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THEMATIC ISSUE

Hydrogeochemical assessment of groundwater quality and associated potential human health risk in Bhadohi environs, India

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Abstract

The current study intended to assess the hydrogeochemical processes and groundwater quality along with the identification of associated health risk by consuming the groundwater in the local population by collecting 70 groundwater samples for premonsoon and postmonsoon in the year 2015. Gibbs plot nominated that majority of the sample of Bhadohi is from rock dominance. The Ca/Mg ratio signifies that carbonate dissolution is the principal reason for Ca in the Bhadohi environs. Relatively high Na/Cl (> 1), K/Cl (> 0.02) and SO_4/Cl (> 0.09) ratios are accredited to the influence of textile effluents on the groundwater. 45% sample in postmonsoon and 40% samples in premonsoon demonstrate high NO_3 values which is exceeding the WHO standard for human drinking. Chronic daily intake (CDI) value demonstrates that the residents of the study region are at risk of nitrate contamination originated health hazards. About 48.5% of groundwater samples show a high concentration of iron. The HPI profile shows that 32% of the sample has high HPI values, 17% of the sample has a medium range of HPI, and 51% of the sample has a low value of HPI. Target health quotient values of trace metals in groundwater were in the order of Pb > Mn > Cr > Cd > Cu > Fe > Zn > Ni. The groundwater of the investigative area is fine for irrigation.

Keywords Hydrogeochemistry · Groundwater pollution · Textile industry · Chronic daily intake (CDI) · Heavy metal pollution index (HPI) · Target health quotient (THQ)

Introduction

Groundwater is one of the great natural resources on earth. Moreover, water has seemed like an infinite and ample resource that describes human, social and economic progress. Groundwater chemistry of any region is extensively directed by geological formations and anthropogenic activities (Madhav et al. 2018a; Tiwari et al. 2020). Natural features which have control on water chemistry include precipitation form and amount, geological typeset of watershed and aquifer, climatic conditions and different rock–water interface events in the aquifer (Elangovan et al. 2018). However, the natural characteristic of groundwater has gradually downgraded due to various human actions (Kim et al. 2015). Anthropogenic activities which operate the water composition incorporate management of household and industrial wastewater and agricultural runoff (Arnade et al. 1999; Mukate et al. 2019). Urbanization, industrialization and agricultural activities are responsible for nitrate contamination in groundwater (Madhav et al. 2018b). Various health impacts are associated with the higher values of nitrate in drinking water. Non-carcinogenic health hazards of nitrate pollution were measured by Chronic Daily Intake (CDI) in various studies (Tiwari et al. 2015; Madhav et al. 2020).

Textile industries have emerged as a prime source of water pollution. These industries consume a considerable amount of water in their function and, therefore, discharge a significant amount of effluent into the environment, primarily untreated (Madhav et al. 2018b). Furthermore, textile effluents are reported to contain hazardous waste,

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such as degradable organics, surfactants, pH regulating elements, trace metals and dyes (Giorgetti et al., 2011). The occurrence of metals in various paints is necessary for they are responsible for the colour dyes. Cu, Zn, Cr, Ni, Cd, Pb, and Mn are the different heavy metals allied with diverse dyes (Madhav et al. 2018b). Heavy metal contamination in groundwater is a big challenge as a high concentration of heavy metals imposes an adverse effect on human health. Human disclosure to textile dyes has resulted in lung and skin nuisances, body aches, innate deformities and nausea (Mathur et al. 2012). Heavy metal contamination in groundwater employing several indices such as HPI and THQ was done by various researchers (Tiwari et al. 2015; Pawar and Pawar 2016; Ahamad et al. 2018). In the current assessment, an attempt has been made to identify the sources of ions in the groundwater and find out various hydrogeological processes affecting groundwater chemistry. An endeavour has been prepared to find out the impact of textile effluents on groundwater composition. Multiple indices are applied to determine the aptness of water for drinking and irrigation purposes. The adverse health impact of nitrate and heavy metals on human health are also analyzed in this study.

Study area

Bhadohi

Bhadohi has situated between 25.12° and 25.32° North Latitudes and 82.12° to 82.42° East Longitudes. Bhadohi is a recognized textile hub in north India. A significant number of textile industries are positioned and operational in Bhodohi city and adjacent areas, and treated and untreated effluents is usually used in agricultural activities. Large industries are situated in industrial zones but small in medium size industries are scattered in the city and creating big environmental crisis. Figure 1 shows the location map of the investigative region. The study area has a subtropical type climate with a clear monsoon effect. Three distinct seasons, namely, summer, rainy and winter occurs in this region. The average annual rainfall of the study area is around 1020 mm (Raju et al. 2011; Mohan et al. 2011; Madhav et al. 2018a). Jayad, Kharif and Rabi are three major crops in this region (CGWB 2013). The reliance of the whole region on the groundwater is the key motive behind the selection of this particular study area. An additional reason to prefer this region is its multifaceted land use pattern and high population density. A relatively small area shows different land-use patterns. Groundwater is being used for housing, irrigation as well as industrial purposes in this region.

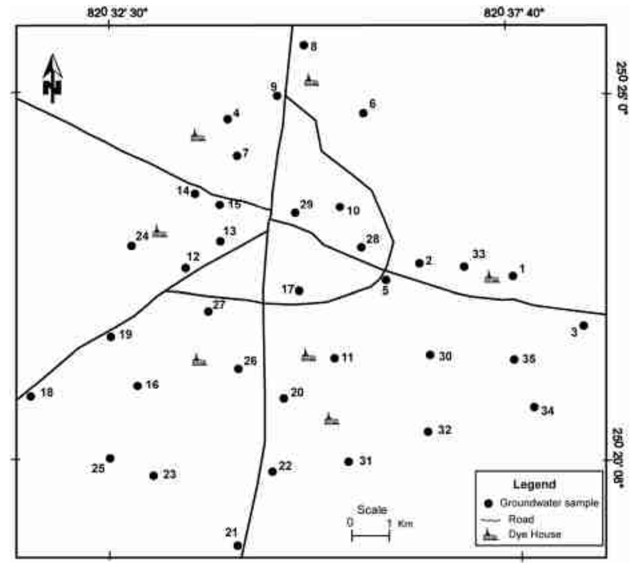

Fig. 1 Location map of the study area

Geology and hydrogeology

Bhadohi environs are situated in central Ganga Alluvial plain. The alluvial plain of the investigative town is geologically alienated into three diverse zones, i.e., older alluvial upland, newer alluvial plain and Holocene to Recent active channels and floodplains with a gentle slope. The unconsolidated close to surface Pleistocene to recent fluvial sediments covering the more significant part of the Ganga plains are usually potential aquifers. The discontinuous sand and clay layers have formed a multilayer aquifer structure in the study region (Shukla and Raju 2008; Raju 2012; Madhav et al. 2018a).

Material and method

Sampling pattern, sample containers, and storage of samples

Samples collection performs a crucial part in concluding the quality of data produced. Standard techniques and sample collection are essential to obtain good results (APHA 2005).

