



Contamination level, source identification and health risk evaluation of potentially toxic elements (PTEs) in groundwater of an industrial city in eastern India

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Abstract The present investigation explores the spatial and seasonal variations in potentially toxic element (PTEs) concentrations and contamination level assessment of groundwater samples in and around the Asansol industrial city, eastern India. The representative samples of groundwater from 24 different locations were analyzed for pH, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH) and PTEs, e.g., Pb, Cu, Cd, Zn, Fe and Cr for pre-monsoon and post-monsoon. The pH level of examined groundwater samples is under the desirable limit with few exceptions (S5, S11 and S16 in pre-monsoon and S12 in post-monsoon). The recorded values for Pb, Cd, Fe and Cr in many sampling stations found higher than the prescribed limits of Indian

standards (IS 10500: 2012) in both the seasons. The mean contamination factor (C_f) for PTEs in the groundwater is in the order of $Cr > Fe > Cd > Pb > Cu > Zn$ and $Fe > Cr > Cd > Pb > Cu > Zn$, with mean contamination index (C_d) value of 2.83 and 2.72 in pre-monsoon and post-monsoon season, respectively, indicating moderate level of contamination in the examined area. Geospatial depiction of HPI values shows high level of contamination during pre-monsoon (58.3% sampling sites) and post-monsoon (45.8% sampling sites) in majority of sampling sites. Further, application of multivariate statistical analysis ascertains that the PTEs in groundwater are majorly derived from anthropogenic activities such as open-cast mining, thermal power plants, iron and steel

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industries, sponge iron and other metallurgical industries, and leachate from urban and industrial wastes along with limited contribution from geogenic and lithogenic sources. The health risk assessment demonstrates that the non-carcinogenic risk (due to PTEs) in adults is in the sequence of $Cr > Cd > Pb > Fe > Cu > Zn$, while for children the order is $Cr > Pb > Cd > Fe > Cu > Zn$ for both the seasons. The results also reveal higher chance of occurrence of carcinogenic risk due to Cr (ILCR $> 1.0E-04$) for children and adults in both the seasons.

Keywords Groundwater quality · Potentially toxic elements (PTEs) · Pollution indices · Health risk assessment · Geospatial techniques · Multivariate analysis

Introduction

The scarcity of potable drinking water is one of the serious environmental concerns worldwide, which is evident in many parts of India including the State West Bengal. In India, still majority of the rural population do not have the facility to access properly treated consumable water and often use untreated groundwater (dug wells and tube wells) without any awareness or proper knowledge about the negative health impacts (Ghosh et al., 2010). India ranks first in groundwater utilizing nation and having world's 18% population with approximately 4% of the world's renewable water resources (Brindha et al., 2020). Therefore, the monitoring of groundwater, mainly for dissolved trace elements (TEs), is very important as these metals may aggravate susceptibility to cancer in human health (Madhav et al., 2018). In India, approximately 85% of the domestic requirement in rural areas, 55% for irrigation water and over 50% of industrial and urban requirements is fulfilled by groundwater resources (Herojeet et al., 2015). Industrial development and urban expansion are the foremost aspects for discharging contaminants into the environment and diminish groundwater quality (Raja et al., 2021). Considering the above fact, the assessment of the spatial and temporal variations in groundwater quality has become an obligatory prerequisite to the rapidly developing countries like India with high population density.

In recent times, several research works have been conducted in different parts of India to explore the deterioration of groundwater quality due to PTE contamination in mining and industrial areas such as lignite mining area of Birbhum District in West Bengal (Hossain & Patra, 2020), coal mining areas of West Bokaro, Jharkhand (Prathap & Chakraborty, 2019; Tiwari et al., 2016), Obra, Renukoot and Anpara industrial hubs of Sonbhadra District (Ahamad et al., 2020), North Karanpura coalfield of Jharkhand (Neogi et al., 2018), Korba coal mining area of Chhattisgarh (Singh et al., 2017), Bhatinda industrial hubs of Punjab (Kumar et al., 2020). Apart from these, several research investigations also showed that the surface and groundwater resources are severely polluted by PTEs due to the burning of fossil fuel, fertilizers, industrial discharges, agricultural activities and vehicular emissions in rural, urban and industrial clusters in many parts of the world (Torghabeh et al., 2020). Al-Khashman and Jaradat (2014) studied the groundwater quality of Ma'an area and find potential metal contamination due to larger agricultural activities. Ganiyu et al. (2021) explored the toxic metal pollution and associated health risks in groundwater samples of Ibadan metropolis area in Nigeria. De León-Gómez et al. (2020) studied the groundwater quality of the Nuevo Leon area situated in Mexico City and explored the risk allied with PTE contamination which mainly derived from wastewater from industrial clusters, agricultural and livestock activities.

Besides, the PTE contamination in groundwater has become another major concern area because of its toxicity even at trace concentrations (Momodu & Anyakora, 2010). Some potentially toxic elements (PTEs) are considered as essential elements for several bio-physiological functions, but they may lead to several health effects when present in excess quantities (Prasad et al., 2014; Prasanna et al., 2011). Though safe and good quality of groundwater is major concern for public consumption and health, PTE contamination due to both natural and anthropogenic activities leads to significant deterioration of such water resources (Al-Khashman, 2008). Geochemical weathering of parent rocks and leachates from soil are the two major prime natural sources of PTEs in groundwater bodies while various industrial and agricultural activities considered as anthropogenic sources may introduce larger quantities of PTEs in groundwater resources than the threshold limit for human

consumption. Accumulation and recalcitrance of PTEs in groundwater and transfer through the food chain initiate acute and chronic diseases in humans and animals (Torghabeh et al., 2020). The elevated concentrations of PTEs in drinking water tend to accumulate in human tissues and reach toxic levels, which would have an impact on human health (Raja et al., 2021). Therefore, the monitoring of groundwater, mainly for dissolved trace elements (TEs), is very important as these metals may aggravate susceptibility to cancer for the existing population (Madhav et al., 2018). Though these PTEs are naturally available in the earth's crust, they found higher concentrations in groundwater due to several natural and anthropogenic processes. Decline in groundwater quality due to PTEs is influenced by mineral dissolution, weathering of bedrock, soil–water interaction, precipitation frequency, groundwater flow, dissolution/precipitation reaction, quality and quantity of the infiltration water, recalcitrant time and the type of aquifer (Ahamad et al., 2020). Moreover, contributions from anthropogenic sources result in elevated PTEs in groundwater which includes leachates from unplanned dumping site of urban wastes and overburden materials, discharges of industrial/domestic wastewaters, excavation and mining activities, radial discharges from heavy vehicles, etc. (Hossain & Patra, 2020).

Major anthropogenic sources of PTE contamination are mining, discharge of untreated or partially treated effluents from industries and disposal of domestic sewage (Ahamad et al., 2020; Nouri et al., 2008; Zakhem & Hafez, 2015). Geogenic sources of PTEs in groundwater occur due to leaching from ground strata and weathering of rocks (Dijkstra et al., 2004; Hossain & Patra, 2020). Therefore, the assessment of PTEs in groundwater is of great importance in the context of potential health effects and ecological risk. Such investigations also help to suggest the extent of pollution levels, implementation of proper measures and restoration of groundwater resources in the study area.

Further, excessive use of groundwater for cultivation, direct discharge of mine water and industrial effluents in crop land resulted bioaccumulation of PTEs in vegetables and crops. These PTEs are transported via food chain when get absorbed in different parts of organisms/human and subsequently result various health hazards (Herojeet et al., 2015;

Shil & Singh, 2019; Wang et al., 2017). PTEs can be exposed to human health in three different pathways, i.e., direct intake, inhalation and dermal absorption through the skin from various environmental medium such as soil, dust and water Gope et al., 2017; Hossain & Patra, 2020; Pobi et al., 2020). Principally dermal absorption and ingestion are the main routes of PTEs contaminated groundwater exposure on human body (Hossain & Patra, 2020). Chronic exposure to PTEs can cause carcinogenic health hazards to the human. The probability of adverse health effects on human due to PTEs can be measured through health risk assessment models developed by USEPA. Previous research works in the study area were mostly focused on hydrochemical features and metal concentrations in groundwater in Asansol industrial areas (Gupta et al., 2008; Roy, 2017), but limited attention was given to health risk assessment. Henceforth, to cover up the gap, an attempt has been made to evaluate the contamination level and furnish in-depth information about the potential health risks related to PTEs in groundwater of the study area. The health risk of PTEs in groundwater is assessed through ingestion and dermal contact pathway in the present study. Therefore, nowadays it is becoming very important to measure PTE concentration and potential health risk to safeguard water resources and regulate pollution level (Wang et al., 2017).

In this backdrop, the primary objectives of the present investigation are (1) to explore the level of contamination of PTEs in the groundwater to determine the influence of industrial and mining activities, (2) to examine the suitability of the groundwater for drinking with the help of different pollution evaluation indices, viz., HPI, HEI and C_d , and finally (3) to provide information on the impact of seasonal changes on the distribution patterns of PTEs in the study regime and associated human health risk through the geostatistical method.

Materials and methods

Description of the study area

Demographically, Asansol industrial city (23.68°N and 86.99°E) is situated at western part of State West Bengal and in close proximity to the Eastern Coalfield region with registering a total population of around

11,56,387 (Indian Census, 2011). Moreover, Asansol urban area is the second most populous in West Bengal and 39th most populous City in India (Indian Census, 2011). Asansol Municipal Corporation (AMC) consists of 106 wards and governs the Asansol Sadar subdivision, Burnpur Notified Area Authority, the rural parts under the Asansol block development community and coalfield areas. The study area spreads over an area of 326.48 sq. km. with an altitude of 111 m from the sea level, lined with Damodar River (on the south) and Ajay River (on the north) and surrounded by the hills of Chhotonagpur and Santhal Parganas (Fig. 1). The area mainly faces two distinct seasons, i.e., pre-monsoon (dry summer), in which temperatures are ranging between 40 and 45 °C, and post-monsoon, in which temperatures are hovering between 16 and 20 °C. The observed soil type of the study area is predominantly hard laterite, with possessing limited alluvial segments along the edges of the rivers. The main source of drinking water is

supplied from river Damodar (after going through proper treatment) in the Asansol municipal area, but in rural parts of colliery belt people are still relying on groundwater for drinking and household uses.

