



# Geostatistical appraisal of water quality, contamination, source distribution of potentially toxic elements (PTEs) in the lower stretches of Subarnarekha River (Odisha), India, and health risk assessment by Monte Carlo simulation approach

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Received: 16 August 2023 / Accepted: 26 October 2023 / Published online: 16 January 2024  
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**Abstract** In the present study, the status of water quality, environmental contamination in the lower stretch of Subarnarekha River with respect to potentially toxic elements (PTEs), its seasonal distribution, and ecotoxicological health impacts were investigated. For this purpose, a combination of indexing approaches and geospatial methods was used. The estimated water quality index (WQI) has shown that

the river water falls under “moderate to very poor” category during the pre-monsoon and “moderate to poor” category in the post-monsoon season. The abundance of PTEs (Pb, Cu, Ni, Cd, Fe, and Cr) was on the higher side during the pre-monsoon in comparison with the post-monsoon season. The results of contamination index ( $C_d$ ) and heavy metal evaluation index (HEI) explain that Subarnarekha River has low-to-moderate levels of contamination with PTEs in the majority of sampling sites. However, HPI indicated that the river water is moderate-to-highly contaminated with PTEs in both seasons. Principal component analysis (PCA) and cluster analysis (CA) reveal that anthropogenic sources are prime contributors to PTEs contamination in Subarnarekha River. The potential non-cancerous health concerns for child and adults due to Cr and Pb in some sampling stations along the river stretch have been observed. The carcinogenic risk (CR) has been established for Cr, Pb, and Cd in Subarnarekha River with Cr ( $> 10^{-4}$ ) as the most unsafe element. Monte Carlo simulation (MCS) indicates a high risk of cancer hazards due to Cr (values  $> 1E-04$ ) in present as well as future for both child and adults.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10653-023-01815-1>.

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**Keywords** River water quality · Heavy metal pollution index (HPI) · Geostatistical analysis · Carcinogenic risk (CR) · Monte Carlo simulation (MCS) · Health risk assessment

## Introduction

Rivers are undoubtedly the potential surface water source for human survival and serve as a socio-economic indicator for the advancement of a country. Additionally, river water essentially serves as a resource for maintaining environmental integrity and is entitled to preserve the fundamental requirements for public health safety and aquatic life that have been recognized by numerous earlier studies globally (Bhuiyan et al., 2015; Islam et al., 2020). Last few decades, several works have been done on evaluation the riverine water quality for the use on drinking, agricultural, industrial, recreational purposes and allow accelerating the monitoring programme for conservation and protection of surface water quality (Şener et al., 2017). The degradation of river water quality has been triggered by numerous anthropogenic activities, including the discharge of domestic wastewater, industrial operations, agriculture runoff, mining operations, vehicular pollution, the dumping of solid waste, etc. (Han et al., 2016; Jabbo et al., 2022; Zhai et al., 2022), as well as numerous natural processes like soil and bedrock erosion, precipitation, volcanic emission, soil–water interaction, and seasonal effects (Kazi et al., 2009; Subramani et al., 2005). Rapid urbanization, industrialization, and several human activities have been identified as the main sources of river water pollution (Kumar et al., 2019a; b). According to the UNEP (2021) report, 3 billion people worldwide are at a high risk of contracting a water-borne illness (Chorol and Gupta, 2023). As a result, assessing and monitoring river water quality based on its hydrogeochemical characteristics is crucial to determining whether it should be used for home, agricultural, or industrial purposes. It also enables planners and decision-makers to take corrective action and restore the river's ecosystem.