Groundwater samples (35 each in premonsoon and postmonsoon in the year 2015) were collected from bore wells and hand tubes. The groundwater was collected from shallow aquifers with an average depth of 40 m. The values of some parameters and concentration of some parameters, for instance, pH, EC, and HCO_3 measured on-site. Water samples collected in plastic bottles were utilized for determining major anions and silica. For water samples, total hardness and Ca were measured by EDTA titrimetric mode and Mg by calculation method. Total alkalinity, HCO_3, and Cl were also determined by the titrimetric method. Na and K were be measured by flame photometer, NO_3, SO_4 and SiO_2 by UV spectrophotometer. 60 ml water was taken in the postmonsoon season for the investigation of heavy metals in groundwater and preserved by adding four drops of HNO_3 to maintain pH 2. Heavy metal concentrations of the groundwater were examined by Atomic Absorption Spectrophotometer (M series AAS, Thermo Scientific, Cambridge, UK) with Air-Acetylene Flame**.** The analytical precision for the precise measurements of ions was determined by formulating electrical neutrality (EN %), which is adequate at ± 5% (Appelo and Postma 2004). All the samples have EN % values within ± 5% in both the seasons:

$$\text{EN \%} = \left[\left(\sum \text{Cation} + \sum \text{Anion}\right) / \left(\sum \text{Cation} - \sum \text{Anion}\right)\right] \times 100. \quad (1)$$

Chronic daily intake (CDI)

The Chronic daily intake (CDI) values can be computed by the following formula **(**Miri et al. 2018; Adimalla et al. 2020):

$$\text{CDI} = (\text{Cw} \times \text{DI} \times \text{EF} \times \text{EP})/(\text{BW} \times \text{AT}), \quad (2)$$

where Cw is equal to the values of NO_3 in water, DI is per day water intake (L/day), EF is exposure constancy (days/year), EP is the mean exposure time (years), BW is average body weight (kg) and AT is the average time (days). Here DI is 2, 1.5 and 0.8 L; EP is 40, 10 and 1 year, and BW is 70, 40 and 10 kg for an adult, children, and infants, respectively (Qasemi et al. 2018; Adimalla et al. 2020, 2021).

Hazard quotient (HQ) value is calculated as a division of the indicated dose to the reference dose as specified in the following formula (Radfard et al. 2018):

$$\text{HQ} = \text{CDI}/\text{RfD}, \quad (3)$$

where RfD is the reference dose of $NO_{3,}$ i.e., 1.6 mg/kg/day. If the HQ value is more than 1 are cause adverse health consequences on the exposed person.

Residual sodium carbonate (RSC)

RSC is utilized to identify the harmful effects of CO_3 and HCO_3 on the water for farming function (Eaton 1950). RSC can be approximated by the formula specified below:

$$\text{RSC} = \left(\text{CO}_3 + \text{HCO}_3\right) - (\text{Ca} + \text{Mg}), \quad (4)$$

where ionic values are taken in meq/l.

Percentage of sodium (% Na)

The % Na is found by the formula given below:

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

where ionic values are taken in meq/l.

Sodium adsorption ratio (SAR)

The SAR value is calculated by Richard (1954) equation:

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

where all the ionic values are articulated in meq/l.

The heavy metal pollution index

HPI is a grading system that offers the collective outcome of various heavy metals in general water class (Tiwari et al. 2015; Raja et al. 2021). HPI is a significant way for the estimation of water excellence on the origin of heavy metal concentration. HPI has been invented and developed (Mohan et al. 1996) as

$$\text{HPI} = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \quad (7)$$

$$Qi = \frac{\sum_{(i=1)}^{n} \{Mi(-)Ii\}}{\sum_{(i=1)}^{n} (Si - Ii)}, \quad (8)$$

where Qi = sub-index of the ith element; Wi = unit weightage of the ith element; n = number of elements; Mi = examined value of heavy metal of ith element; Ii = ideal value of i element; Si = standard value of the ith element. The critical pollution index of HPI value for intake water as specified by Prasad and Bose (2001) is hundred. On the other hand, a revised scale of 3 groups has been applied in the current work after Edet and Offiong (2002). The groups have been differentiated as low, medium and high for HPI values < 15, 15–30 and > 30, correspondingly.

Target hazard quotient (THQ) and potential human health risk

THQ in the course of water intake is computed according to the US Environmental Protection Agency (US EPA 2000) formula as pursue:

$$THQ = \left(EFr \times ED_{tot} \times SFI \times MCS_{inorg}\right) / (RfD \times BWa \times ATn), \quad (9)$$

where EFr = disclosure regularity (365 days/year); ED = disclosure interval (70 years); SFI = water intake rate (5L/ person/day), MCS_{inorg} = value of heavy metal in water (μg/L); BWa = standard body mass (55.9 kg); ATn = time duration (365 days/year X ED_{tot}) and RfD = oral reference dose (μg/kg/day). RfD values for Fe, Mn, Cu, Zn, Pb, Cd, Ni, and Cr are 300, 20, 300, 40, 0.4. 0.5, 20, and 3 in that order (US EPA 2013; Ahamad et al. 2018; Madhav et al. 2020). The collective non-carcinogenic outcome for more than 1 element can be expressed by Hazard Index (HI):

$$HI = \sum_{i=1}^{n} HQ. \quad (10)$$

The non-carcinogenic toxic hazard is measured to be low if the THQ and HI value is < 1. When it is > 1, a probable health hazard may happen.

Results and discussion

General geochemistry

The statistical chart of physiochemical constituents and ionic ratios are accessible in Table 1.

Hydrogeochemical facies

Gibbs (1970) projected two plots to identify the hydrogeochemical processes concerning atmospheric rainfall, rock–water interface, and evaporation over the command on groundwater chemistry. Gibbs diagram are the graphs of ratio of cations [(Na + K)/(Na + K + Ca)] and anions [Cl/ (Cl + HCO_3)] against to TDS. Gibbs plot nominated that all the sample of Bhadohi is from rock dominance in premonsoon. In contrast, in postmonsoon, all the samples are rock dominance except one sample, which lies in evaporation control (Fig. 2a, b).

Piper diagram is practised to identify the similarity and differences in water composition and categorized into specific water categories based on dominant ions. It is observed that in postmonsoon, 71.42% samples are of no dominance type, 11.42% samples are of Na + K type, 11.42% samples are of Mg type, and 5.71% samples are of Ca type, while in premonsoon, 91.42% samples are of no dominance, 5.71% samples are of Ca type, and 2.85% samples are of Ca type