Geology and hydrogeological framework of the study area

The geology of the study area and its surroundings belongs to the consolidated Gondwana group, recent to Quaternary age. The upper Gondwana only consists of super Panchet formation. This group indicates a petrological variation and is made up of basaltic lavas with inter-trappean clay. The igneous intrusive is the result of Post-Gondwana. Raniganj block has a random coal seam, which is a part of the Raniganj formation. Lower Gondwana has Talchir, Barakar, Raniganj and Panchet formation. The core component in lower Gondwana group is alluvium and laterite deposition (Singh et al., 2010). The major lithology of

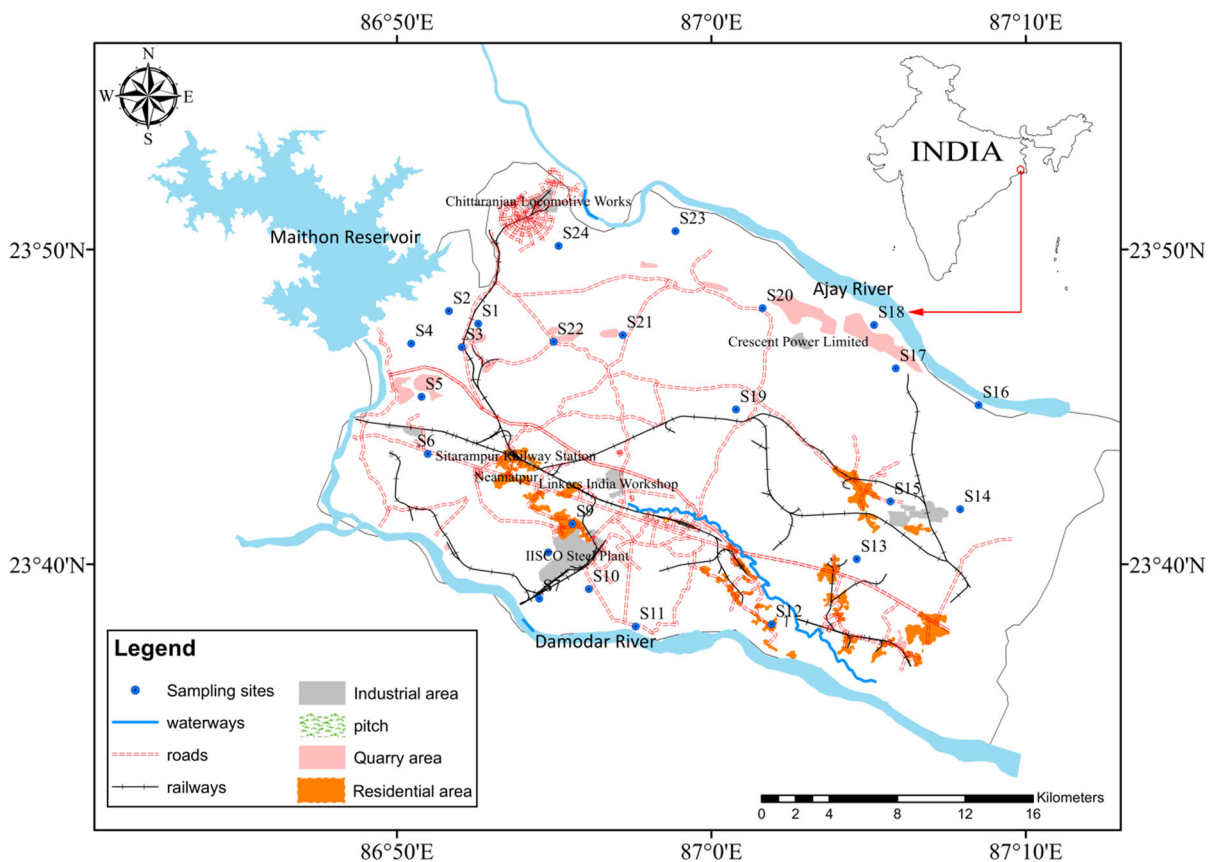


Fig. 1 Geographical location of groundwater sampling stations in the study area, Asansol, West Bengal, India

lower Gondwana division is made up primarily of shales and sandstones with occasional layers of grits and very wide occurrence of coal (Fig. 2). The entire area is affected by many structural features, like dip, strike and oblique fault. Some of these faults have the same time period as the deposition and coalification period. It has been extensively intruded by ultrabasic and basic rocks. The ultrabasic rock occurs as sill and dykes. The most prominent dyke in this region is Salma dyke.

The geological setting of the area has serious impact of lateral and vertical movement of groundwater as it illustrated in the contour map (Fig. 3). Mainly, it is highly influenced by major fault and lineament. The presence of igneous rock (basic and ultramafic rocks) in some part enjoys high yield of groundwater movement. Less permeable parts of the sedimentary rock (sandstone, shale and siltstone) yield a steady supply of water. The sudden interruption of rock contact has given risen to complex aquifer setting of the study area (Adhikari et al., 2013). Groundwater flows toward south–southeast direction at the vicinity of Damodar River. In contrast, the part of areas nearby the Ajay river has the flow north to northwest direction. A great depression is present in the Ethora and Barabani sites of study area. This is due to steep flow in the middle than the peripheral regions. The western part of the region show very significantly high gradient (10–20 m) in comparison with other localities. In contrast, flow gradient is moderate (5–10 m) in the eastern part of study area.

Sample collection and analysis

To assess the groundwater quality, 24 sampling sites were selected strategically considering the land use and landform variability, which covers the Asansol urban, suburban, rural parts, industrial zone and coal mine areas. All the sampling locations are depicted in Fig. 1. The groundwater samples were collected on the monthly interval basis covering two distinct seasons, i.e., pre-monsoon and post-monsoon. Before sampling, 1-L polyvinyl chloride sample bottles were rinsed several times with deionized water followed by sample water. These sterilized PVC bottles were used to fill sample water up to its mouth to prevent entrapment of any air in water samples (Al-Khashman & Jaradat, 2014). The pH, electrical conductivity (EC) and total dissolved solid (TDS) were analyzed on field

using portable analyzer (HI 9813-6). During pH measurement, portable analyzer was calibrated using standards pH buffer solutions (pH 4 and 7). Prior to physicochemical analysis, the water samples were preserved in an ice-crested cooler under 4 °C to avoid any kind of chemical/biological reaction in sample water (Ganiyu et al., 2021). Quantitative analysis of other water quality parameters was performed in laboratory within 48 h according to American Public Health Association (APHA, 1998). For quantification of PTEs (Pb, Cu, Zn, Cd, Fe and Cr), water samples were collected in separate containers and added with 1 ml concentrated HNO₃ to prevent the precipitation of PTEs and subsequently analyzed for their concentrations in atomic absorption spectrophotometer (AAS: Varian 220FS).

Statistical interpretations

The results are furnished with the help of descriptive statistics and conventional graphical methods. To analyze the relative interdependency of measured water parameters and to identify their possible sources, multivariate applications such as Pearson correlations, principal component analysis (PCA) and cluster analysis (CA) were performed by using SPSS version 20.0 software for pre-monsoon and post-monsoon seasons. Further, the hierarchical CA was performed on the normalized data set to group the analyzed variables using Ward's method with Euclidean distances as a measure of similarity.

Quality control and assurance

Standard method of analysis and quality control assurances including instrumental recalibration, triplicate data collection and result analysis, and percentage of recovery examination during PTE quantification with the standard reference material was done as recommended by APHA (1998). During the entire study process, proper care was taken in the sample collection, preservation and analysis. High-purity reagents and standard solutions (E-Mark, AR grade) were used for laboratory analysis, and ultrapure water (resistivity = 18.2 MΩcm⁻¹) was used for instrument calibration and preparation of intermediate standards/solutions. All laboratory glassware were treated with diluted HNO₃ solution (2%), rinsed with deionized water and kept in the oven overnight under

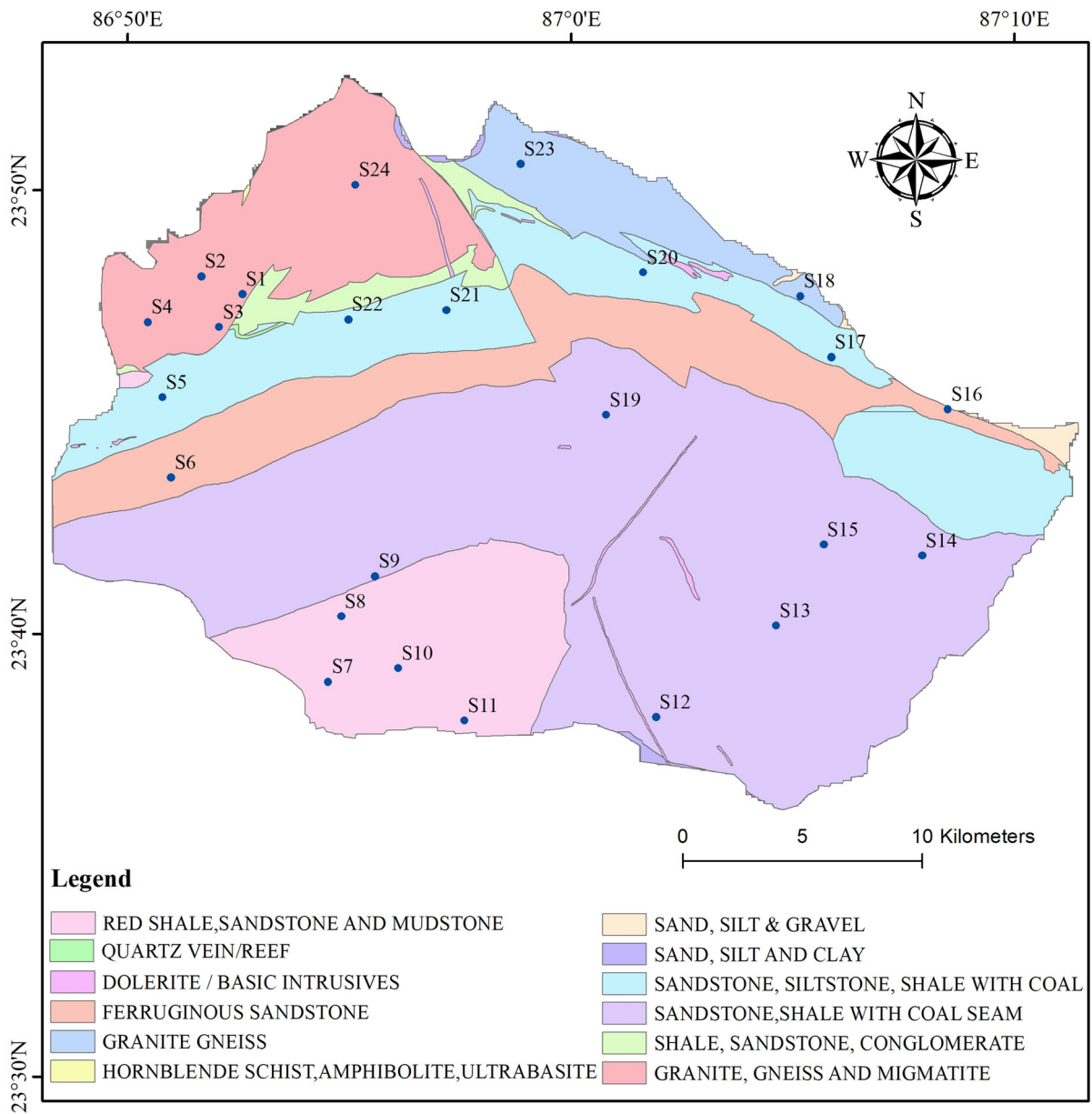


Fig. 2 Geo-lithological map of the study area

40 °C to avoid any type of contamination. In the laboratory, collected water samples were filtered through 0.45 µm millipore membrane filter papers (WHA7404002) and analyzed for physicochemical parameters. Each analysis for water samples was done in triplicates to ensure the reliability of obtained results. Reagent blank determinations were used to correct the instrument readings. Standards and blank solutions were run subsequently after every 10

samples to check the accuracy of the instrument (AAS: Varian 220FS). Analyzed results for PTEs were checked with respect to standard reference materials (NIST1640a), and recovery results were 95–98% of certified values for the inspected PTEs. The recovery rates of each PTEs were 95.3, 95.1, 96.4, 95.5, 98.0 and 97.2% for Cd, Cr, Cu, Fe, Pb and Zn, respectively. Reproducibility of analytical results was within 5%