Several approaches have been periodically used to assess the water physicochemical properties, including potentially toxic elements (PTEs) and the status of water quality. The water quality index (WQI) is a widely used method for assessing water quality that aggregates a number of measured water parameters into a single numerical value (Singh et al., 2018). However, solely relying on WQI may not be sufficient to understand the pollution characteristics, especially the risk to human health due to heavy metals and PTEs (Şimşek and Mutlu, 2023). PTEs

concentration in riverine ecosystem is now one of the most serious threats due to their higher accumulation, recalcitrance, biomagnification, and toxicity (Ali and Khan, 2019; Sahoo and Sahu, 2022). Among them, a few trace elements (like as Fe, Cu, Co, and Mn) are essential in smaller quantities for several physiological and metabolic activities in living organisms, while larger concentrations of these elements can cause serious health issues (Setia et al., 2020). Excessive use of river water for agricultural purposes is the most prominent route of transfer/bioaccumulation of PTEs in vegetables/crops. Subsequent transportation of such PTEs to human through food chain accelerates their accumulation in different parts of human/organism causing severe health hazards (Panda et al., 2021). As a result, many researchers also evaluate the qualitatively and quantitatively of PTE content in river water and their assimilative impacts on human health (Bhuiyan et al., 2015; Islam et al., 2020; Shan et al., 2021). Several indexing approaches such as degree of contamination ( $C_d$ ), heavy metal evaluation index (HEI), and heavy metal pollution index (HPI) on PTEs concentration of surface waters explore the level of toxicity and indicate the quality of water (Sahoo and Sahu, 2022). Various tools such as multivariate analysis, viz., Pearson's correlation analysis, principal component analysis (PCA), hierarchical cluster analysis (HCA), and geospatial interpolation might provide comprehensive information to discriminate the potential sources of PTEs in river water from surrounding point and non-point sources.

Chronic exposure to PTEs through ingestion and dermal absorption can cause cancerous and non-cancerous health effects in humans. Among other PTEs, Cr, Pb, and Cd are known as possible carcinogens and could potentially represent a concern because of their toxic, genotoxic, and cancer-causing actions (Jiang et al., 2021; Sadeghi et al., 2022). According to reports, drinking unsuitable water contributes to roughly 20% of all cancer cases worldwide (Chorol and Gupta, 2023; Balali-Mood et al., 2021). Therefore, estimating the potential health risks associated with total PTE concentrations in river water is becoming increasingly relevant (Ozoko et al., 2022).

Subarnarekha is a rain-fed river in eastern India that provides water to millions of people in Jharkhand, West Bengal, and Odisha. It originates at Nagri village in Ranchi district, Jharkhand, and flows past important industrial centres like Jamshedpur,

Chaibasa, and Bhadrak before joining the Bay of Bengal at Kirtania port in Odisha. The river's total length from its sources to its outlet in the Bay of Bengal is 446.12 kms, of which 79 kms are in Odisha. It is the smallest of India's 14 major river basins. The rain-fed river covers a drainage area of 18,951 km<sup>2</sup>, lies between 21° 33 'N to 23 °32 'N and 85 °09 'E to 87 °27 'E, and comprises 0.4% of total surface water resources in the country (Giri and Singh, 2015). This river is the lifeline for many tribal communities, residing on the riverbanks, following agricultural practises, and fishing for their livelihood. Contamination of the river water with respect to PTEs can be a major environmental concern, as their entry to human body can pose a serious health hazard.

Thus, the primary goals of current investigation were to assess the following:

- Evaluation of water quality and distribution of PTEs in Subarnarekha River on a spatio-temporal scale.
- To classify the contamination level and identify the sources and factors that influence the PTEs in Subarnarekha River water.
- Carcinogenic and non-carcinogenic risk evaluation of PTEs through diverse exposure paths using health risk assessment tool.
- Monte Carlo simulation approach to validate and reduce uncertainty in health risk analysis