Table 1 Range of chemical parameters of groundwater in Bhadohi environs

Quality Parameter	WHO limit 2011	Range Min.–Max. (Mean)		% samples Exceeding the permissible limit WHO 2011	
		Postmonsoon	Premonsoon	Postmonsoon	Premonsoon
pH	9.2	6.82–8.1 (7.59)	6.70–8.18 (7.41)	–	–
TDS (mg/L)	1500	464–1174 (670)	420–899 (636)	–	–
TH (mg/L)	–	196–648 (373)	240–585 (371)	–	–
Ca (mg/L)	200	34–180 (70.23)	32–124 (68.91)	–	–
Mg (mg/L)	150	16.10–108.05 (48.24)	25.61–98.67 (48.48)	–	–
Na (mg/L)	200	39.7–174 (90.54)	23.30–154.90 (79.45)	–	–
K (mg/L)	12	2.2–15.6 (4.96)	1.20–13.80 (5.04)	2.85	2.85
HCO_3 (mg/L)	600	240–548 (411.66)	176–536 (395.77)	–	–
SO_4 (mg/L)	600	15.9–102.9 (47.32)	10.62–96.30 (44.39)	–	–
Cl (mg/L)	600	42–250 (94.25)	48–234 (86.97)	–	–
F (mg/L)	1.5	0.17–1.9 (0.61)	0.10–2.10 (0.47)	8.57	5.71
NO_3 (mg/L)	50	10.6–198.6 (70.54)	13.12–205.39 (67.60)	45.71	42.85
Ca/ Mg	–	0.28–3.32 (1.15)	0.3–2.19 (0.94)	–	–
Na/Cl	–	0.38–3..32 (1.65)	0.45–2.96 (1.5)	–	–
HCO_3/ (HCO_3 + SO_4)	–	0.72–0.096 (0.87)	0.66–0.97 (0.87)	–	–
K/Cl	–	0.03–0.66 (0.25)	0.01–0.12 (0.06)	–	–
SO_4/ Cl	–	0.09–1.15 (0.42)	0.1–1.36 (0.42)	–	–

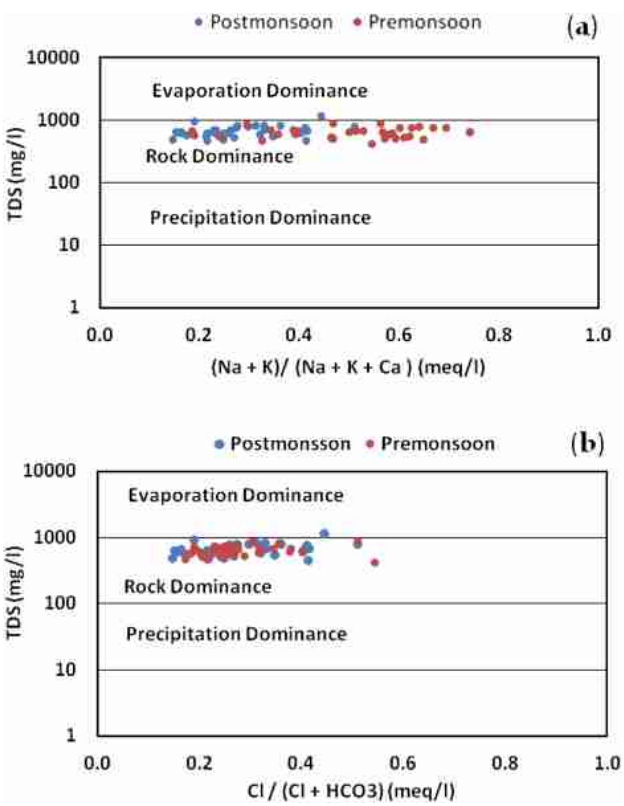

Fig. 2 Mechanism controlling groundwater chemistry: **a** Gibbs 1 and **b** Gibbs 2

of cation facies. On the other hand in postmonsoon 91.42% samples are of HCO_3 type, 5.71% samples are of no dominance type 2.85% samples are of Cl types, while in premonsoon, 91.42% sample is of HCO_3 type, 2.85% samples are of no dominance, and 5.71% sample is of Cl type of anion facies (Fig. 3).

Hydrogeochemical processes

In Bhadohi Ca/Mg ratio varies from 0.28 to 3.32 (mean 1.15) in postmonsoon and 0.30 to 2.19 (mean 0.94) in premonsoon (Table 1). Therefore, carbonate weathering is the main cause of Ca in groundwater in the investigative region. In carbonate weathering, dolomite weathering is dominant over calcite weathering. However, some samples are above the ratio line 2, representing silicate weathering is also adding Ca in the groundwater at a small quantity (Karunanidhi et al. 2020). The role of weathering on groundwater chemistry can be identified by a plot between TZ^+ and HCO_3. 1:1 ratio between TZ^+ and HCO_3 is the indication of considerable control of weathering on groundwater composition (Kim et al. 2004; Umar and Alam 2012**)**. In the current study graph between TZ^+ and HCO_3 (Fig. 4a) reveals the predominance of ion cascade near the 1:1 line recommending that mineral weathering is a major cause of ions in the groundwater in Bhadohi. A high comparative ratio of $HCO_3/(HCO_3+SO_4)$ (Fig. 4b) of the groundwater is the signal of carbonate weathering (Raju 2012; Husain et al. 2020). In, Bhadohi the ratio between $HCO_3/(HCO_3+SO_4)$ fluctuates from 0.72 to 0.96 with an average of 0.87 in postmonsoon and 0.66–0.97 with an average of 0.87 in premonsoon (Table 1). If the Na/Cl ratio is > 1, it indicates that silicate weathering is contributing Na in water (Meyback 2003; Jalali 2010; Husain et al. 2020). In Bhadohi it ranges from 0.38 to 3.32 (mean 1.65) in postmonsoon and 0.45 t 2.96 (mean 1.50) in premonsoon (Table 1). It indicates that silicate weathering is also contributing Na in groundwater.

The cation exchange progression is also a vital occurrence that acts a significant function to decide the groundwater quality. A graph between [(Na + K)–Cl] and [(Ca + Mg–(HOC_3–SO_4)] informs about the opportunity of the ion exchange process. If the cation exchange process is not occurring, all the data should plot close to the origin (Mc Lean et al. 2000; Mthembu et al. 2020). If cation exchange is dominant in the aquifer, there is a linear relationship between [(Na + K)–Cl] and [(Ca + Mg)–(HOC_3–SO_4)] with a slope of -1 (Jalali 2007; Karunanidhi et al. 2020). In the Bhadohi region, the postmonsoon data plot posses a slope1.06, and in premonsoon data, the plot posses a slope 0.98. This relation signifies that the ion exchange process is also contributing ions in the aquifer (Fig. 4c).

Anthropogenic contribution of ions

The geochemical signature of groundwater pollution owing to municipal household and industrial effluents is evident, because municipal household and industrial effluents have a comparatively elevated Na/Cl (> 1), K/Cl (> 0.02) and SO_4 /Cl (> 0.09) ratio (Ghabayen et al. 2006; Prasanna et al. 2011; Etikala et al. 2020). In Bhadohi average Na/Cl ratio is 1.646 and 1.499, K/Cl ratio 0.052 and 0.056, and SO_4/Cl ratio is 0.420 and 0.419 in postmonsoon and premonsoon, respectively (Table 1). The high proportion of Na/Cl is may be due to the application of NaCl in textile industries as a water softener and percolation of textile effluents in groundwater (Babu et al. 2007; Patel et al. 2016). The high ratio of SO_4 /Cl advocates the addition of SO_4 by the breakdown of organic material present in textile effluents. Na_2SO_4 also utilized in textile processing, which added more SO_4 to the groundwater (Sarayu and Sandhya 2012; Mountassir et al. 2013; Aleem et al. 2020). The study area shows high values of NO_3 with a mean value of 70.54 and 67.60 mg/L in postmonsoon and premonsoon season, respectively. Based on WHO (2011) classification, 45.71% samples in postmonsoon and 42.85% samples in premonsoon samples show NO_3 values beyond the permissible limit (Table 1). If the amount of NO_3 in groundwater is more than 13 mg/l, it is believed to be