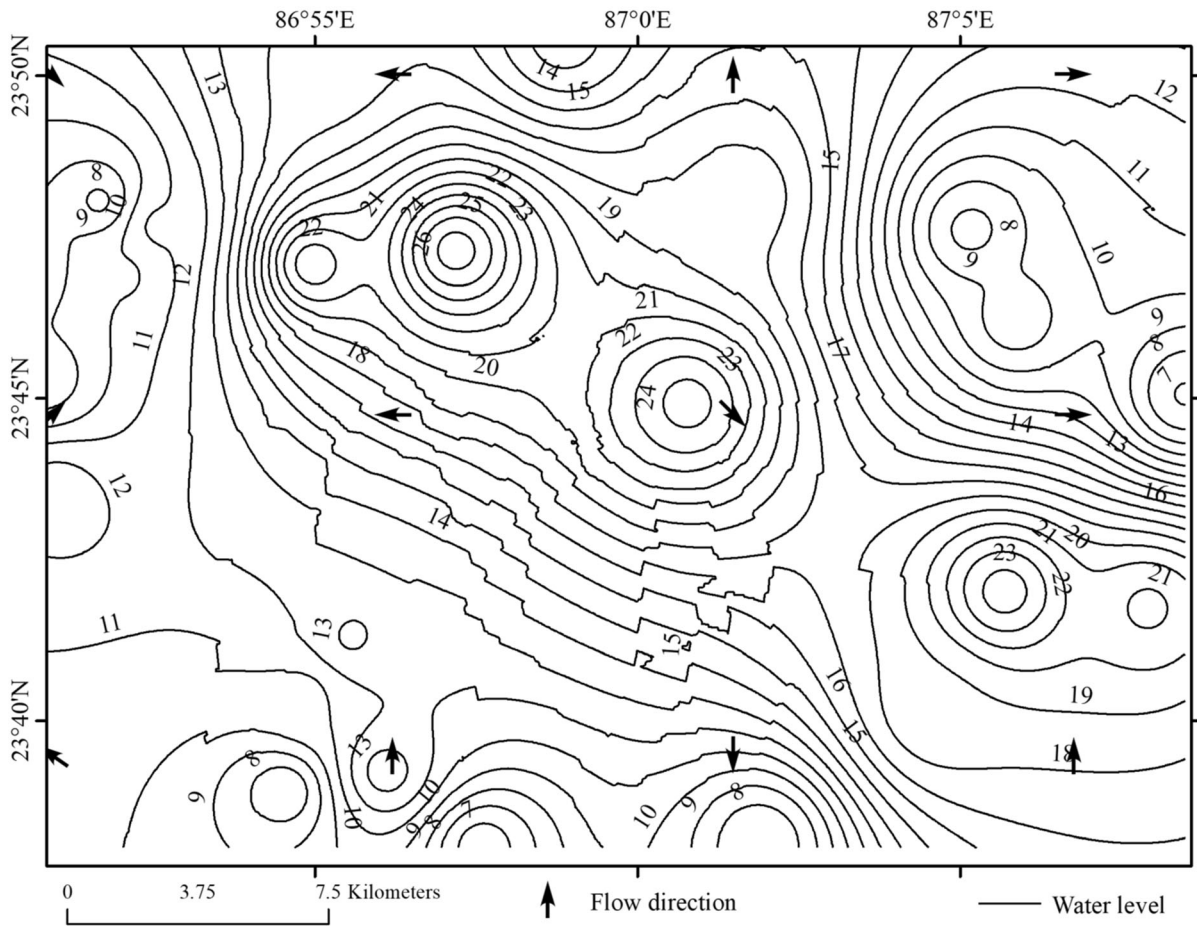


Fig. 3 Groundwater framework of the study area

standard error (SE) level of certified values for each metal.

Methodology

Several approaches have been developed to estimate of the quality of groundwater with respect to PTEs (Prasad et al., 2014; Zakhem & Hafez, 2015). In this study, the degree of contamination (C_d), heavy metal evaluation index (HEI) and the heavy metal pollution index (HPI) were used to examine the suitability of the groundwater for human consumption by comparing the level of heavy metal with prescribed Indian standards (IS10500: 2012). Human health risk assessment of PTEs in the groundwater is used to explore the current carcinogenic risks and suitability for human consumption.

Degree of Contamination (C_d)

The degree of contamination (C_d) is widely used to evaluate the drinking water quality and to observe the collective effects of various quality parameters. The C_d has been proposed by Backman et al. (1997) and is calculated by following equations:

$$C_d = \sum_{i=1}^n C_f^i \tag{1}$$

where

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \tag{2}$$

where C_{fi} , C_{Ni} and C_{Ai} define the contamination factor, the maximum permissible concentration and the analytical value, respectively, of i th component. N and C_{Ni} signifies the ‘normative value’ and standard permissible concentration (SPC), respectively.

Heavy metal evaluation index

The heavy metal evaluation index (HEI) provides an overall quality of the water with respect to heavy metal concentrations (Edet & Offiong, 2002; Prasanna et al., 2012). The HEI is calculated using the formula:

$$HEI = \sum_{i=1}^n H_c / H_{mac} \quad (3)$$

where H_c and H_{mac} indicate the detected value of PTEs and the maximum permissible concentration (MAC) of the i th parameter, respectively.

Heavy metal pollution Index

Heavy metal pollution index (HPI) is another useful technique used frequently by the researchers to assess the overall quality of water in relation to PTEs for drinking and domestic uses (Kumar et al., 2012; Mohan et al., 1996; Prasad et al., 2014). The calculated HPI depicted the composite influence of individual PTE on the total quality of groundwater. The assigned weight on selected PTEs varies between 0 and 1. HPI in the study area is determined by using the mean PTE concentrations in pre- and post-monsoon season, and the details of the calculation are presented in Table 1,

in where unit weightage (W_i), standard permissible value (S_i), monitored metal concentration value (M_i) and highest desirable value (I_i) has been considered. Mohan et al. (1996) introduced HPI calculation by using the following equation:

$$HPI = \frac{\sum_{i=1}^n W_i * Q_i}{\sum_{i=1}^n W_i} \quad (4)$$

where Q_i , W_i and n denote the sub-index, unit weightage and the number of considered parameters, respectively, of i th component.

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{(S_i - I_i)} * 100 \quad (5)$$

where M_i , I_i and S_i represent the detected value of PTE, the ideal value and the standard value of the i th parameter, respectively. The sign (–) designates the numerical dissimilarity of the two values, ignoring the algebraic sign. In general, pollution indices are assessed for any particular practice of the water. The critical pollution index value of HPI for drinking water is 100.

Non-carcinogenic health risks assessment

The quantification of human health risk due to the presence of toxic metals in groundwater is performed in this study as suggested by USEPA (US Environmental Protection Agency, 2004). To estimate the potential risk of non-carcinogenic health hazards, two set of people, i.e., adults and children were considered through dual key exposure corridors, namely the direct

Table 1 Calculation of HPI for groundwater during pre-monsoon and post-monsoon in the study area

PTEs	Mean concentration (M_i) (µg/L)		Highest permitted values for drinking water (S_i) (µg/L)	Unit weightage (W_i)	Sub-index (Q_i)		$W_i \times Q_i$	
	Pre-monsoon	Post-monsoon			Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
Pb	10.06	7.88	10	0.1000	100.57	78.77	10.057	7.877
Cu	13.74	11.38	1500	0.001	2.52	2.56	0.003	0.003
Zn	49.47	39.80	15,000	0.0001	49.51	49.60	0.005	0.005
Cd	3.44	2.61	3	0.3000	114.50	87.05	34.351	26.115
Fe	438.82	591.51	300	0.003	146.27	197.17	0.439	0.592
Cr	112.26	90.96	50	0.0200	224.52	181.93	4.490	3.639

Mean HPI = 116.35 (pre-monsoon) and 90.14 (post-monsoon)

ingestion and dermal absorption (Wang et al., 2017). The quotient of human health hazards (HQ) for non-carcinogenic risk of individual PTEs is formulated by dividing chronic daily intake (CDI) values of individual PTEs with their respective chronic reference doses (R_fD) (Chen et al., 2018; Shil & Singh, 2019). The hazard index (HI) value is obtained by sum of all the HQs of every distinct PTEs from both the exposure paths (Wang et al., 2017).

The values of $CDI_{Ingestion}$ and CDI_{Dermal} for both adults and child were evaluated by the following Eqs. (6) and (7) (Hossain & Patra, 2020; USEPA, 2004).

$$CDI_{Ingestion} = \frac{C_i \times IR \times EF \times ED}{BW \times AT} \tag{6}$$

$$CDI_{Dermal} = \frac{C_i \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \tag{7}$$

where C_i ($\mu\text{g/L}$) is the concentration of individual metal, IR is the ingestion rate (for adults and children is $2.5 \text{ L}\cdot\text{day}^{-1}$ and $0.64 \text{ L}\cdot\text{day}^{-1}$, respectively), exposure frequency (EF) is 365 days/year, exposure duration (ED) for adults and children is 60 years and 6 years, respectively, body weight (BW) for adults is 60 kg (Gope et al., 2018) and children 15 kg (Wang et al., 2017), the average time (AT) is $ED \times 365$ days/year, SA is the skin area ($18,000 \text{ cm}^2$ for adults and 6600 cm^2 for children), exposure time (ET) (0.58 h/day for adults and 1 h/day for children) and K_p (cm/h) is the dermal permeability coefficient of the metal(loid)s in water (Table 2). The unit transfer factor (CF) has value 1×10^{-3} for water (Shil & Singh, 2019; USEPA, 2010).

$$HQ_{Ingestion} = \frac{CDI_{Ingestion}}{R_fD_{Ingestion}} \tag{8}$$

$$HQ_{Dermal} = \frac{CDI_{Dermal}}{R_fD_{Dermal}} \tag{9}$$

The value for the chronic reference dose of ingestion ($R_fD_{Ingestion}$) and dermal (R_fD_{Dermal}) ($\mu\text{g/L}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$) is mentioned in Table 2.

$$HI = \sum HQs \tag{10}$$

Here the value of HI is < 1 which suggests minor adverse health effects and the value ≥ 1 which means the metal has greater probability of adverse health effect on the people (Wagh et al., 2018).

Carcinogenic health risk assessment

The assessment of carcinogenic risk is performed by means of incremental lifetime cancer risk (ILCR) method that introduced by USEPA (2004). The ILCR is formulated by multiplying of chronic daily intake (CDI) with cancer slope factor (CSF) (Hossain & Patra, 2020), as in Eq. (11),

$$ILCR = CDI \times CSF \tag{11}$$

Pb, Cd and Cr are pondered as prospective carcinogens and their carcinogenic toxicity assessment have been calculated in this investigation. The value of $CSF_{Ingestion}$ for Pb, Cd and Cr ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$) is mentioned in Table 2 (Shil & Singh, 2019; USEPA, 2004). The value of $CR > 1 \times 10^{-4}$ is considered as intolerable, while $CR < 1 \times 10^{-6}$ signifies no substantial health effect for a single carcinogenic metal (USEPA, 1989).

