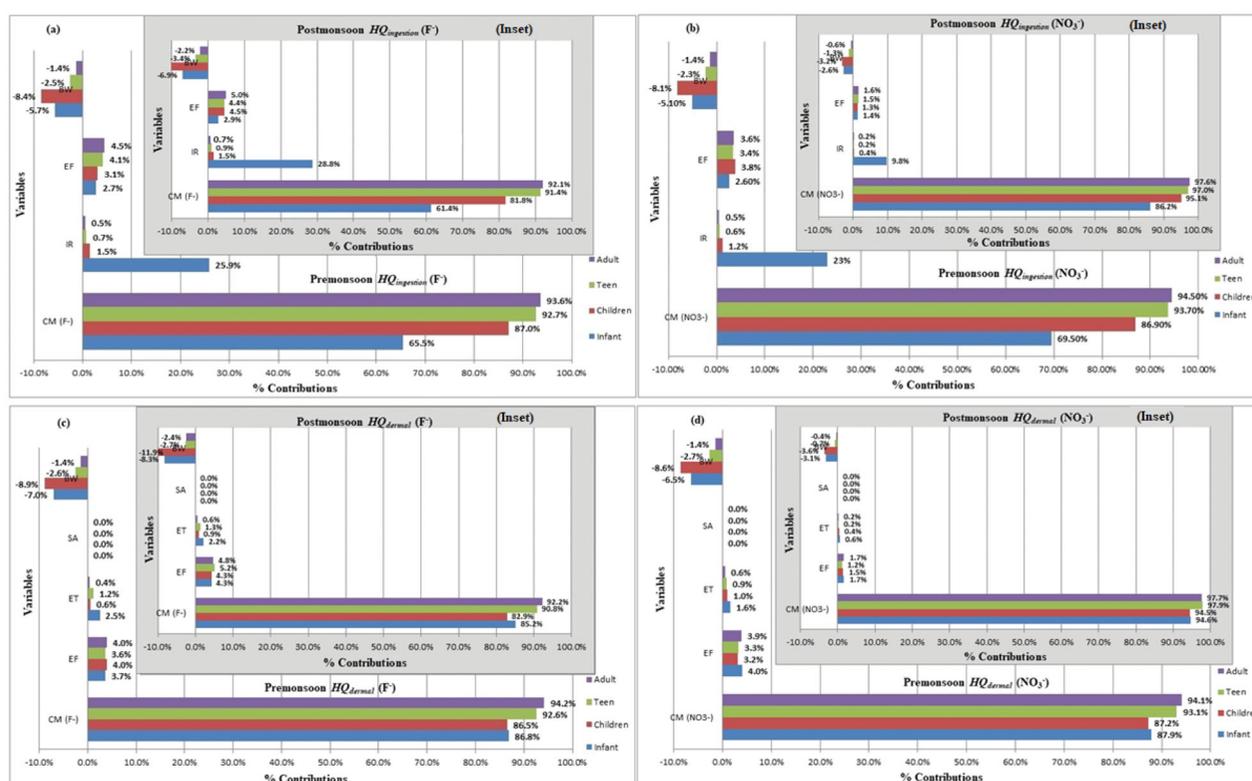
that infants (0.6 – 11.3 times) are more vulnerable than the other population groups and children (0.6 times) more than teens and adults, which is unable to predict by the point estimation method. Therefore, it is noteworthy that the probabilistic simulation method appraises the holistically credible risk scenarios on target subpopulations that may be limited by the deterministic method. Liu *et al.* (2022) suggest that the health risk assessment in groundwater through probabilistic simulation provides comprehensive results than that of deterministic method in different age groups in China. The overall non-carcinogenic health risks in the different population groups are higher in pre monsoon season as compared to post monsoon period due to higher concentration of  $\text{NO}_3^-$ . The present study ascertain that minor populations (infants and children) are more vulnerable to non-carcinogenic risks than those of teens and adults (Figure 6). This is because minor populations show higher sensitivity and poor resilience to withstand the harmful contaminants due to lower body weights. Similar studies on the non-carcinogenic health risks in different population groups elsewhere too report that infants and children are susceptible high risk than those of teens and adults. Examples are: Baqiao District, China (Guo *et al.* 2022), Muktsar district, Punjab, India (Sangwan *et al.* 2021), Jalandhar district, Punjab (Singh *et al.* 2020a), surface water in Taizhou city, Zhejiang Province, China (Zhang *et al.* 2022) and water supply reservoirs in Taizhou City, East China (Yin *et al.* 2021).