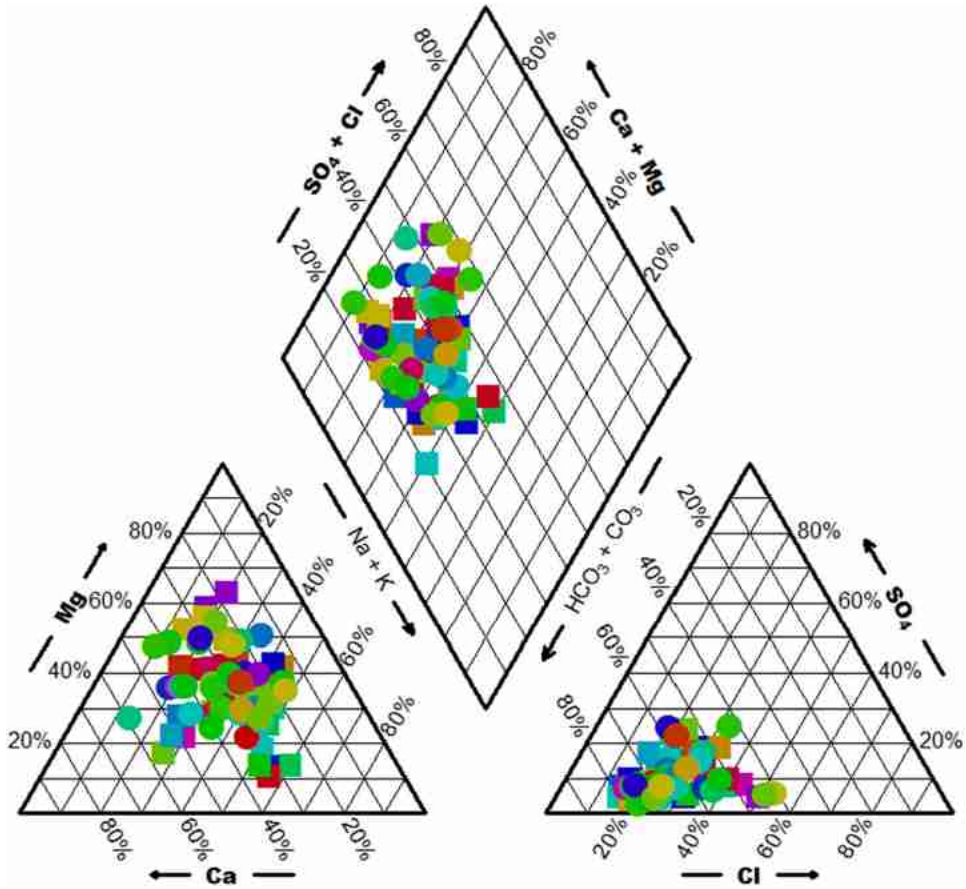

Fig. 3 Relative ionic composition (after Piper 1944) (square symbols represent post-monsoon and circular symbols represent pre-monsoon samples)

polluted by human conducts and described human-induced values (Jalali 2010). Both point sources (municipal sewage) and non-point sources (farming activities) are contributing NO_3 in the vadose zone of aquifers (Ahamad et al. 2018; Nazneen et al. 2019; Us Saba and Umar 2021). The spatial distribution of NO_3 shows a higher concentration in a central area of the city. The high concentration of NO_3 in the central area of the town is due to the presence of some settling ponds which contain textile effluents released by different dye houses. The spatial distribution of NO_3 in Bhadohi (Fig. 5a, b) shows more variation in premonsoon as compare to the postmonsoon. In postmonsoon poor discharge system of the city leads to more percolation of contaminated water and homogenized the NO_3 concentration in the whole town.

Categorization of groundwater for domestic use

Physiochemical parameters of groundwater of the study area evaluated with guidelines recommended by WHO (2011) to figure out the appropriateness of groundwater for drinking and household use (Table 2). Groundwater is categorized based on its TDS values to presume the excellence for consumption and household use (Davis and DeWiest 1966; Freeze and Cherry 1979). Under Davis and DeWiest (1966) categorization, 96% samples in postmonsoon and 100% samples in premonsoon are permissible for drinking reason. Under Freez and Cherry (1979) categorization, 97% of samples in postmonsoon and all the samples in premonsoon fit into a freshwater class. On the basis of Sawyer and Mc. Cartly (1967) cataloguing 71% samples in postmonsoon and 74% samples in premonsoon belong to the very hard category in Bhadohi (Table 2).

Evaluation of non-carcinogenic hazard intensity of nitrate (NO_3)

High NO_3 concentration in drinking water is related to health difficulties, such as methemoglobinemia (Blue baby syndrome) in newborns stomach cancer in adults (Madhav et al. 2020; Adimalla et al. 2020). NO_3 reduces to NO_2 by oxidizing the ferrous ion of haemoglobin in the ferric state and forms methemoglobin. Cancer-causing nitroso compounds are formed in the human body when NO_3 reacts with amines and amides (Ahamad et al. 2018). In the current investigation, the non-carcinogenic health hazard for human in diverse age factions was made by the NO_3 contamination in water. The model used for carrying out health hazard evaluation is under the non-carcinogenic

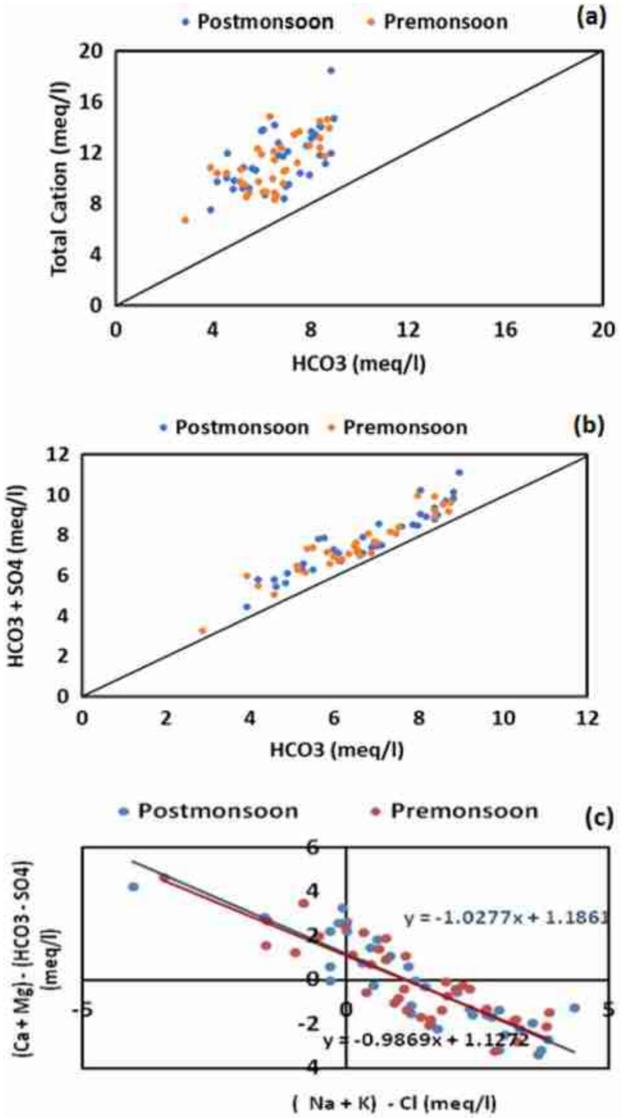

Fig. 4 Ionic relationships: **a** HCO_3 and Total Cations (TZ^+); **b** HCO_3 and (HCO_3+SO_4) and **c** [(Ca + Mg)–(HCO_3+SO_4)] and [(Na + K)–Cl]

hazard quotient model recommended by the United States Environmental Protection Agency (USEPA 2013).