Table 2 Permeability coefficient (K_p), reference dose (R_fD) and cancer slope factor (CSF) of different PTEs

Metal	K_p (Cm/h)	R_fD ingestion ($\mu\text{g/L}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$)	R_fD dermal ($\mu\text{g/L}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$)	CSF ($\text{mg/L}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$)
Pb	10^{-4}	1.4	0.42	0.0085
Cu	10^{-3}	40	8	–
Zn	6×10^{-4}	300	60	–
Cd	10^{-3}	0.5	0.025	0.38
Fe	10^{-3}	700	140	–
Cr	10^{-3}	3	0.075	0.5

Results and discussion

The statistical summary of measured water parameters and PTEs in groundwater samples is presented in Table 3 and compared to Indian standards for drinking water. The results show notable variations in the examined samples collected from different sites with respect to their chemical characteristics. The spatial variation of pH (Table 3) in the examined water samples ranges from 6.64 to 7.76 in pre-monsoon and 6.84 to 8.65 in post-monsoon season, indicating neutral to slightly alkaline nature of the waters. The observation shows an increasing trend in pH during post-monsoon season and in very few occasion exceeds the drinking water standards (e.g., sampling site S7). Electrical conductivity (EC), an indicative of dissolved ion concentrations, varies from 118 to 902 $\mu\text{S}\cdot\text{Cm}^{-1}$ in pre-monsoon and 124 to 1225 $\mu\text{S}\cdot\text{Cm}^{-1}$ in the post-monsoon (Table 3), which is very much within the desirable drinking water standards. The values for EC in groundwater are on higher side during the post-monsoon season, which can be attributed to the dissolution of minerals, leaching and influx of runoff water during the rainy season. Total dissolved solids range from 96.80 to 968 mg/L in pre-monsoon and 83.3 to 862 mg/L in post-monsoon. Among all the

sampling stations, 80% groundwater falls under the desirable categories of drinking water. The increase in mean TDS values from pre-monsoon to post-monsoon is probably due to higher dissolution, mineralization, leaching of ions and the influx of runoff water during the monsoon season. Substantial deviations in EC and TDS values can be linked to geochemical processes like ion exchange, mineralization, dissolution of sediment/soil and precipitation (Ehya & Marbouti, 2016). Besides the influence of human activities, discharge of industrial and mine wastewater, leachates from overburden materials, dispose urban wastes result in increased ionic and dissolve solids in groundwater (Hosseinfard & Mirzaei Aminian, 2015; Zakhem & Hafez, 2015). The total hardness (TH as CaCO_3) in the groundwater samples ranges from 82.56 to 486 and 56 to 500 mg/L during pre-monsoon and post-monsoon, respectively, where 37.50% and 33.33% sampling stations exceed the drinking water quality standards in the respective seasons. The results show the level of Cl^- concentrations within the range of 65.15–312.70 mg/L (mean 132.97 mg/L) in pre-monsoon and 60.25–276.85 mg/L (mean 114.74 mg/L) during post-monsoon. Majority of sampling stations (87.50% in pre-monsoon and 91.67% in post-monsoon) shows Cl^- content under

Table 3 Statistical summary of physicochemical parameters and PTE concentrations compared with drinking water standards

Parameters	Pre-monsoon				Post-monsoon				BIS limit (2012)	
	Min	Max	Mean	SD	Min	Max	Mean	SD	Desirable limit	Permissible limit
<i>Major ions (mg/L)</i>										
pH	6.64	7.76	7.25	0.23	6.84	8.65	7.61	0.40	6.5–8.5	No relaxation
EC ($\mu\text{S}\cdot\text{Cm}^{-1}$)	118.00	902.00	354.46	213.25	124	1225	422.38	314.35	–	–
TDS	96.80	968.00	337.34	242.06	83.3	862	276.20	222.17	500	2000
TH	82.56	486.00	191.77	112.67	56	500	174.60	140.00	200	600
HCO_3^-	38.62	264.82	105.16	61.67	36.78	298.55	115.93	76.16	–	–
Cl^-	65.15	312.70	132.97	71.19	60.25	276.85	114.74	60.47	250	1000
SO_4^{2-}	25.25	286.24	88.53	78.36	18.25	217.62	73.81	68.41	200	400
<i>Potentially toxic elements (PTEs) ($\mu\text{g/L}$)</i>										
Pb	2.32	34.72	10.06	6.68	2.08	21.24	7.88	3.87	10	No relaxation
Cu	4.55	30.76	13.74	4.72	3.14	16.98	11.38	3.23	50	1500
Zn	30.48	98.35	49.47	18.86	23.86	71.48	39.80	14.35	5000	15,000
Cd	0.15	5.43	3.44	1.35	0.126	4.632	2.61	1.42	3	No relaxation
Fe	258.34	1056.65	438.82	160.85	298.35	1263.54	591.51	249.48	300	No relaxation
Cr	38.46	256.08	112.26	65.18	32.66	238.48	90.96	55.70	50	No relaxation

the safe limit of water for human consumption. The concentration of SO_4^{2-} in the study area is found to vary from 25.25 to 286.24 mg/L (mean 88.53 mg/L) in pre-monsoon and 18.25 to 217.62 mg/L (average 73.81 mg/L) in post-monsoon. The values of SO_4^{2-} are mostly as per the desirable standards with few exceptions (S7, S9, S15 in pre-monsoon and S7 in post-monsoon).

PTE concentrations in groundwater samples

The statistical summary of PTE concentration in groundwater samples in different seasons is presented in Table 3. The concentration of Pb ranges from 2.32 to 34.72 $\mu\text{g/L}$ (mean 10.06 $\mu\text{g/L}$) in the pre-monsoon and 2.08 to 21.24 $\mu\text{g/L}$ (mean 7.88 $\mu\text{g/L}$) in the post-monsoon season, exceeding the desirable standards in 25 and 17% of sampling sites in respective season. The values of Cu ranges from 4.55 to 30.76 $\mu\text{g/L}$ in the pre-monsoon and 3.14 to 16.98 $\mu\text{g/L}$ in the post-monsoon, which is well under the desirable water quality standards. In this study, Zn concentration ranges from 30.48 to 98.35 $\mu\text{g/L}$ (average 49.47 $\mu\text{g/L}$) and 23.86 to 71.48 $\mu\text{g/L}$ (average 39.80 $\mu\text{g/L}$) in pre-monsoon and post-monsoon seasons, respectively, and is very much within the prescribed standards. Cd is a minor metallic element in the earth's crust and naturally present in groundwater. The concentration of Cd ranges from 0.15 to 5.43 and 0.13 to 4.63 $\mu\text{g/L}$ in pre-monsoon and post-monsoon, respectively. The level of Cd exceeds the desirable limit for drinking water for 75% of sampling sites in pre-monsoon and 62.5% sampling sites in post-monsoon. The measured concentrations for Fe ranges from 258.34 to 1056.65 $\mu\text{g/L}$ (average 438.82 $\mu\text{g/L}$) in the post-monsoon and 298.35 to 1263.54 $\mu\text{g/L}$ (average 591.57 $\mu\text{g/L}$) in the pre-monsoon season, exceeding the desirable standards for the maximum no of sample stations (91.67 and 95.83%, respectively) in both seasons (Table 3). Excessive Fe content in groundwater is mostly emerged through the weathering of rocks and opencast mining processes (Kumar et al., 2010). The elevated Fe content in the groundwater may be attributed to coal mines wastewater and leachate from overburden dumps of coal mines of the study area and from effluent discharge from Sponge iron and Ferro Alloy industries (Mahato et al., 2014; Tiwari et al., 2016). Measured values for Cr are found to be within the range of 38.46–256.08 $\mu\text{g/L}$ in pre-monsoon and

32.66–238.48 $\mu\text{g/L}$ in post-monsoon season (Table 3), which is very much higher than the prescribed Indian standards. The Cr concentrations exceeded the permissible limit of 87.50 and 79.17% of sampling sites in pre-monsoon and post-monsoon season, respectively. Higher values of Cr can be linked to opencast mining process and geological process such as weathering, soil erosion in study area. The overall results demonstrate elevated PTEs in groundwater in pre-monsoon season as compared to the post-monsoon (except Fe and Cr). The measured values of Pb (6 out of 24 Sites), Cd (18 of 24), Fe (22 of 24), Cr (21 of 24) in pre-monsoon and Pb (4 out of 24), Cd (15 of 24), Fe (23 of 24), Cr (19 of 24) in post-monsoon exceed the recommended standards for drinking water (Table 3). However, the level of Cu and Zn are well underneath the specified standard for both the seasons.

Pollution evaluation indices of the groundwater samples

In the present study, three pollution indices such as degree of contamination (C_d), heavy metal evaluation index (HEI) and heavy metal pollution index (HPI) are calculated using Indian standards for drinking water (2012) as reference value. The statistical outcomes of different indices are presented in Table 4. The results of contamination factor (C_f) for PTEs are Pb (– 0.77 to 2.47), Cu (– 0.997 to – 0.979), Zn (– 0.998 to – 0.993), Cd (– 0.951 to 0.809), Fe (– 0.14 to 2.52), Cr (– 0.23 to 4.12) and Pb (– 0.79 to 1.12), Cu (– 0.998 to – 0.989), Zn (– 0.998 to – 0.995), Cd (– 0.958 to 0.544), Fe (– 0.01 to 3.21), Cr (– 0.35 to 3.77) during pre-monsoon and post-monsoon seasons, respectively (Table 5). The mean C_f of PTEs in the groundwater is in the order of Cr (1.25) > Fe (0.46) > Cd (0.15) > Pb (0.01) > Cu (– 0.99) > Zn (– 1.00) in pre-monsoon and Fe (0.97) > Cr (0.82) > Cd (– 0.13) > Pb (– 0.21) > Cu (– 0.99) > Zn (– 1.00) in post-monsoon season. The degree of contamination (C_d) for PTEs ranges from 0 to 6.64, with a mean value of 2.19 in pre-monsoon, and 0 to 6.39, with a mean value of 2.03 in post-monsoon season (Fig. 4a, b). The results (with respect to C_d values) demonstrate that the level of metal contamination in majority of the sampling site is low in both the seasons, whereas moderate degree of contamination is noted for site S7, S10 and S22 in pre-monsoon and S7, S8 and S10 in post-monsoon season.

Table 4 Classification of water quality based on modified categories of pollution indices

Pollution indices	Pre-monsoon					Post-monsoon				
	Category	Degree of pollution	No. of samples	% of Samples	Sampling sites	Category	Degree of pollution	No. of samples	% of Samples	Sampling sites
HPI	< 55	Low	02	8.33	S23, S24	< 55	Low	08	33.33	S23, S16, S24, S2, S3, S1, S19, S5
	55–110	Medium	08	33.33	S19, S2, S1, S3, S16, S11, S4, S12	55–110	Medium	05	20.83	S12, S6, S4, S18
	> 110	High	14	58.33	S5, S20, S17, S6, S21, S14, S8, S10, S18, S15, S13, S9, S22, S7	> 110	High	11	45.83	S17, S20, S21, S14, S13, S10, S15, S22, S8, S9, S7
HEI	< 8	Low	19	79.17	S24, S23, S19, S16, S2, S3, S12, S11, S4, S5, S1, S6, S18, S15, S13, S20, S17, S21, S14	< 8	Low	21	87.5	S23, S24, S16, S19, S2, S3, S5, S1, S12, S18, S4, S6, S13, S15, S22, S9, S11, S17, S20, S21, S14
	8–15	Medium	05	20.83	S8, S9, S22, S7, S10	8–15	Medium	03	12.5	S10, S8, S7
	> 15	High	Nil	Nil	Nil	> 15	High	Nil	Nil	Nil
C_d	< 5	Low	21	87.5	S19, S24, S23, S16, S12, S3, S5, S4, S11, S2, S6, S1, S18, S15, S13, S20, S17, S21, S14, S8, S9	< 5	Low	21	87.5	S19, S16, S24, S12, S23, S18, S5, S3, S1, S4, S6, S2, S13, S15, S22, S9, S11, S17, S20, S21, S14
	5–10	Medium	03	12.5	S22, S7, S10	5–10	Medium	03	12.5	S10, S7, S8
	> 10	High	Nil	–	–	> 10	High	Nil	–	–

The calculated HEI values range from 2.35 to 10.51 with a mean value of 5.87 in pre-monsoon and 2.36 to 10.31 with a mean value of 5.46 in post-monsoon (Fig. 5). From the results, it is observed that no groundwater sample falls under the highly contaminated category in pre-monsoon and post-monsoon seasons. Only 20.83% (S8, S9, S22, S7, S10) of sampling sites in pre-monsoon and 12.5% (S10, S8, S7) in post-monsoon seasons are classified as

moderately contaminated, while contamination level is low for the rest of the sampling stations (Fig. 5). The similar findings for the C_d and HEI confirm the impacts of the anthropogenic activities such as discharges from mining, industries and leachates of overburden due to opencast coal mining in the aforementioned areas.