## Materials and methods

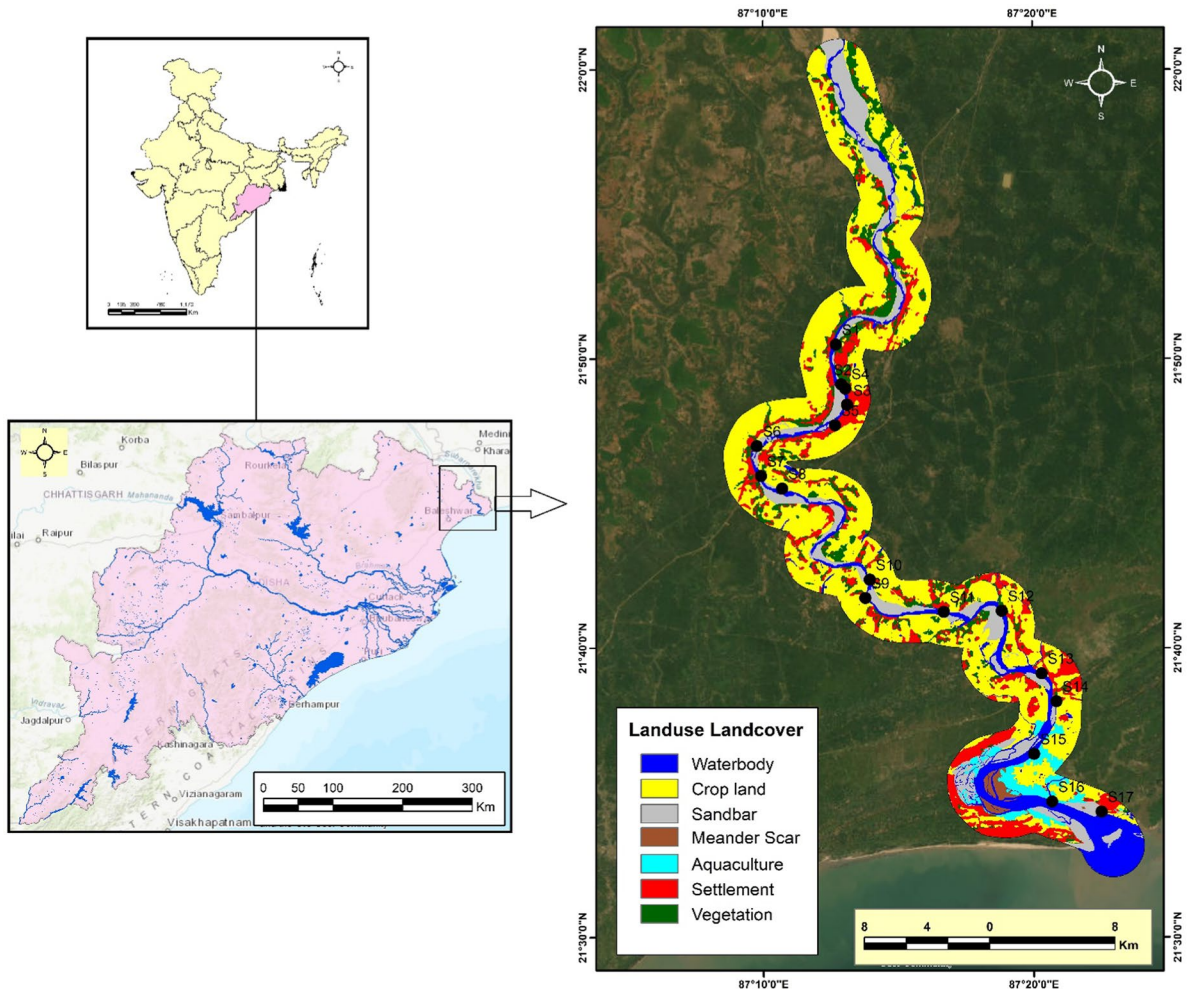
### Sampling, analysis and quality assurance

For this research study, field samples were collected at different sampling stations along the lower stretches of the Subarnarekha River in the State of Odisha, covering about 79 km, starting from Balasore district to its termination to Bay of Bengal. To evaluate the river water quality, 17 sampling sites were strategically selected considering the accessibility of the river in view of land use patterns and landform variability, such as village areas, agricultural areas, fish depots, jetty and port areas (Fig. 1). The river water samples were collected during the period of 2021–2022, covering two distinct seasons, i.e. pre-monsoon and post-monsoon, respectively. The representative samples were collected

in sterilized and washed 1 L PVC bottles up to its mouth to prevent entrapment of any air in the sample bottles. The representative water samples were collected at least 0.5 m below the surface level of the water to avoid atmospheric influences. Thereafter, the samples were kept in an ice box under 4 °C and shifted to the laboratory for further physico-chemical analysis.