CDI values for three varied age divisions are presented in Table 3.

If the HQ value is more than 1 are cause adverse health outcomes on the exposed human being. The result illustrates that HQ values of NO_3 range from 0.19 to 3.55 and 0.23–3.67 for adults, 0.25–4.65 and 0.31–4.81 for children and 0.53–9.93 and 0.66–10.27 for an infant in postmonsoon and premonsoon correspondingly. The HQ values were more than one for 45 and 40% adult, 54 and 45.7% children and 88.6 and 85.7% infants in postmonsoon and premonsoon, respectively, signifying the groundwater have

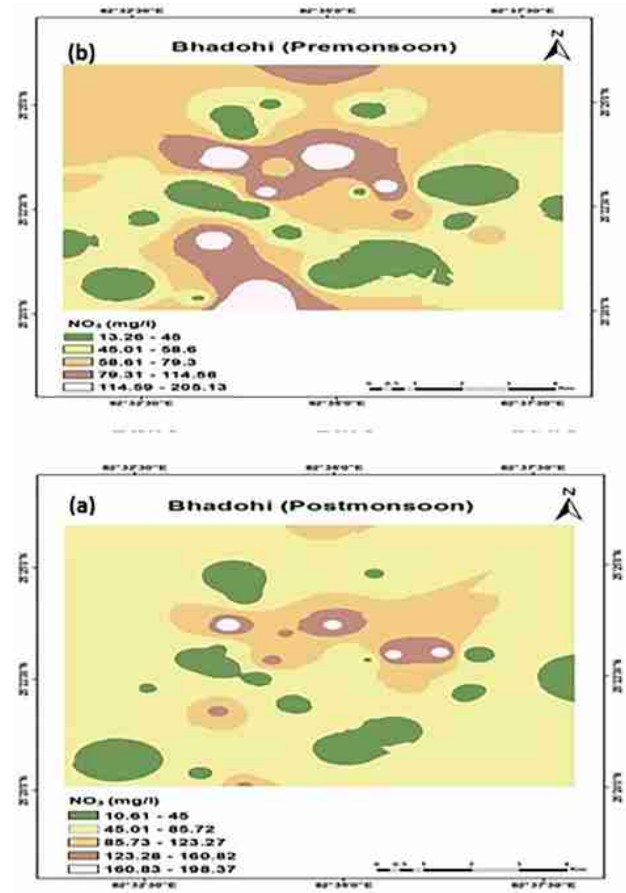

Fig. 5 Spatial distribution of NO_3: **a** Post-monsoon season and **b** Premonsoon season

unpleasant health outcomes on those exposed persons of particular age factions (Table 3).

Categorization of groundwater for irrigation

Based on RSC, water can be graded in 3 classes, such as safe, marginally suitable and unsuitable. In Bhadohi, 85% in postmonsoon and 88% samples in the premonsoon lie in the safe category (Table 2).

EC and % Na plays a crucial function to conclude the appropriateness of groundwater for irrigation function. The higher concentrations of Na in water will transform soil permeability; as a result, the soil becomes tough to plough (Jeevanandam 2012; Madhav et al. 2020).

Salinity (EC) hazard

Long-term irrigation enhances the salinity of the soil. Increase salinity is damaging to soil and plant as high salinity limit the selection of crop, hampers seed germination, decreases the harvest yield and eradicates the indigenous

Table 2 Categorization of groundwater for different purposes

Parameter	Range	Classification	(% of samples)	
			Postmonsoon	Premonsoon
TDS (Davis and DeWiest 1996)	< 500	Desirable for drinking	8.57	8.57
	500–1000	Permissible for drinking	88.58	91.43
	1000–3000	Useful for agriculture	2.85	–
TDS (Freeze and Cherry 1997)	< 1000	Fresh water	97.15	100
	1000–10,000	Brackish water	2.85	–
	10,000–100,000	Saline water	–	–
	> 100,000	Brine water	–	–
Hardness (Sawyer and Mc. Cartly, 1967)	< 75	Soft	–	–
	75–150	Slightly hard	–	–
	150–300	Moderately hard	28.58	25.72
	> 300	Very hard	71.42	74.28
% Na (meq/l)	0–20	Excellent	14.28	11.42
	20–40	Good	48.57	60
	40–60	Permissible	34.28	28.57
	60–80	Doubtful	2.85	–
	> 80	Unsuitable	–	–
SAR (meq/l)	0–10	Excellent	100	100
	10–18	Good	–	–
	18–26	Fair	–	–
	> 26	Poor	–	–
RSC (meq/l)	< 1.25	Good	85.69	88.57
	1.25–2.5	Medium	11.43	8.57
	> 2.5	Bad	2.86	11.43
EC (µS/cm)	< 250	Low salinity hazards	–	–
	250–750	Medium salinity hazard	–	2.85
	750–2250	High salinity hazard	100	97.15
	> 2250	Very high salinity hazard	–	–

flora (Misra and Mishra 2007). Based on EC values, Richard (1954) classified the irrigational water into four groups. Low salinity group (C1), medium salinity group (C2), high salinity group (C3) and Very High salinity (C4). All the samples lie in high salinity hazard in postmonsoon, while in premonsoon, 2.85% samples lies in medium salinity hazard and 97.15% samples in high salinity hazard (Table 2). High salinity is may be due to the leaching of textile effluents into the groundwater (Prabha et al. 2013; Madhav et al. 2020).

Alkalinity hazards (Sodium)

The Na hazard is articulated in the term of Sodium adsorption ratio. Long-term application of water containing elevated SAR demolishes the physical structure of the soil (Umar et al. 2001). On the basis of SAR, water can be categorized into four groups as S-1 (< 10), S-2 (10–18), S-3 (18–26) and S-4 (> 26). In Bhadohi, all the samples in both seasons are lies in the S-1 type (Table 2).

Wilcox (1948) projected a model of groundwater categorization for irrigation founded on % Na and EC in a diagram form. Wilcox (1948) graded the water in five separate degrees of appropriateness for irrigation. In the present study, 88.58% of samples are good to permissible, and 11.42% of samples are admissible to unsuitable in postmonsoon, and all the samples are good to acceptable in premonsoon (Fig. 6).