The mean values of the examined PTEs (Pb, Cu, Zn, Cd, Fe and Cr) in groundwater samples are used to

Table 5 Contamination factors (C_f) of PTEs during pre- and post-monsoon in the groundwater samples

Location no	C_f											
	Pb		Cu		Zn		Cd		Fe		Cr	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
S1	-0.17	-0.33	-0.992	-0.993	-0.998	-0.998	-0.12	-0.58	0.70	0.55	0.46	0.24
S2	-0.31	-0.44	-0.991	-0.994	-0.997	-0.998	-0.35	-0.82	0.33	0.61	0.56	0.31
S3	-0.14	-0.27	-0.992	-0.994	-0.997	-0.998	-0.05	-0.63	0.21	0.53	0.39	0.11
S4	-0.10	-0.37	-0.991	-0.992	-0.997	-0.998	0.07	0.15	0.22	0.58	0.45	0.12
S5	0.03	-0.25	-0.989	-0.993	-0.998	-0.998	0.14	-0.57	0.09	0.56	0.42	0.00
S6	-0.10	-0.20	-0.992	-0.992	-0.996	-0.996	0.28	0.08	0.23	0.69	0.54	0.12
S7	2.47	1.12	-0.989	-0.990	-0.996	-0.997	0.61	0.22	0.59	2.52	2.21	2.44
S8	-0.12	-0.21	-0.979	-0.989	-0.997	-0.998	0.23	0.34	0.23	3.21	4.12	2.84
S9	0.43	0.24	-0.990	-0.991	-0.995	-0.996	0.76	0.54	0.93	0.75	2.60	0.77
S10	-0.15	-0.21	-0.989	-0.990	-0.997	-0.998	0.25	0.10	2.52	2.15	3.87	3.77
S11	-0.21	-0.24	-0.992	-0.992	-0.998	-0.998	0.09	0.01	0.35	0.69	0.39	2.25
S12	-0.12	-0.16	-0.991	-0.993	-0.998	-0.998	0.11	-0.39	0.35	0.22	0.11	0.23
S13	0.15	-0.07	-0.991	-0.992	-0.995	-0.995	0.62	0.26	0.37	0.53	0.85	0.53
S14	-0.20	-0.24	-0.991	-0.992	-0.997	-0.998	0.29	0.21	1.29	2.01	2.49	1.74
S15	0.13	0.03	-0.991	-0.991	-0.996	-0.997	0.62	0.33	0.46	0.81	0.65	0.33
S16	-0.24	-0.67	-0.992	-0.995	-0.998	-0.998	0.05	-0.95	0.00	0.37	0.34	-0.19
S17	-0.07	-0.14	-0.990	-0.991	-0.995	-0.998	0.14	0.09	0.44	1.56	2.31	1.33
S18	-0.15	-0.15	-0.992	-0.992	-0.995	-0.995	0.72	0.11	0.21	0.26	0.33	0.10
S19	-0.62	-0.74	-0.994	-0.995	-0.998	-0.998	-0.35	-0.39	-0.14	-0.01	-0.11	-0.29
S20	-0.13	-0.19	-0.989	-0.990	-0.995	-0.998	0.12	0.14	0.32	1.53	2.18	1.37
S21	-0.21	-0.22	-0.991	-0.992	-0.998	-0.998	0.22	0.13	0.24	1.89	2.82	1.66
S22	1.42	0.16	-0.990	-0.991	-0.993	-0.995	0.81	0.35	0.76	0.46	2.33	0.56
S23	-0.77	-0.79	-0.996	-0.996	-0.998	-0.998	-0.95	-0.96	0.33	0.45	-0.23	-0.35
S24	-0.69	-0.78	-0.997	-0.998	-0.998	-0.998	-0.84	-0.89	0.09	0.40	-0.21	-0.33

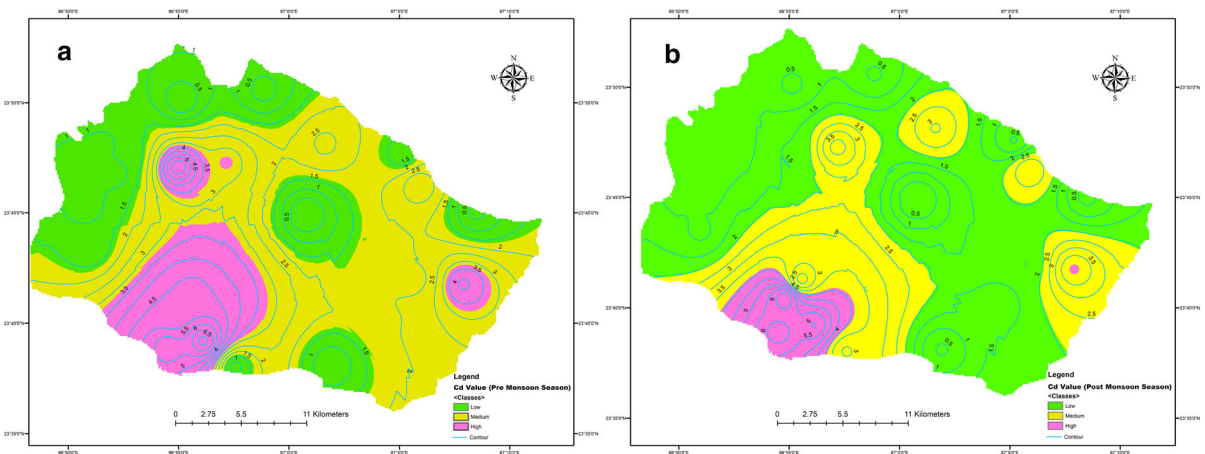


Fig. 4 Geospatial distribution of degree of contamination (C_d) of PTEs during pre- and post-monsoon

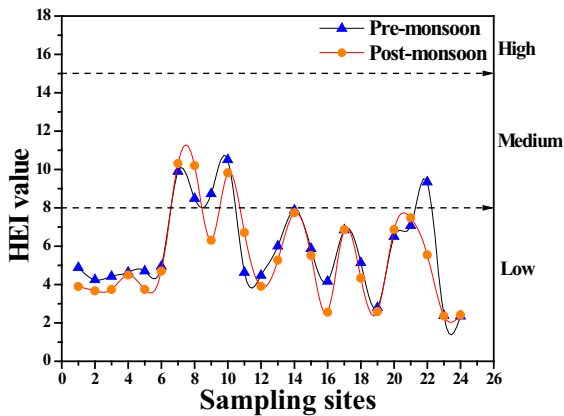


Fig. 5 Spatial variation of heavy metal evaluation index (HEI) for PTEs in different sampling sites

estimate the HPI and evaluate the rationality of the index model (Jahanshahi & Zare, 2015; Prasad et al., 2014). The mean HPI resulted in this study area are 116.35 and 90.14 during pre-monsoon and post-monsoon season, respectively (Fig. 6a, b). The spatial variability of HPI ranges from 13.55 to 211.88 in pre-monsoon and 12 to 154.98 in post-monsoon season (Fig. 6a, b). The calculated HPI demonstrate that 8.33% of sampling stations during pre-monsoon and 33.33% of the sampling stations during post-monsoon are below the critical limit of 100 (Table 4). This inconsistency in results can be explained due to the dilution of groundwater during post-monsoon season. The level of PTEs found to be high for 58.33% sampling sites in pre-monsoon and 45.83% sampling sites in post-monsoon. This situation can be explained due to the leaching of PTEs from ground strata, open dump of mining wastage, seepage of industrial

discharges to groundwater (Prasad et al., 2017). Moreover, these locations are highly influenced by anthropogenic activities such as industrial, mining and urban discharges, and thus make it unsuitable for drinking and other domestic/household uses.

Source evaluation of PTEs in groundwater using multivariate statistical analysis

Exploring the sources of PTEs in groundwater in different sampling stations in the studied region will assist to control groundwater contamination in near future. In general, groundwater contamination due to PTEs can be occurred by several natural and anthropogenic activities. Statistical investigation is often used to evaluate the patterns of distribution, nature of dynamics and interdependency of analyzed variables. The potential sources of PTEs in groundwater might be obtained by employing statistical tools such as correlation study, principal component analysis (PCA) and hierarchical cluster analysis (HCA) (Hossain & Patra, 2020; Vetrimurugan et al., 2017).

Pearson's correlation analysis

Correlation study has been performed between PTEs and other physicochemical parameters in the groundwater samples to examine their relative interdependence on each other (Table 6). Significant positive correlation is observed between pH with EC, SO_4^{2-} and Pb in pre-monsoon and pH with EC, TDS, TH, HCO_3^- , Cl^- and SO_4^{2-} in the post-monsoon season. This may explain that the groundwater quality is influenced by geochemical process and anthropogenic

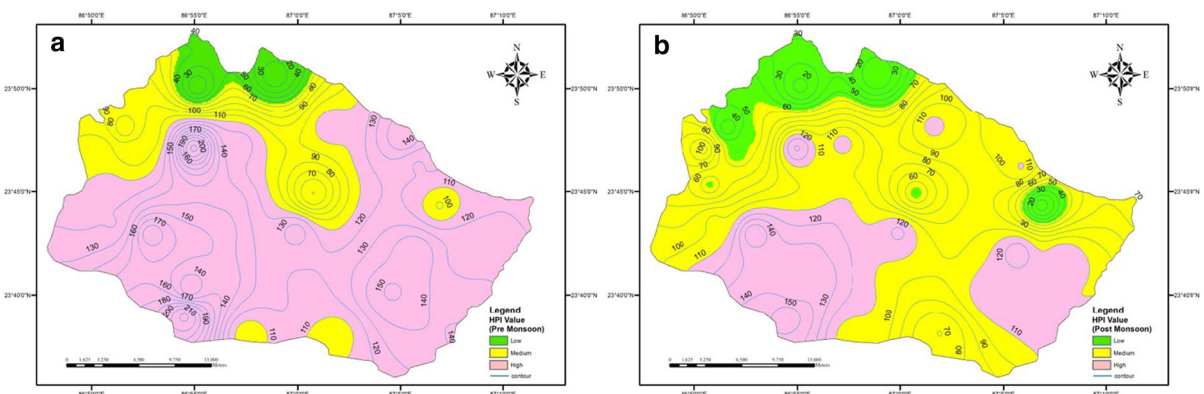


Fig. 6 Geospatial representation of heavy metal pollution index (HPI) during pre- and post-monsoon season

Table 6 Pearson correlation coefficient matrix among the water quality parameters of the groundwater in the study area