#### 6.4. Sensitivity and uncertainty analysis

Sensitivity analysis is employed using the MCS approach to evaluate the input variables that

significantly influenced non-carcinogenic risk prediction. The outcome of sensitivity analysis is presented as tornado plots elucidating the Spearman rank-order correlation coefficient in the percentage scale [Figure 7(a,b,c,d)]. The results of sensitivity analysis for non-carcinogenic  $HQ_{\text{ingestion}}$  confirmed that respective parameter concentration ( $C_M$ ) is the most precedence variable, followed by exposure frequency (EF) and ingestion rate (IR) of groundwater with a minor contribution in children, teens, and adults for both seasons [Figure 7(a&b)]. On the other hand, the sensitivity analysis shows the order of significant variables as  $C_M$ , IR, and EF for infants  $HQ_{\text{ingestion}}$  due to high dependence on water-based liquid diet and less surface area of the body [Figure 7(a&b)]. The non-cancer  $HQ_{\text{dermal}}$  sensitivity analysis outputs reveal the highly significant variables as  $C_M$ , and minor influence by EF, and exposure time (ET). In contrast, surface area (SA) indicates neutral contribution in any specific population groups during the investigational period [Figure 7(c&d)]. However, Body weight (BW) had a negative inference on non-carcinogenic  $HQ$  risk simulation through ingestion and dermal pathways in target population groups.

Uncertainty analysis is crucial to determining the conservatism, ramification, and certainty accuracy level of the risk analysis results (Zhang *et al.* 2019). In this study, the application of MCS is notably enhanced to identify the uncertainties quantification in the non-cancer health risk assessment. Nevertheless, there are still other uncertainties that remain unaccounted in the model input variables, thereby limiting the validity of the whole scenario study. For example, (i) the daily water intake and dermal contact of target population groups are not measured during the groundwater



**Figure 7.** (a, b, c, & d) Tornado plot illustrating sensitivity analysis of input variables to the non-carcinogenic HQ of groundwater (a & b) pre monsoon and post monsoon (inset) of F<sup>-</sup> and NO<sub>3</sub><sup>-</sup> ingestion and (c & d) for dermal contact.

sampling, (ii) body weight of the local population are not evaluated, instead used the representative data of the Indian Council of Medical Research (ICMR) and USEPA, (iii) exposure duration, average time, dermal permeability and conversion factor are considered as the same fixed or similar values for deterministic and probabilistic approach for different subpopulation groups, (iv) the variables data to generate the PDFs using MCS are acquired from the USEPA, and other relevant published works, (v) assuming the specific chemical parameter contents in groundwater are the totally bio-absorbable amount by human body might lead to ambiguity in risk analysis, and (vi) the reference dose (*RfD*) for ingestion and dermal are obtained from USEPA. The present findings shall be considered reliable information of HHRA in the target subpopulation groups in the study area compared to reliance on classification based on their parameter concentrations and prescribed National standards.

## 7. Conclusion

This paper highlights groundwater evolution and geochemical profiling using various graphical interpolations, statistical techniques along with quality assessment for drinking purposes. Further, the comparative evaluations of deterministic and probabilistic

approaches are applied to determine the non-carcinogenic HHRA for F<sup>-</sup> and NO<sub>3</sub><sup>-</sup> through ingestion and dermal pathways. This study profoundly conveyed that the health risk may persist in vulnerable groups, even if health concern parameters concentrations are below their respective guideline limits. Major findings of the present study are as under:

- Concentrations of pH, EC, TH, and Mg<sup>2+</sup> exceed their respective permissible limit at some sites, and ~50% of samples for TDS, TH, Mg<sup>2+</sup>, and Ca<sup>2+</sup> surpassed the acceptable limit that needs to be cautious and requires necessary treatment. The parameters such as, EC, TDS and Na<sup>+</sup> have higher mean values during pre monsoon season indicating enhanced ion exchange processes for mineralization and salinity in aquifers. On the other hand, TH, Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> show elevated mean concentrations during post monsoon season reflecting dissolution of the carbonate and silicate minerals in the percolating rainwater and inverse ion exchange processes in the alluvial aquifers.
- Aquifer chemistry is mainly controlled by water-alluvial interaction and predominant Ca<sup>2+</sup>-Mg<sup>2+</sup>-HCO<sub>3</sub><sup>-</sup> water type. Interionic plots corroborated by PCM that Mg<sup>2+</sup>, Ca<sup>2+</sup>, and HCO<sub>3</sub><sup>-</sup> are influenced by weathering of aquifer minerals, and Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>+</sup>,

and  $\text{SO}_4^{2-}$  by mixed factors. Further, the thermodynamic equilibrium of calcite, dolomite, and aragonite with aqueous phase confirmed their major influence in aquifer chemistry.

- Deterministically and probabilistically estimated  $HQ_{\text{ingestion}}$  and  $HI_{\text{ingestion}}$  indicate that  $\text{NO}_3^-$  is the prominent parameter inducing the plausible risk factor than  $\text{F}^-$  on the local population. Non-cancer risk ( $HQ$  and  $HI$ ) for dermal route depicts trivial health risks and could be derelict. Therefore, ingestion is the dominant pathway associated with non-carcinogenic health risks. The calculated THI depicts that infants and children are more susceptible to health risk than teens and adults by probabilistic simulation for both seasons. Therefore, the probabilistic method enables the appraisal  $RCLs$  of  $HQ$ ,  $HI$ , and THI in the most holistic credible risk scenarios on target subpopulations that may be limited by the deterministic method.

Proper treatment of water prior to use is strongly recommended to safeguard the human health and prevent the vulnerable age groups from being affected by non-cancer risks. Further, implementation of better industrial policies and their strict enforcement shall minimize the spread of water pollution and protect the fragile sub-Himalayan ecosystem from contamination.

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