U S salinity diagram (1954)

More inclusive irrigation aptness study can be achieved by plotting a USSL diagram, where SAR is plotted against EC (Richards 1954). The analytical data plotted on the USSL

Table 3 Chronic daily intake (mg/Kg/day) and HQ values for three different age groups

S. no.	Postmonsoon						Premonsoon					
	CDI (Adult)	HQ	CDI (Children)	HQ	CDI (Infant)	HQ	CDI (Adult)	HQ	CDI (Children)	HQ	CDI (Infant)	HQ
1	0.46	0.29	0.60	0.38	1.29	0.80	0.58	0.36	0.76	0.48	1.62	1.02
2	5.15	3.22	6.77	4.23	14.43	9.02	4.19	2.62	5.51	3.44	11.74	7.34
3	0.52	0.33	0.69	0.43	1.46	0.92	1.21	0.76	1.59	0.99	3.39	2.12
4	0.30	0.19	0.40	0.25	0.85	0.53	0.96	0.60	1.26	0.79	2.70	1.69
5	1.13	0.71	1.49	0.93	3.17	1.98	0.98	0.61	1.28	0.80	2.74	1.71
6	1.20	0.75	1.58	0.99	3.37	2.11	1.10	0.69	1.45	0.90	3.09	1.93
7	0.74	0.46	0.97	0.61	2.07	1.30	0.58	0.36	0.77	0.48	1.63	1.02
8	2.83	1.77	3.71	2.32	7.92	4.95	3.15	1.97	4.14	2.59	8.83	5.52
9	1.29	0.81	1.70	1.06	3.62	2.26	1.21	0.76	1.59	0.99	3.39	2.12
10	4.87	3.04	6.39	3.99	13.62	8.52	4.78	2.99	6.28	3.92	13.39	8.37
11	1.93	1.21	2.54	1.58	5.41	3.38	2.07	1.29	2.71	1.70	5.79	3.62
12	0.67	0.42	0.89	0.55	1.89	1.18	0.48	0.30	0.63	0.39	1.34	0.84
13	1.07	0.67	1.40	0.87	2.98	1.87	1.29	0.81	1.69	1.06	3.61	2.26
14	2.95	1.85	3.87	2.42	8.27	5.17	3.02	1.89	3.96	2.47	8.44	5.28
15	5.67	3.55	7.45	4.65	15.89	9.93	5.87	3.67	7.70	4.81	16.43	10.27
16	3.79	2.37	4.98	3.11	10.62	6.64	4.00	2.50	5.25	3.28	11.20	7.00
17	4.01	2.51	5.27	3.29	11.24	7.03	3.85	2.40	5.05	3.15	10.77	6.73
18	1.29	0.81	1.70	1.06	3.62	2.27	1.18	0.74	1.55	0.97	3.32	2.07
19	1.25	0.78	1.64	1.02	3.49	2.18	1.17	0.73	1.54	0.96	3.29	2.06
20	0.99	0.62	1.30	0.81	2.77	1.73	1.10	0.68	1.44	0.90	3.07	1.92
21	3.71	2.32	4.87	3.04	10.38	6.49	5.43	3.39	7.12	4.45	15.20	9.50
22	1.83	1.14	2.40	1.50	5.12	3.20	4.19	2.62	5.50	3.44	11.73	7.33
23	1.13	0.70	1.48	0.92	3.15	1.97	1.20	0.75	1.58	0.99	3.37	2.11
24	1.63	1.02	2.13	1.33	4.55	2.85	1.44	0.90	1.89	1.18	4.04	2.52
25	0.87	0.55	1.15	0.72	2.45	1.53	0.74	0.46	0.97	0.61	2.07	1.29
26	0.79	0.49	1.03	0.64	2.20	1.38	0.52	0.33	0.69	0.43	1.47	0.92
27	0.55	0.35	0.73	0.45	1.55	0.97	0.37	0.23	0.49	0.31	1.05	0.66
28	1.99	1.25	2.62	1.64	5.58	3.49	2.21	1.38	2.89	1.81	6.18	3.86
29	3.59	2.25	4.72	2.95	10.06	6.29	1.71	1.07	2.25	1.41	4.80	3.00
30	2.68	1.68	3.52	2.20	7.50	4.69	2.39	1.50	3.14	1.96	6.70	4.19
31	0.90	0.56	1.18	0.74	2.51	1.57	0.56	0.35	0.74	0.46	1.57	0.98
32	0.9	0.56	1.18	0.74	2.52	1.58	0.64	0.40	0.84	0.53	1.792	1.12
33	5.10	3.19	6.69	4.18	14.27	8.92	0.50	0.31	0.66	0.41	1.40	0.88
34	2.07	1.30	2.72	1.70	5.81	3.63	1.93	1.21	2.53	1.58	5.40	3.38
35	0.67	0.42	0.87	0.55	1.86	1.17	0.98	0.61	1.28	0.80	2.74	1.71

graph exposes that the majority of the water samples fall in the field of C2S1 and C3S1 water (Fig. 7).

Distribution of heavy metals in groundwater

Fe in groundwater samples ranges from 28.60 to 2016.30 µg/l with a mean value of 388.82 µg/l. 48.57% of samples in the study region are beyond the allowable value of WHO (2011) (Table 4). Iron contamination in groundwater is an outcome of the dissolution of ferruginous minerals in rocks and the leaching of household sewage (Raju et al. 2011). Corrosion of iron utensils utilized in textile industries also adds iron contamination in groundwater (Madhav et al. 2018b). Mn in groundwater samples ranges from 40.40 to 145.00 µg/l, with a mean value of 76.36 µg/l (Table 4). Cu in groundwater samples ranges from 34.50 to 807.00 µg/l, with a mean concentration of 89.87 µg/l (Table 4). According to WHO (2011), the permissible boundary of Cu in drinking water is 2000 µg/l. All the samples in the study area are inside the permissible limit laid by WHO (2011). The primary source of Cu in groundwater is Cu holding dyes utilized in dye houses and textile units (Malik et al. 2008;

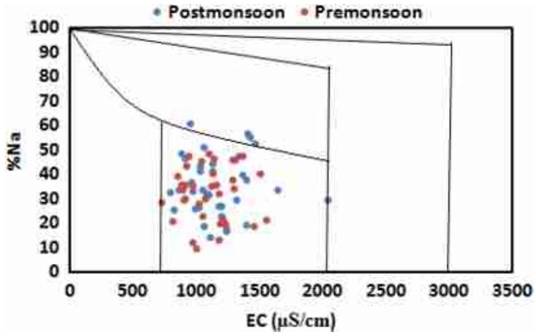

Fig. 6 Categorization of irrigation waters (after Wilcox 1948)

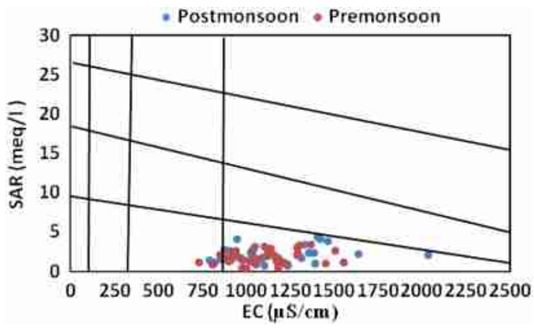

Fig. 7 Categorization of irrigation waters (after USSL 1954)