Variables	pH	EC	TDS	TH	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Pb	Cu	Zn	Cd	Fe	Cr
<i>Pre-monsoon</i>													
pH	1												
EC	0.736	1											
TDS	0.413	0.708	1										
TH	0.478	0.821	0.902	1									
HCO ₃ ⁻	0.449	0.768	0.909	0.917	1								
Cl ⁻	0.475	0.781	0.711	0.736	0.681	1							
SO ₄ ²⁻	0.623	0.847	0.746	0.813	0.732	0.704	1						
Pb	0.571	0.736	0.409	0.568	0.375	0.791	0.734	1					
Cu	0.115	0.345	0.633	0.681	0.581	0.425	0.406	0.306	1				
Zn	0.470	0.651	0.385	0.445	0.445	0.673	0.495	0.571	0.201	1			
Cd	0.374	0.662	0.569	0.624	0.484	0.646	0.592	0.638	0.484	0.718	1		
Fe	0.041	0.160	0.142	0.183	0.078	0.243	0.139	0.191	0.208	0.147	0.284	1	
Cr	0.080	0.320	0.315	0.315	0.225	0.513	0.290	0.383	0.285	0.382	0.504	0.702	1
<i>Post-monsoon</i>													
pH	1												
EC	0.712	1											
TDS	0.597	0.882	1										
TH	0.585	0.830	0.934	1									
HCO ₃ ⁻	0.597	0.895	0.979	0.920	1								
Cl ⁻	0.595	0.654	0.660	0.767	0.655	1							
SO ₄ ²⁻	0.581	0.782	0.841	0.944	0.855	0.756	1						
Pb	0.479	0.527	0.488	0.604	0.478	0.776	0.689	1					
Cu	0.301	0.396	0.501	0.571	0.456	0.522	0.597	0.717	1				
Zn	0.164	0.188	0.272	0.267	0.213	0.359	0.291	0.376	0.343	1			
Cd	0.325	0.479	0.573	0.585	0.548	0.530	0.570	0.655	0.850	0.542	1		
Fe	0.200	0.373	0.490	0.485	0.513	0.423	0.435	0.438	0.657	- 0.181	0.481	1	
Cr	0.088	0.228	0.339	0.358	0.350	0.357	0.313	0.452	0.698	- 0.123	0.547	0.856	1

Values in bold are different from 0 with a significance level alpha = 0.05

activities in both the seasons. High positive correlation also exists for EC–TDS, EC–TH, EC–HCO₃⁻, EC–Cl⁻, EC–SO₄²⁻, TDS–TH, TDS–HCO₃⁻, TDS–Cl⁻, TDS–SO₄²⁻, TH–HCO₃⁻, TH–Cl⁻, TH–SO₄²⁻, HCO₃⁻Cl⁻, HCO₃⁻SO₄²⁻, Cl⁻SO₄²⁻, TDS–Cu and TDS–Cd in both the seasons. This situation can be explained due to their common origin such as anthropogenic contribution, leachates from overburden materials and mining waste, coal mine effluents, industrial and urban waste and wastewater discharges (Banerjee & Gupta, 2013; Loganathan & Ahamed, 2017). Among the PTEs, significant positive correlation is noted between Pb–Zn, Pb–Cd, Zn–Cd, Cd–Cr

and Fe–Cr in pre-monsoon; and Pb–Cu, Pb–Cd, Cu–Cd, Cu–Fe, Cu–Cr, Zn–Cd, Cd–Cr and Fe–Cr in post-monsoon (Table 6). This observation may be due to similarities in their geochemical distribution and behavior pattern as they sourced from a common origin (Dash et al., 2016).

Principal component analysis (PCA)

The PCA is performed on the analyzed results (normalized data set) of water parameters and PTEs to identify the potential sources of contamination during pre-monsoon and post-monsoon seasons. The

summary of PCA analysis including eigenvalues, total, cumulative variance values are presented in Table 7. The results execute three factors (eigenvalue > 1) accounting 80% and 84.22% of the total variation during the pre-monsoon and post-monsoon. The first component (PC1) contributes 56.49% of variance and strongly loaded with EC, TDS, TH, Cl^- , SO_4^{2-} , moderately with Pb, Cd, and weekly loaded with pH, Cu, Zn in pre-monsoon, whereas in post-monsoon PC1 accounts 58.67% of variance and strongly comprises with EC, TDS, TH, HCO_3^- , SO_4^{2-} , moderately with Cl^- , Pb, Cd, Zn and weekly loaded with pH. Therefore, this first component (PC1) seems to be associated with anthropogenic sources such as mining activities, setting up coal-based thermal power plants, establishing iron and steel industries, and disposing of mining and urban wastes in the studied region (Ehya & Marbouti, 2016; Tiwari et al., 2017). PC2, accounts for 12.81%, execute positive loading for Fe and Cr in pre-monsoon, while moderate loading of Cr and week loading of Fe in post-monsoon with 14.58% of total variance. The outcome in PC2 can be linked to weathering of the earth's crust and leachates from overburden materials and sponge iron industries (Tiwari et al., 2016). The third component (PC3) depicts minor loading of Cu in pre-monsoon and Zn in post-monsoon (accounts for 10.70

and 10.97% of the total variance, respectively), and may be due to the combine influence of seasonal factors and natural process such as weathering, mineral dissolution which influence the groundwater chemistry in the study area.

Hierarchical cluster analysis (HCA)

The CA is used for grouping water quality parameters or sampling locations by looking at similarities in their chemical compositions and their interdependency (Routroy et al., 2013; Shrestha & Kazama, 2007). The dendrograms of the analyzed parameters and sampling locations for the pre- and post-monsoon seasons are shown in Fig. 7, and Fig. 8a, b depicts dendrograms for groundwater sampling locations. Dendrogram explores three statistically significant clusters of measured variables for pre-monsoon and post-monsoon season.

During the pre-monsoon season, cluster 1 (C1) (sampling sites 16, 5, 21, 4, 3, 1, 12, 17, 10, 6, 11, 2) describes a close association with pH, Cd, Pb, Cu, Zn and Cl^- , and cluster C2 (sampling sites 18, 15, 20, 19, 24, 23, 8, 22, 7, 13, 9) confirms the elevated level of EC, TDS, TH, HCO_3^- and SO_4^{2-} (Fig. 7a, b). The statistical outcome for C1 and C2 correlates reasonably with PC1 and PC3, which may be corresponded to

Table 7 Varimax rotated factor loadings matrix for groundwater parameters

Variables	Component (pre-monsoon)			Component (post-monsoon)		
	PC1	PC2	PC3	PC1	PC2	PC3
pH	0.391	0.078	0.214	0.421	0.162	0.014
EC	0.838	0.025	0.045	0.704	0.125	0.053
TDS	0.712	0.040	0.154	0.805	0.056	0.039
TH	0.828	0.034	0.090	0.861	0.039	0.017
HCO_3^-	0.691	0.091	0.114	0.792	0.056	0.068
Cl^-	0.781	0.009	0.011	0.685	0.012	0.012
SO_4^{2-}	0.766	0.036	0.006	0.821	0.038	0.002
Pb	0.587	0.008	0.167	0.598	0.022	0.100
Cu	0.341	0.001	0.380	0.567	0.249	0.082
Zn	0.473	0.020	0.172	0.119	0.061	0.695
Cd	0.615	0.060	0.009	0.578	0.085	0.180
Fe	0.080	0.652	0.022	0.389	0.393	0.129
Cr	0.240	0.612	0.005	0.288	0.597	0.034
Eigenvalue	7.34	1.67	1.39	7.63	1.90	1.43
Variability (%)	56.49	12.81	10.70	58.67	14.58	10.97
Cumulative %	56.49	69.30	80.00	58.67	73.25	84.22

The values highlighted in bold represent higher loading in particular components and show larger correlations with extracted PC

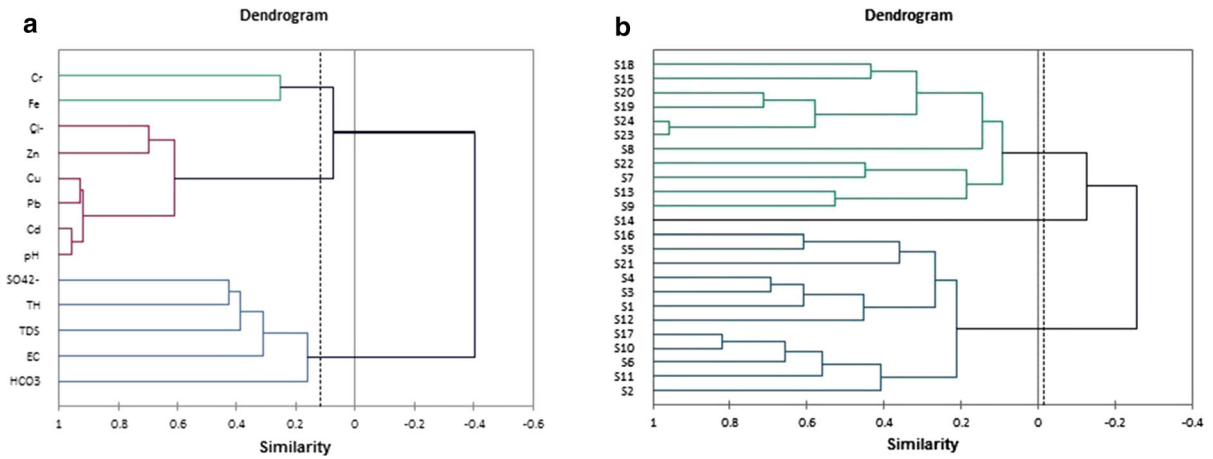


Fig. 7 Dendrograms of **a** the analyzed parameters and **b** the sampling locations for pre-monsoon season

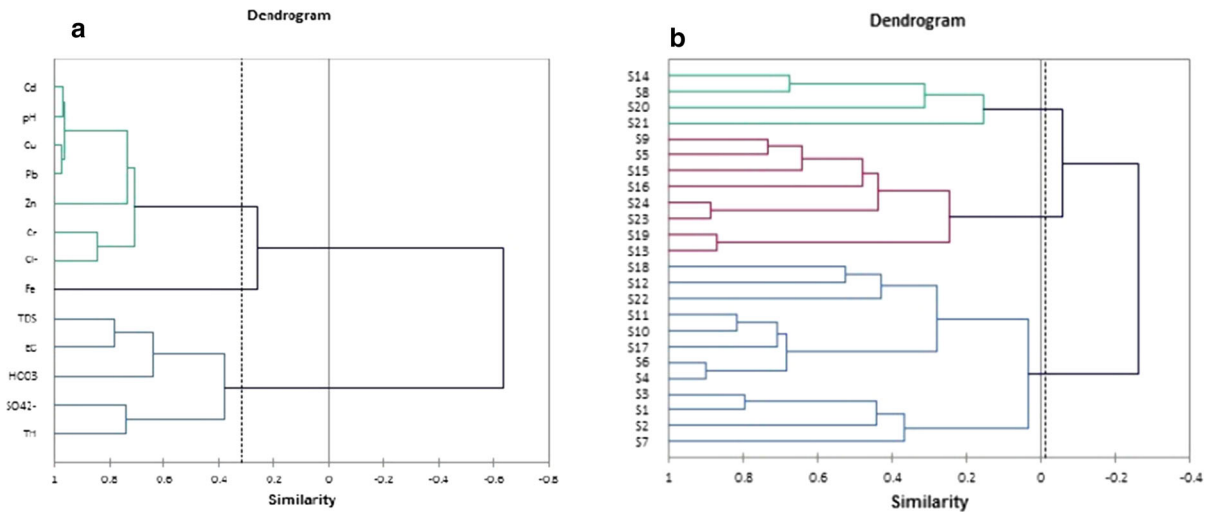


Fig. 8 Dendrograms of **a** the analyzed parameters and **b** the sampling locations for post-monsoon season

the mixed factor, i.e., anthropogenic activities such as coal mining, discharges from iron and steel industries, coal fired thermal power plant, stone crushers, sponge iron, ferro alloy and electroplating industries, leachate from overburden materials, urban/industrial waste dumping sites, and partially influenced by seasonal and natural process like geochemical weathering and soil–water interaction. Cluster 3 (C3) is represented by the single sample station (14), indicating higher levels of Fe and Cr. The outcome for C3 can be attributed to discharges from adjacent sponge iron industries and also due to the erosion/weathering of the earth’s crust and bedrock materials which affirms the findings of PC2.