In this study, a total of 14 physicochemical parameters were analysed, and all analyses were performed in triplicate. Among the parameters, pH, temperature, electrical conductivity (EC), total dissolved solids (TDS), and dissolved oxygen (DO) were immediately analysed in situ by using portable hand analyser (Systronics 371). All the sample bottles were kept in an ice box under 4 °C and shifted to the laboratory immediately. Remaining physicochemical parameters such as total hardness (TH), total suspended solids (TSS), total alkalinity (TA), biological oxygen demand (BOD), chemical oxygen demand (COD), sodium (Na<sup>+</sup>), calcium (Ca<sup>2+</sup>), potassium (K<sup>+</sup>), chloride (Cl<sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and phosphate (PO<sub>4</sub><sup>3-</sup>) were analysed as per APHA (2012) guidelines. Atomic absorption spectroscopy (AAS) was used to measure six metals: iron (Fe), manganese (Mn), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn). Throughout the analysis, the analytical protocols of the APHA (2012) Standard Methods for the Examinations of Water and Wastewaters were followed.

The geological composition of the studied basin area primarily consists of recent alluvium deposits. The upper part of the river basin possesses substantial mineral reserves, which has prompted the development of mineral-based industries along the river stretch (Giri and Singh, 2015). Climatically, the region experiences a maximum temperature of approximately 31.5 °C, while the minimum temperature recorded is around 20.5 °C. The overall annual rainfall in this area amounts to 1383.3 mm. To achieve the land use and landcover classification at the 2 km buffer zone on both sides of the river, a supervised classification approach using the maximum likelihood method (ArcMap 10.8) with a Kappa coefficient of 86% was employed. This process helped to categorize and identify different land use and landcover classes within the designated study area.



**Fig. 1** Study area with sampling sites of Subarnarekha River

### Quality assurance

Special attention has been made to avoid contamination and to increase the data's confidence in terms of bias and variability. All glassware and apparatus were sterilized with 10% HCl and rinsed with Millipore ultra-pure water multiple times. Millipore ultra-pure water is used to prepare reagents and stock solutions. Merck-GR grade chemicals were used to prepare the reagent solutions. To achieve reliable outcomes, all instruments were carefully calibrated, and bank samples for every single metal parameter were prepared from their stock solutions. The reference materials (RM 1643E) supplied from the National Institute of Standards and Technology were meticulously

followed. For each examined metal, the margin of error was < 5%.

### Indexing approach

#### *Water quality index (WQI)*

The WQI reflects the combined influences of different physicochemical parameters and assesses the geogenic and anthropogenic influences on several key parameters that eventually effects on drinking water quality (Gupta et al., 2016; Kumar et al., 2019a, b). Hence, to calculate the WQI in this study, 11 physicochemical water parameter such as pH, EC, TDS, TA, TH, DO,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  have been

considered for both pre- and post-monsoon season, and their prescribed limits recommended by WHO (2006) and BIS (2012) are mentioned in Table 1. The definite weightage ( $W_a$ ) for each parameter is assigned between 1 and 5 according to its relative influence on the overall water quality (Table 1). In step 1, the relative weight ( $W_r$ ) is calculated from the following equation.

$$W_r = W_{ai} / \sum_{i=1}^n W_{ai}$$

where  $W_r$  and  $W_a$  represent the relative weightage and the assigned weightage of each physicochemical parameter where  $n$  denotes the number of parameters.

In step 2, a quality rating scale ( $Q_i$ ) for each parameter is formulated as:

$$Q_i = \left[ (C_i - V_i) / (S_i - V_i) \right] \times 100$$

where  $Q_i$  is the quality rating;  $C_i$  the concentration of each chemical parameter;  $V_i$  is the ideal value of each parameter which is taken 0 for all except pH (7) and DO (14.6);  $S_i$  is the standard permissible limit prescribed by WHO (2006) and BIS (2012) for each parameter.