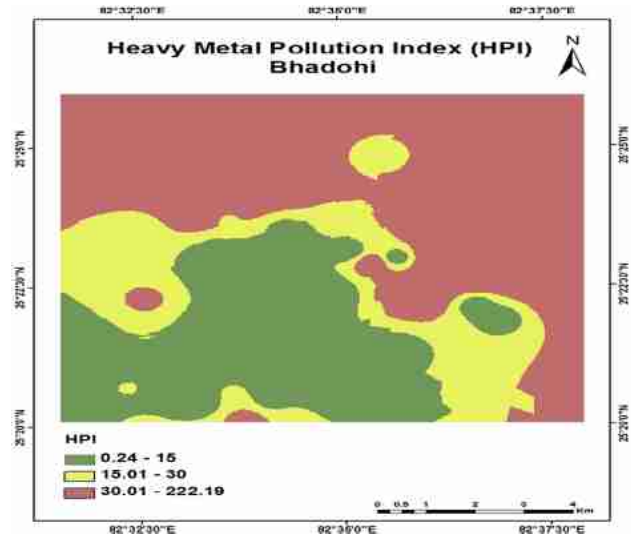

Fig. 8 Spatial distribution of HPI in the study area

Aleem et al. 2020). Zn in groundwater samples ranges from 20.40 to 1201.00 μg/l with a mean value of 158.18 μg/l (Table 4). All the samples in the study region were inside the permissible limit laid by WHO (2011). Pb in groundwater samples ranges from 1.20 to 77.60 μg/l with a mean value of 15.80 μg/l (Table 4). 23.33% of samples are above the allowable limit of WHO (2011). Vehicular emission and leaded paint are the primary sources of Pb in the study region (Kumari and Maiti 2020). Lead in drinking water is also due to the corrosion of lead pipes and leaded paints and as impurities in chemicals used in textile processing (Madhav et al. 2020). Cd in groundwater samples ranges from BDL to 6.10 μg/l with a mean value of 1.60 μg/l (Table 4). 11.42% of samples are above the permissible limit of WHO (2011). The source of Cd in groundwater is from a verity of industries includes pigment, electroplating, and smelting (Hutton 1983; Kanwar et al. 2020). Ni in groundwater

Table 4 Heavy metals in groundwater and their comparison with WHO (2011) standard

Heavy metal	Range Min.–Max (Mean)	WHO (2011) Permissible Limit (μg/l)	Sample no. and % of sample Exceeding Permissible Limit WHO (2011)	
			Sample no	% sample
Iron (μg/l)	28.60–2016.30 (388.82)	300	2–8,14,21, 24–28,30–31,35	48.57
Manganese (μg/l)	40.40–145.00 (76.36)	500	–	–
Copper (μg/l)	34.50–807.00 (89.87)	2000	–	–
Zinc (μg/l)	20.40–1201.00 (158.18)	4000	–	–
Lead (μg/l)	1.20–77.60 (15.80)	10	1,5,7,10,24,25, 30	20
Cadmium (μg/l)	BDL–6.10 (1.60)	3	1,7,14, 21,33	14.28
Nickel (μg/l)	1.70–24.50 (6.61)	20	7,8, 16, 19, 21,30	17.14
Chromium (μg/l)	BDL to 52.40 (11.41)	50	1,4,8	8.57
HPI	0.24–222.19 (33.06)	–	–	–

Table 5 Target Hazard Quotient (THQ) and Potential Human Health Risk (HI) in Bhadohi

S. NO	Fe	THQ	Mn	THQ	Cu	THQ	Zn	THQ	Pb	THQ	Cd	THQ	Ni	THQ	Cr	THQ	HI
1	256.10	0.076	145.00	0.648	73.50	0.164	120.10	0.036	34.50	7.715	6.10	1.091	4.50	0.020	52.40	1.562	11.313
2	439.40	0.131	77.80	0.348	45.60	0.102	33.50	0.010	1.20	0.268	0.00	0.000	0.00	0.000	0.00	0.000	0.859
3	376.80	0.112	100.40	0.449	87.70	0.196	55.60	0.017	3.40	0.760	0.00	0.000	5.60	0.025	17.10	0.510	2.069
4	2016.30	0.601	67.50	0.302	66.50	0.149	162.00	0.048	00.00	0.000	0.20	0.036	0.00	0.000	54.60	1.628	2.764
5	482.70	0.144	113.70	0.508	54.40	0.122	78.50	0.023	65.50	14.647	0.00	0.000	3.40	0.015	10.80	0.322	15.781
6	896.00	0.267	89.70	0.401	77.50	0.173	637.60	0.190	2.30	0.514	0.50	0.089	3.30	0.015	3.00	0.089	1.740
7	431.50	0.129	99.80	0.446	99.80	0.223	99.80	0.030	32.60	7.290	3.40	0.608	24.50	0.110	11.20	0.334	9.169
8	371.50	0.111	102.00	0.456	73.20	0.164	523.40	0.156	4.50	1.006	1.20	0.215	7.80	0.035	12.30	0.367	2.509
9	124.60	0.037	89.80	0.402	109.00	0.244	334.20	0.100	0.00	0.000	0.00	0.000	3.50	0.016	7.34	0.219	1.017
10	123.40	0.037	97.50	0.436	77.00	0.172	123.40	0.037	37.10	8.296	0.70	0.125	2.30	0.010	4.24	0.126	9.240
11	28.60	0.009	67.50	0.302	65.60	0.147	77.80	0.023	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.480
12	98.80	0.029	77.60	0.347	78.00	0.174	66.40	0.020	0.00	0.000	0.20	0.036	5.50	0.025	2.18	0.065	0.696
13	245.10	0.073	66.70	0.298	77.40	0.173	46.70	0.014	1.70	0.380	0.00	0.000	0.00	0.000	0.00	0.000	0.939
14	376.20	0.112	87.50	0.391	88.70	0.198	66.50	0.020	7.80	1.744	4.50	0.805	3.60	0.016	9.45	0.282	3.569
15	145.60	0.043	77.80	0.348	81.80	0.183	40.40	0.012	5.60	1.252	0.90	0.161	4.40	0.020	5.27	0.157	2.176
16	302.00	0.090	56.70	0.254	67.50	0.151	550.00	0.164	3.50	0.783	0.00	0.000	4.80	0.021	0.00	0.000	1.463
17	200.10	0.060	52.30	0.234	44.50	0.100	33.40	0.010	2.70	0.604	0.00	0.000	2.70	0.012	0.00	0.000	1.019
18	152.80	0.046	44.50	0.199	78.20	0.175	24.50	0.007	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.427
19	112.30	0.033	100.40	0.449	77.80	0.174	77.40	0.023	4.80	1.073	1.70	0.304	7.80	0.035	6.36	0.190	2.282
20	283.70	0.085	55.60	0.249	57.80	0.129	93.50	0.028	1.20	0.268	0.00	0.000	0.00	0.000	0.00	0.000	0.759
21	345.70	0.103	66.90	0.299	68.80	0.154	98.90	0.029	5.60	1.252	3.20	0.572	23.10	0.103	3.39	0.101	2.615
22	170.80	0.051	67.80	0.303	50.50	0.113	263.40	0.079	1.20	0.268	1.50	0.268	4.50	0.020	0.00	0.000	1.102
23	147.00	0.044	41.50	0.186	65.80	0.147	166.30	0.050	3.20	0.716	0.60	0.107	2.60	0.012	1.14	0.034	1.295
24	774.90	0.231	87.60	0.392	60.60	0.136	77.50	0.023	45.50	10.174	0.50	0.089	3.10	0.014	1.56	0.047	11.106
25	1103.10	0.329	67.50	0.302	55.60	0.124	85.50	0.025	77.60	17.352	0.20	0.036	2.70	0.012	0.00	0.000	18.181
26	741.20	0.221	141.10	0.631	34.50	0.077	33.70	0.010	0.00	0.000	0.00	0.000	3.60	0.016	2.74	0.082	1.037
27	329.90	0.098	50.50	0.226	80.70	0.180	56.70	0.017	1.60	0.358	0.10	0.018	0.00	0.000	0.00	0.000	0.897
28	495.80	0.148	45.60	0.204	82.50	0.184	43.40	0.013	0.00	0.000	0.00	0.000	0.00	0.000	0.00	0.000	0.549
29	132.40	0.039	65.50	0.293	37.80	0.085	37.10	0.011	0.00	0.000	0.30	0.054	0.00	0.000	0.00	0.000	0.482
30	650.40	0.194	87.40	0.391	74.30	0.166	77.50	0.023	43.10	9.638	3.00	0.537	27.60	0.123	4.77	0.142	11.214
31	345.60	0.103	40.40	0.181	44.80	0.100	60.60	0.018	3.60	0.805	0.00	0.000	3.50	0.016	0.00	0.000	1.223
32	123.40	0.037	45.90	0.205	55.60	0.124	77.50	0.023	0.00	0.000	0.00	0.000	2.70	0.012	0.00	0.000	0.402
33	178.50	0.053	55.70	0.249	66.70	0.149	66.70	0.020	2.70	0.604	5.60	1.002	0.00	0.000	15.5	0.462	2.539
34	203.40	0.061	60.60	0.271	78.90	0.176	20.40	0.006	0.00	0.000	0.00	0.000	1.70	0.008	0.00	0.000	0.522
35	403.00	0.120	78.90	0.353	80.50	0.180	45.50	0.014	2.50	0.559	0.00	0.000	0.00	0.000	0.00	0.000	1.226