The results obtained from CA in post-monsoon execute 3 clusters (Fig. 8a, b). The first cluster (C1) is the larger group of sampling locations (18, 12, 22, 11, 10, 17, 6, 4, 3, 1, 2,7), strongly associated with pH, Cd, Cu, Pb, Zn, Cr, Cl⁻, and the second cluster C2 (sampling station nos. 9, 5, 15, 16, 24, 23, 19, 13) is linked with EC, TDS, TH, HCO₃⁻ and SO₄²⁻ (Fig. 8a, b). These clusters (C1 and C2) correspond well with PC1 and PC3. It signifies that the contamination of sampling locations is mainly due to anthropogenic factor such as coal mine effluents, leachates from overburden materials and mining waste, industrial wastewater, urban waste and sewage activities, along with seasonal variations (Loganathan & Ahamed,

Table 8 Spatial distribution of the hazard index (HI) values of PTEs for adults and child during pre- and post-monsoon season in the study area

Sites	Hazardous (CI)												
	Pb				Cu				Zn				
	Pre		Post		Pre		Post		Pre		Post		
	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	
S1	0.238	0.254	0.193	0.206	0.012	0.013	0.011	0.011	0.005	0.005	0.004	0.004	
S2	0.197	0.210	0.161	0.172	0.014	0.014	0.009	0.009	0.006	0.006	0.004	0.004	
S3	0.247	0.264	0.208	0.223	0.013	0.013	0.010	0.010	0.005	0.006	0.005	0.005	
S4	0.256	0.274	0.181	0.193	0.013	0.014	0.013	0.013	0.005	0.006	0.005	0.005	
S5	0.296	0.317	0.213	0.228	0.018	0.018	0.011	0.011	0.004	0.004	0.004	0.004	
S6	0.256	0.274	0.228	0.244	0.013	0.013	0.013	0.013	0.009	0.009	0.008	0.009	
S7	0.992	1.062	0.607	0.650	0.017	0.017	0.016	0.017	0.008	0.009	0.005	0.005	
S8	0.250	0.268	0.227	0.243	0.031	0.033	0.017	0.018	0.005	0.006	0.005	0.005	
S9	0.408	0.436	0.353	0.378	0.015	0.015	0.013	0.014	0.011	0.011	0.007	0.008	
S10	0.242	0.259	0.226	0.242	0.017	0.018	0.015	0.016	0.006	0.007	0.004	0.005	
S11	0.225	0.240	0.216	0.231	0.012	0.013	0.012	0.012	0.005	0.005	0.004	0.004	
S12	0.253	0.271	0.241	0.257	0.014	0.014	0.011	0.012	0.005	0.005	0.004	0.004	
S13	0.328	0.350	0.267	0.286	0.014	0.015	0.013	0.013	0.010	0.010	0.009	0.010	
S14	0.228	0.244	0.218	0.233	0.015	0.015	0.013	0.013	0.005	0.005	0.005	0.005	
S15	0.322	0.345	0.295	0.316	0.014	0.014	0.014	0.014	0.007	0.008	0.006	0.006	
S16	0.219	0.234	0.093	0.100	0.013	0.013	0.007	0.008	0.005	0.005	0.004	0.005	
S17	0.266	0.285	0.246	0.264	0.016	0.017	0.014	0.014	0.009	0.010	0.005	0.005	
S18	0.244	0.261	0.242	0.259	0.012	0.013	0.012	0.012	0.010	0.011	0.010	0.010	
S19	0.110	0.118	0.075	0.081	0.009	0.010	0.008	0.008	0.005	0.005	0.004	0.005	
S20	0.249	0.267	0.233	0.249	0.017	0.018	0.015	0.015	0.009	0.010	0.005	0.005	
S21	0.225	0.241	0.224	0.240	0.013	0.014	0.012	0.012	0.005	0.005	0.004	0.005	
S22	0.693	0.741	0.331	0.354	0.015	0.016	0.014	0.015	0.013	0.014	0.010	0.010	
S23	0.066	0.071	0.059	0.064	0.006	0.007	0.005	0.006	0.004	0.004	0.003	0.003	
S24	0.088	0.094	0.064	0.069	0.005	0.005	0.003	0.003	0.004	0.005	0.004	0.004	
Cd	Fe				Cr								
Pre		Post		Pre		Post		Pre		Post			
Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
0.229	0.230	0.109	0.110	0.030	0.031	0.027	0.029	1.137	1.083	0.961	0.916		
0.170	0.171	0.046	0.046	0.023	0.024	0.028	0.030	1.215	1.157	1.021	0.973		
0.247	0.249	0.097	0.098	0.021	0.022	0.027	0.028	1.081	1.030	0.859	0.818		
0.278	0.280	0.299	0.301	0.021	0.022	0.028	0.029	1.123	1.070	0.868	0.827		
0.296	0.298	0.112	0.113	0.019	0.020	0.027	0.029	1.106	1.054	0.775	0.738		
0.331	0.333	0.281	0.283	0.021	0.023	0.030	0.031	1.198	1.141	0.873	0.832		
0.418	0.420	0.316	0.318	0.028	0.029	0.061	0.065	2.492	2.375	2.676	2.549		
0.321	0.322	0.347	0.349	0.021	0.023	0.074	0.077	3.980	3.792	2.987	2.846		
0.458	0.460	0.401	0.403	0.034	0.036	0.031	0.032	2.795	2.663	1.372	1.307		
0.324	0.326	0.286	0.288	0.062	0.065	0.055	0.058	3.787	3.608	3.707	3.532		
0.284	0.285	0.263	0.265	0.024	0.025	0.029	0.031	1.083	1.031	2.525	2.406		
0.289	0.291	0.159	0.160	0.024	0.025	0.021	0.022	0.862	0.821	0.957	0.911		

Table 8 continued

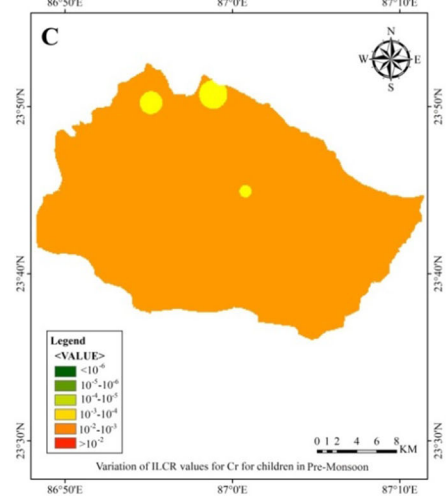
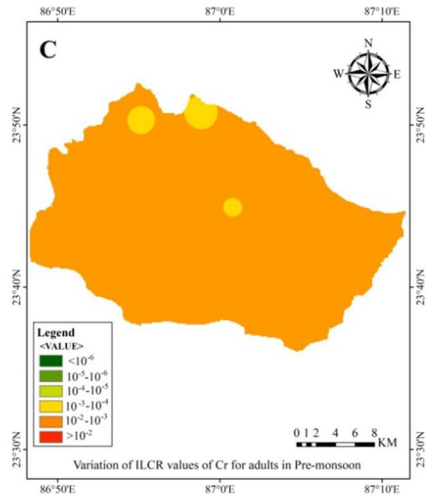
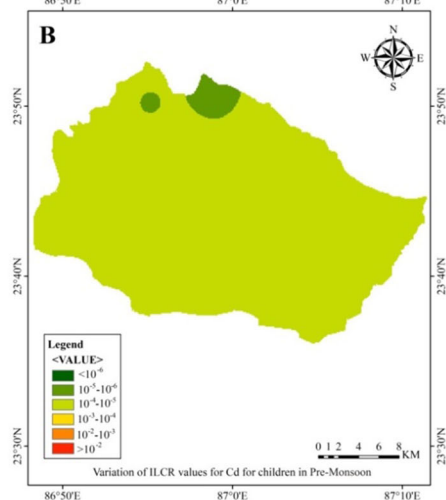
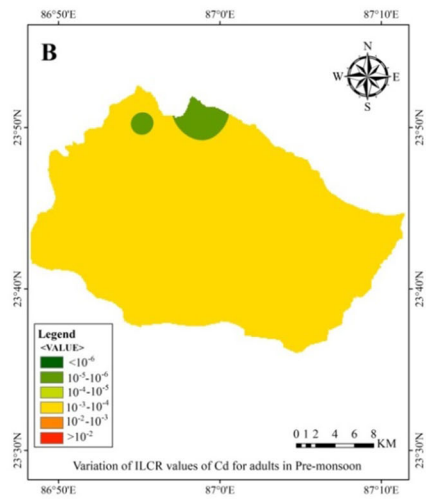
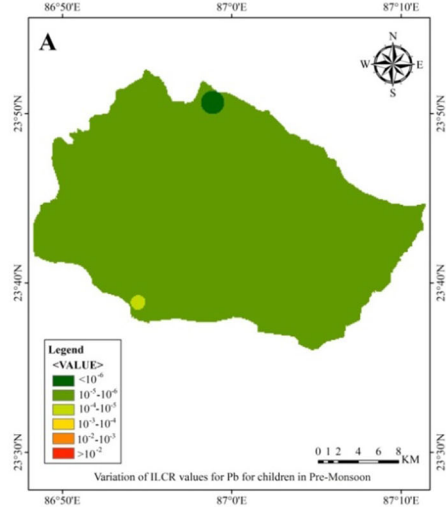
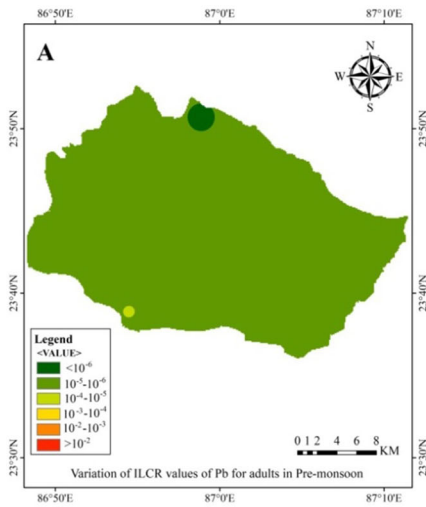
Cd				Fe				Cr			
Pre		Post		Pre		Post		Pre		Post	
Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
0.421	0.423	0.326	0.328	0.024	0.025	0.027	0.028	1.438	1.370	1.192	1.136
0.335	0.337	0.315	0.317	0.040	0.042	0.053	0.055	2.713	2.584	2.132	2.031
0.420	0.423	0.345	0.347	0.025	0.027	0.032	0.033	1.283	1.222	1.031	0.983
0.273	0.275	0.012	0.012	0.017	0.018	0.024	0.025	1.038	0.989	0.631	0.601
0.297	0.298	0.284	0.286	0.025	0.026	0.045	0.047	2.574	2.452	1.813	1.727
0.448	0.451	0.289	0.291	0.021	0.022	0.022	0.023	1.036	0.987	0.851	0.811
0.169	0.170	0.158	0.159	0.015	0.016	0.017	0.018	0.694	0.661	0.554	0.528
0.290	0.292	0.296	0.297	0.023	0.024	0.044	0.046	2.468	2.351	1.842	1.755
0.317	0.318	0.294	0.296	0.022	0.023	0.051	0.053	2.971	2.831	2.065	1.968
0.470	0.473	0.349	0.352	0.031	0.032	0.026	0.027	2.591	2.469	1.215	1.157
0.013	0.013	0.011	0.011	0.023	0.024	0.025	0.027	0.598	0.570	0.508	0.484
0.042	0.042	0.028	0.029	0.019	0.020	0.025	0.026	0.615	0.586	0.520	0.495

2017). Cluster C3, the smallest group of sampling stations (14, 8, 20, 21), is distinguished by high level of Fe and correlates well with PC2. Cluster C3 is mainly controlled by the geogenic factor and can be corresponded with mineral dissolution and rock–water interactions which regulate the characteristics of groundwater in the study area (Tiwari et al., 2016). The identical combinations of water parameters obtained in PCA and CA confirm that the groundwater quality and characteristics are strongly influenced by natural process as well as anthropogenic factors.