Finally in step 3, computing the WQI, the sub-indices (SI) are the firstly determined for each chemical parameter, which is then now used to determine the overall WQI as per the following equation:

$$SI_i = W_r * Q_i$$

$$WQI = \sum SI_i$$

The computed WQI was categorized owing the suggested categorization of water quality (Singh et al., 2018) as: excellent (WQI < 25), good (WQI: 25–50), moderate (WQI: 51–75), poor (WQI: 76–100), and very poor (WQI > 100).

### Evaluation of PTEs contamination in river water using pollution indices

#### Contamination index ( $C_d$ )

The degree of contamination ( $C_d$ ) is extensively used to evaluate the drinking water quality and to detect the composite influences of various quality parameters (Panda et al., 2021; Singh et al., 2017). In this study, the composite effects of PTEs are summarized with a single numerical value, suggesting the water quality for the drinking water purposes. The  $C_d$  is firstly established by Backman et al. (1997) and is formulated by the below equations:

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

**Table 1** Relative weight of physicochemical parameters of Subarnarekha River

Parameters	WHO stand-ards (2006)	BIS standards (2012)		Weight ( $w_i$ )	Relative weight ( $W_r$ )
		Desirable	Permissible		
pH	6.5–8.5	6.5–8.5	NX	4	0.100
EC ( $\mu\text{S}/\text{cm}$ at 25 °C)	2000	250	NX	5	0.125
TDS ( $\text{mg L}^{-1}$ )	1000	500	2000	4	0.100
TA ( $\text{mg L}^{-1}$ )	200	200	600	2	0.050
TH ( $\text{mg L}^{-1}$ )	–	200	600	2	0.050
DO ( $\text{mg L}^{-1}$ )	5	$\geq 5$	NX	5	0.125
$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	250	250	1000	3	0.075
$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	200	200	400	4	0.100
$\text{NO}_3^-$ ( $\text{mg L}^{-1}$ )	50	45	NX	5	0.125
$\text{PO}_4^{3-}$ ( $\text{mg L}^{-1}$ )	0.3	–	–	2	0.050
Fe ( $\mu\text{g L}^{-1}$ )	300	300	NX	4	0.100
				40	1.000



where

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \quad (2)$$

where  $C_{fi}$ ,  $C_{Ni}$ , and  $C_{Ai}$  define the contamination factor, the upper permissible value and the analytical value of  $i$ th component, respectively.  $N$  and  $C_{Ni}$  signify the “normative value” and standard permissible concentration (SPC), respectively.

### Heavy metal evaluation index (HEI)

The heavy metal evaluation index (HEI) also delivers an overall quality status for the drinking purposes with respect to PTEs concentration like HPI (Edet & Offiong, 2002; Singh et al., 2017), and the HEI is formulated by the following equation:

$$HEI = \sum_{i=1}^n M_i/S_i \quad (3)$$

where  $M_i$  defines the examined value of PTEs and  $S_i$  represent the maximum permissible concentration of the  $i$ th component as per standards guideline of BIS (2012).

### Heavy metal pollution index (HPI)

The heavy metal pollution index (HPI) is a well-known tool to estimate overall quality of with respect to PTEs concentration (Panda et al., 2021, Ahamad et al., 2020, Kumar et al., 2019a, b). The HPI was initially established by Mohan et al. (1996) and suggested weighted arithmetic mean methods via two step indexing approaches to estimate it. In first step, establish a rating scale with assigned weightage for the studied PTEs (i.e. Pb, Cu, Ni, Cd, Fe, and Cr). Then, the pollution parameters are chosen to calculate pollution index of the study area. The estimated HPI value represented the composite effect of each PTE concentration on the overall quality where the assigned weight on studied PTEs lies in between 0 and 1. The HPI is computed by using the following equations:

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

where  $W_i$  and  $n$  represent the unit weightage and the number of selected PTEs.  $Q_i$  denotes the sub-index of the  $i$ th component and is formulated by

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

where  $M_i$ ,  $S_i$ , and  $I_i$  denote the monitored value of PTE, the standard value, and the ideal value of the  $i$ th component, respectively. The sign  $(-)$  defines the numerical divergence among two values, disregarding the algebraic sign. The critical pollution index value of HPI is set at 100 for drinking water.