samples ranges from 1.70 to 24.50 µg/l with a mean value of 6.61 µg/l (Table 4). 17.14% of samples exceed the permissible limit of WHO (2011). Ni-based dyes are the source of Ni in the groundwater of the study area (Madhav et al. 2018b). Cr in groundwater samples ranges from BDL to 52.40 µg/l with a mean value of 11.41 µg/l (Table 4). 8.57% of samples are above the allowable limit of WHO (2011). The application of Cr containing dyes in textile industries is a key source of pollution in groundwater (Sanyal et al. 2015; Aleem et al. 2020). A wide range of variations in the concentrations of heavy metals in groundwater samples is due to the difference in the proximity of water samples from textile industries and effluents settling ponds.

In Bhadohi, the HPI value for groundwater samples ranges from 0.24 to 222.19, with a mean value of 33.06 (Table 4). Based on individual groundwater sample, 5% of samples show the HPI values above the critical index values of 100. While based on Edet and Offiong (2002) classification, 51% of samples are low HPI, 17% of samples are medium HPI, and 32% of samples are with high HPI values. The spatial distribution of HPI shows the distribution of heavy metals in the study region (Fig. 8). The northern part of the study area shows high values of the HPI. High values of HPI in the north part of the study area are due to the industrial zones and settling ponds. The groundwater in the southern zone of the city did not show much pollution load.

It indicates that soil is undersaturated with heavy metals and not releasing heavy metals in the groundwater at these sites. In the south part of the city, most of the dye houses are of small size and scattered in agricultural fields, so groundwater of these areas shows relatively low HPI values.

The THQ has classically demonstrated the human health risk originated by heavy metal revelation. THQ is anticipated for the estimation of the probable human health hazard from the exposure by various researchers (USEPA 1986; Pawar and Pawar 2016; Madhav et al. 2020). THQ is typically a non-cancer hazard evaluation mode founded on a relation between the approximate dose of pollutant and the reference dose underneath, which will not be any significant hazard (Tiwari et al. 2020; Mthembu et al. 2020; Raja et al. 2021). The values of THQs of the deliberated metals from the groundwater of Bhadohi are concise in Table 5. THQ values of heavy metals in Bhadohi were set up in the command of Pb > Mn > Cr > Cd > Cu > Fe > Zn > Ni. The THQ of metals varies from Fe (0.009–0.601 with a mean of 0.116), Mn (0.181–0.648 with a mean of 0.345), Cu (0.077–0.244 with a mean of 0.155), Zn (0.006–0.190 with a mean of 0.041), Pb (0.0–17.352 with a mean of 2.524), Cd (0.000–1.090 with a mean of 0.176), Ni (0.000–0.123 with a mean of 0.020), Cr (0.000–1.628 with a mean of 0.226) (Table 4.31). It is observed that Fe, Mn, Cu, Zn, and Ni metals exhibit THQ values less than 1, while Pb (34.28), Cd (2.85%) and Cr (5.71%) illustrating > 1 THQ values in the Bhadohi. The HI value of metals fluctuates from 0.402 to 18.181 with a mean of 3.56. The high TQH value of Pb, Cd, and Cr are associated with the possible health risk (Mthembu et al. 2020). 68.57% of samples in Bhadohi show HI greater than one value.

Conclusion

Compositional relationships have been used to investigate the source of solute and prove the effective hydrogeochemical procedures accountable for the various ions in the groundwater. After the analysis of different physicochemical parameters, it is observed that the majority of samples in both seasons fall under the section of alkaline earth and week acidic conditions (Ca–Mg–HCO_3 type). Based on the Gibbs plot, the hydrogeochemical process of samples specified that majority of the samples are from rock dominance. Carbonate weathering is the main contributor to the ions in the aquifer. 45% samples in postmonsoon and 40% samples in premonsoon have NO_3 values ahead of the permissible limit, which desires curative means earlier than consumption. Human exposure to NO_3 through ingestion was in the subsequent direct Infant > Children > Adult. The groundwater of the Bhadohi region shows the contamination of Fe, Cd, Ni, and Cr. Contamination of Cr, Cd and Ni in groundwater samples is due to the application of metal-based dyes used in textile industries. In Bhadohi, the mean HPI came out to be 33.02. 5% of samples show the HPI values above the critical index values of 100. It is observed that Fe, Mn, Cu, Zn, and Ni metals exhibit THQ values less than 1, while Pb (34.28%), Cd (2.85%) and Cr (5.71%) showing more than 1 THQ. 68.57% of groundwater samples in Bhadohi offer HI greater than one value.

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Declarations

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Conflict of interest On behalf of all the co-authors, the corresponding author reports no declarations/conflicts of interest.

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