Health risk assessment

The results for health risk assessment in the present study reveal ingestion as the prime pathway of metal exposure for groundwater compared to dermal contact for child and adults both (Table 8). Cr emerged as most unsafe among other studied metals in the present study. Based on HI values, the order of risk in adults is Cr > Cd > Pb > Fe > Cu > Zn in pre-monsoon as well as post-monsoon season, while for children the order is Cr > Pb > Cd > Fe > Cu > Zn in both the seasons. Cr poses maximum health risk (HI > 1) for child and adult in both the seasons; however, the risk level falls down at all the sampling sites in post-

monsoon season. Based on results, Pb appears to be second most unsafe toxic element for child with highest value in site 7 (1.062) which represents HI value > 1 in pre-monsoon season leading to non-carcinogenic risk. Site 7 also indicated HI value close to 1(0.992) for Pb in adults in pre-monsoon season. Likewise, Cr and Pb, and all the PTEs display noticeable decrease in health risk in post-monsoon as compared to pre-monsoon (Table 8). HI of all the examined PTEs bears a higher value for children than the adults in both the seasons, displaying that children are more prone to be affected than the adults except for Cr where adults are more prone to risk in comparison with children. Similar finding was also reported by Wang et al. (2017) on Huaihe River, Anhui, China, although they have no exception with Cr. Present findings are in disagreement with Shil and Singh, (2019) on Mahananda River, India. In this study, maximum HI values of PTEs (Pb, Cu, Zn, Cd, Fe and Cr) are noted in sites 7, 8, 9, 22, 10 and 8 in pre-monsoon, and in sites 7, 8, 22, 9, 8 and 10 in post-monsoon for children. For adults, the results show following pattern: sites 7, 8, 22, 22, 10 and 8 in pre-monsoon and sites 7, 8, 22, 9, 8 and 10 in post-monsoon season for Pb, Cu, Zn, Cd, Fe and Cr, respectively.



◀ **Fig. 9** Geospatial distribution of incremental lifetime cancer risk (ILCR) for adults and child during pre-monsoon season

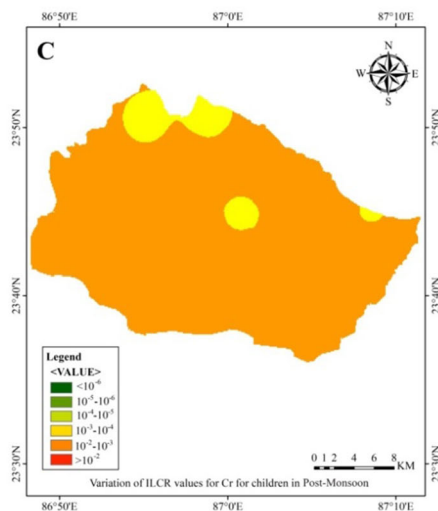
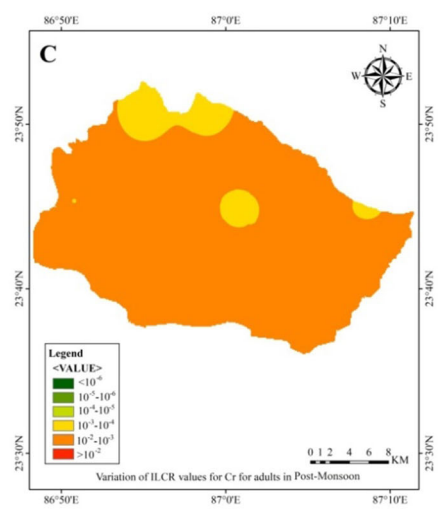
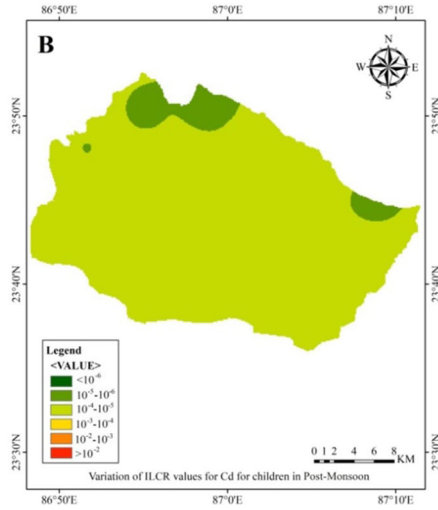
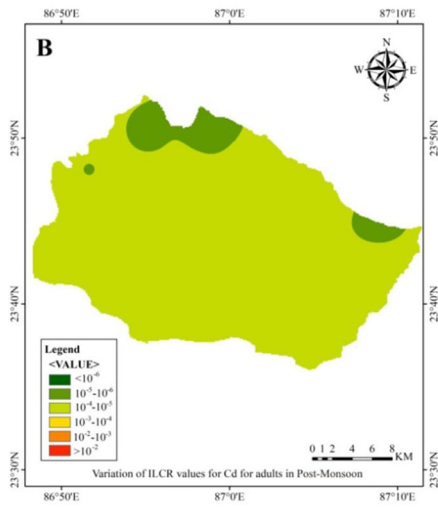
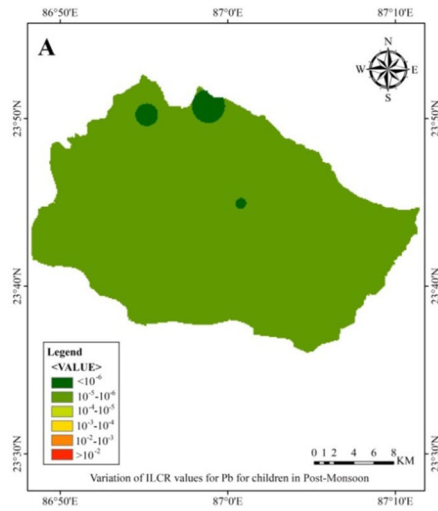
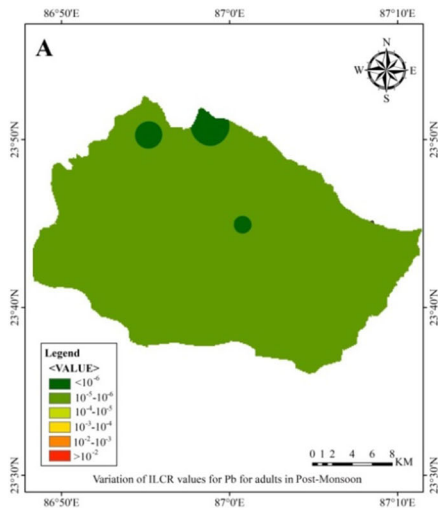
In the present study, carcinogenic risk has been calculated through ingestion pathway only as the availability of reference doses only for ingestion pathway (i.e., for Pb, Cd and Cr among the studied PTEs), and the ILCR values of PTEs in two distinct seasons for both adult and child are presented in Figs. 9 and 10, respectively. ILCR values for carcinogenic risk from PTEs indicate the presence of cancer risk for child and adults in the following order: Cr > Cd > Pb. The ILCR value > 1.0E-06 indicates chance of occurrence of cancer risk in near future while ILCR > 1.0E-04 indicates the presence of carcinogenic risk. The highest carcinogenic risk is observed at S7, S8 and S22 from Pb (child—1.3E-05; adult—1.2E-05), Cd (child—8.8E-05; adult—8.2E-05) and Cr (child—5.5E-03; adult—5.1E-03), respectively, in pre-monsoon season for child and adults both (Fig. 9). In post-monsoon, ILCR values (Fig. 10) display higher cancer risk for Cr, Cd and Pb (S10: child—5.1E-03, adult—4.8E-03; S9: child—7.5E-05, adult—7.0E-05; and S7: child—7.7E-06, adult—7.2E-06). Site 7 among all the sampling stations has emerged as critically unsafe for child and adult in both the seasons due to potential toxicity of Pb in the near future. For Cd, Site 22 (in pre-monsoon) and Site 9 (in post-monsoon) and for Cr Site 8 (in pre-monsoon) and Site 10 (in post-monsoon) are recognized as unsafe for both children and adults in forthcoming time. Cr is the only toxic element which poses a threat to cancer risk in present time.

Conclusion

The present study identifies the detailed scenario of contamination zoning, source evaluation and associated health risk assessment with PTEs in groundwater samples using geospatial and multivariate applications in the studied region. The measured values for Pb and Cu in groundwater are very much within the permissible limits, whereas Fe, Cd and Cr concentrations are found to be higher than the recommended drinking water quality standards in both the seasons. The measured values of Cd (81.25% sampling stations in

pre-monsoon and 75% sampling stations in post-monsoon) and Cr (100% sampling stations in both seasons) fail to comply the desirable limits for drinking water quality. The results of contamination index (C_d) show that the majority of the sampling sites fall under medium to high contamination level in pre- and post-monsoon seasons. Statistical analysis reveals that PTEs in groundwater majorly derived from anthropogenic sources like mining activities, industrial discharges and leachates from overburden materials and solid waste disposal sites and partially associated from geogenic sources such as weathering of bedrock, soil erosion and soil–water interaction. The health risk assessment reveals the maximum chance of occurrence of non-carcinogenic risk is from Cr followed by Cd and Pb for both child and adults. ILCR model indicated that in the present situation the carcinogenic risk in the study area is only due to the Cr for both child and adults; but there is also probable chance of occurrence of carcinogenic risk due to exposure to Cd and Pb in near future.

Therefore, it is essential to constant monitoring and evaluation of groundwater quality with respect to PTEs to distinguish the pollution level at different sampling locations to realize the current status of groundwater, taking into consideration the sharp increase in anthropogenic activities and urban development in the examined area. It is of prime importance to monitor the quality of groundwater as it is considered a primary source for drinking water. For better management of groundwater resources in the study area, it is strongly recommended that a detailed study should be conducted to allocate the groundwater use in various sectors. In-depth study on transport of contaminant and residence time of PTEs in groundwater can be important to identify the source/location of groundwater contamination and to establish suitable remediation scheme. Thus, the obtained results from this study may also useful as reference for policy and decision makers to impose proper groundwater management practices in the study area. Further research and investigation to develop low-cost in situ remediation methods and more reasonable action plan need to be taken by the government, scientific community and engineers to solve the groundwater contamination problems and to ensure supply of consumable water in the studied region. Moreover, regular monitoring and risk assessment of PTEs in groundwater are essential to develop suitable remedial



◀ **Fig. 10** Geospatial distribution of incremental lifetime cancer risk (ILCR) for adults and child during post-monsoon season

schemes and/or preventive measures before irremediable damages occur.

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Authors’ contributions GP had contributed to conceptualization, methodology, validation, data curation, formal analysis, visualization and writing the original draft preparation. KKP was involved in methodology, formal analysis, software, investigation and writing the original draft preparation. SG and MG took part in software, formal analysis, reviewing and editing. AKR conducted the application of GIS software, formal analysis, and data interpretation and representation. SN carried out supervision, visualization, investigation, validation, reviewing and editing.

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Declarations

Conflict of interest The authors declare that there are no conflict of interests.

Consent for publication The authors are hereby giving the consent the publication of manuscript as well as experimental data (represented in tabular, graphical and image forms). The authors also ensure that the manuscript or the experimental results/data have not been submitted elsewhere for the publication.

Availability of data and material The authors ensures about the transparency of data obtained through experimental results and will be able to provide the data on demand.

Human or Animal Rights This research study does not involve any experiment on animals or biological material.

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