### Statistical analysis

Principal component analysis (PCA) and hierarchical cluster analysis (HCA) were accomplished in SPSS (SPSS V.20.0) software to recognize the likely primary sources of PTEs and physicochemical factors in the Subarnarekha River water samples. In PCA, the “varimax with Kaiser normalization” rotation method and the “principal component” extraction method were applied based on eigenvalues larger than 1. Ward’s approach was used to compute the HCA using squared Euclidian distance.

### GIS interpolation

Spatial interpolation of HPI and WQI indices were made by using IDW (inverse distance weighting) interpolation technique in ArcMap 10.8 platform. This method facilitated the creation of spatially continuous maps representing the HPI and WQI values across the study area, based on the sampled data.

### Human health risk assessment

#### Non-carcinogenic risk

According to the USEPA (1989), the health risk assessment (HRA) is a classic tool for assessing the possible effects of harmful chemicals over a given time period. According to Gope et al., (2017, 2020), Yadav et al. (2019) and Rahman et al. (2020), the HRA index has been used to estimate probabilistic hazard in various environmental medium for different inorganic and organic pollutants. The hazard quotient (HQ) was calculated using the non-carcinogenic risk to human health when water is ingested ( $HQ_{ing}$ ) and in contact with the skin ( $HQ_{derm}$ ). When HQ is less than 1, there are no harmful consequences; however, if HQ is

equal to or more than 1, non-cancerous risk or harmful impacts on human health are a matter of concern (Wang et al., 2017). The hazard index (HI) value is calculated by adding the HQs from each exposure routes for individual PTE. According to Panda et al. (2021),  $HI > 1$  generally denotes a high hazard effect, while  $HI < 1$  symbolizes a low risk. Here, hazard index is calculated for Cd, Cu, Cr, Fe, Pb, and Zn to determine the non-carcinogenic health risk. According to USEPA (2004), the following equations were used to determine chronic/chemical daily intake from ingestion ( $CDI_{ing}$ ) and chronic/chemical daily intake from dermal contact ( $CDI_{derm}$ ):

$$CDI_{ing} = \frac{C_m \times IR \times EF \times ED}{BW \times AT} \tag{6}$$

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

where  $C_m$  ( $\mu\text{g/L}$ ) is the concentration of each PTE, IR represents ingestion rate, EF is exposure frequency, ED denotes exposure duration, BW is body weight (BW), AT stands for average time, SA denotes the skin area, ET represents the exposure time, and  $K_p$  is the dermal permeability coefficient of the PTEs in water. The values of all the parameters are mentioned in Supplementary Table 1a and b. The unit conversion factor (CF) has value  $1 \times 10^{-3}$  for water (Panda et al., 2021).

By dividing the chronic daily intake (CDI) values of various PTEs by the corresponding chronic reference doses ( $R_fD$ ) ( $\mu\text{g/L/kg/day}$ ), the hazard quotient (HQ) for non-carcinogenic risk of each PTE was calculated. HI was calculated by summing  $HQ_{ing}$  and  $HQ_{derm}$  of each PTE (Wang et al., 2017).

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

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

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

### Carcinogenic risk (CR)

The incremental lifetime cancer risk (ILCR) model (USEPA, 2004) is used to assess the carcinogenic risk in the present investigation. The ILCR is calculated by multiplying the cancer slope factor (CSF) with chronic daily intake (CDI), as shown in Eq. (11).

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

In this present study, the carcinogenic toxicity of Pb, Cd, and Cr has been assessed as these substances are thought to be potential carcinogens. The CSF values of Cd, Pb, and Cr ( $\mu\text{g/kg/day}$ ) for ingestion pathway is mentioned in Supplementary Table 1b. If a single carcinogenic PTE has a CR value  $> 1 \times 10^{-4}$ , which is considered as intolerable, whereas a CR value  $< 1 \times 10^{-6}$  indicates no significant health effects (Panda et al., 2021).

### Uncertainty analysis by Monte Carlo simulation (MCS)

To reduce the ambiguity and investigate the possible risks of pollutants in food, air, water, and other environmental components, Monte Carlo simulation (MCS) was performed (Chorol and Gupta, 2023). The probabilistic approach is based on MCS, whereas the deterministic approach is based on point estimations (Kilavi et al., 2021). A statistical tool called MCS measures the inconsistency and uncertainty resulting from the input parameters in human health risk assessment. The oracle crystal ball (version 11.1.2.3.000) software was used in the present study to calculate the uncertainty in the carcinogenic risk analysis data using 1,00,000 iterations with the help of Excel programme. Plotting histograms of the probability distribution of carcinogenic risks and analysing their 95th percentile values helped to diminish the uncertainty in carcinogenic risk estimation. All the parameters used in MCS is illustrated in Supplementary Table 2.

## Results and discussions

### Characterization and spatio-temporal variations in measured river water parameters

The descriptive statistical summary of physicochemical parameters and PTEs concentration from 17 locations of lower stretches of Subarnarekha River for pre- and post-monsoon seasons is presented in Table 2. Again, the water quality parameter is compared with Indian standards for drinking water quality. The pH is a lead parameter which may influence for precipitation, co-precipitation, mobilization, and sorption of other significant cationic and anionic of water quality parameters in riverine ecosystem. In our study, the pH is ranging 6.25–7.25 and 7.30–7.9 during pre- and post-monsoon, respectively, suggesting the river water in slightly acidic to normal in range. The EC value of river water ranges from 480 to 804  $\mu\text{S}/\text{cm}$  in pre-monsoon and 392–514  $\mu\text{S}/\text{cm}$

(mean 452.65  $\mu\text{S}/\text{cm}$ ) in post-monsoon that depicts the clear seasonal variation of ionic load derived by anthropogenic inputs and industrial influx (Gupta et al., 2016). Commonly, the TDS value indicates the sum of cationic and anionic contents in water. TDS ranges 226–367 mg/L and 356–428 mg/L during pre- and post-monsoon seasons, respectively. Comparatively, the higher TSS and TDS value in post-monsoon suggests the higher influx agricultural runoff, untreated sewerage, and industrial effluents dumping (Suthar et al., 2010). The DO content varies among 3.7–4.4 mg/L in pre-monsoon and 4.7–5.3 mg/L in post-monsoon reflecting the higher dissolution of oxygen in river water during post-monsoon season because lower temperature favours the said phenomenon (Kumar et al., 2013). The concentration of  $\text{SO}_4^{2-}$  of river water samples is varied significantly from 126.45 to 176.6 mg/L in the pre-monsoon season and varied from 103.8 to 157 mg/L in the post-monsoon season, respectively. Generally,

**Table 2** Statistical description of physicochemical parameters and PTE concentrations of Subarnarekha River during pre- and post-monsoon and comparative standard guidelines for drinking water

Parameters	Pre-monsoon				Post-monsoon				BIS standards (2012)	
	Min	Max	Mean	SD	Min	Max	Mean	SD	Desirable limit	Permissible limit
<i>Physicochemical parameters and major ions (mg L<sup>-1</sup>)</i>										
pH	6.25	7.25	6.74	0.29	7.30	7.90	7.62	0.19	6.5–8.5	No relaxation
Temperature (°C)	28.80	30.80	30.13	0.61	26.70	27.90	27.30	0.36	–	–
EC ( $\mu\text{S Cm}^{-1}$ )	480.00	804.00	628.82	89.65	392.00	514.00	452.65	33.92	2000	No relaxation
TSS	108.00	149.00	129.88	11.73	181.00	258.00	214.53	23.14	–	–
TDS	226.00	367.00	280.24	41.23	356.00	428.00	392.76	21.28	500	2000
TA	36.60	66.70	53.84	9.29	27.30	52.70	38.41	7.70	200	600
TH	85.50	225.40	119.06	41.24	68.79	127.50	92.66	18.46	200	600
DO	3.70	4.30	4.07	0.20	4.70	5.30	5.06	0.19	$\geq 5$	No relaxation
BOD	2.32	5.25	3.58	0.99	1.40	2.70	1.97	0.41	–	–
COD	82.50	147.60	107.37	23.37	67.00	138.00	96.35	23.06	–	–
Cl <sup>-</sup>	34.80	56.50	45.08	5.51	26.70	39.20	32.51	3.71	250	1000
SO <sub>4</sub> <sup>2-</sup>	126.45	176.60	151.04	15.84	103.80	157.00	130.49	16.26	200	400
NO <sub>3</sub> <sup>-</sup>	1.75	4.64	3.01	0.87	0.59	1.04	0.80	0.13	45	No relaxation
PO <sub>4</sub> <sup>3-</sup>	1.15	3.12	2.04	0.57	0.84	1.90	1.39	0.39	–	–
<i>PTEs (<math>\mu\text{g L}^{-1}</math>)</i>										
Pb	16.00	39.00	27.82	6.18	11	39	19.71	7.52	10	No relaxation
Cu	22.00	41.00	30.59	6.07	10	54	22.94	13.32	50	1500
Ni	18.00	71.00	41.53	14.83	11	31	18.82	4.53	20	No relaxation
Cd	0.00	3.00	0.82	0.95	ND	3	0.41	0.87	3	No relaxation
Fe	392.00	965.00	590.71	182.18	224	562	331.76	89.63	300	No relaxation
Cr	42.00	92.00	67.71	15.68	26	65	37.47	11.39	50	No relaxation



the  $\text{SO}_4^{2-}$  contents in river water indicates the level of pollution and define the anthropogenic contribution. The highest  $\text{SO}_4^{2-}$  contents noted at S13 (176.6 mg/L during pre-monsoon) and S15 (157 mg/L during post-monsoon) reveal that these locations are polluted because of industrial discharges in the river stream. Although, 100% sampling locations have the  $\text{Cl}^-$  concentration below the recommended guideline for drinking water (BIS, 2012).

#### Distribution and seasonal variations of PTEs concentration in Subarnarekha River water

The descriptive statistics of measured PTE concentrations in river water samples for pre- and post-monsoon season is presented in Table 2. The mean value of Pb, Cu, Ni, Cd, Fe, and Cr during pre-monsoon season is 27.82, 30.59, 41.53, 0.82, 590.71, and 67.71  $\mu\text{g/L}$ , respectively, while those in post-monsoon is 19.71, 22.94, 18.82, 0.41, 331.76, and 37.47  $\mu\text{g/L}$ , respectively. Analytical results clearly show that the concentration Pb in river water ranges 16–39  $\mu\text{g/L}$  and 11–39  $\mu\text{g/L}$  in pre- and post-monsoon season, respectively, and 100% sampling locations are exceeded the desirable standards of drinking water quality. The variation of Cu concentration is 22–41  $\mu\text{g/L}$  and 10–54  $\mu\text{g/L}$  during pre- and post-monsoon seasons, respectively, which is well under the desirable water quality standards (except S16 in post-monsoon).

#### Evaluation of water quality of Subarnarekha River using WQI

The WQI values were computed using eleven physicochemical parameters of the river Subarnarekha for pre- and post-monsoon seasons. The calculated WQI values of river water is between 68.43 and 117.30 during pre-monsoon with a mean value of 87.41 which suggests the water quality are lies among “moderate” to “very poor” category. During post-monsoon, the WQI value ranges within 54.43 to 83.04 with an average value of 68.14 that reflects the quality of river water falls in “moderate” to “poor” category. In addition, the WQI value  $> 100$ , i.e. “very poor” category was observed at S3(104.29), S16(115.10), and S17(117.30) which may be due to higher discharges of industrial effluents and municipal waste dumping.

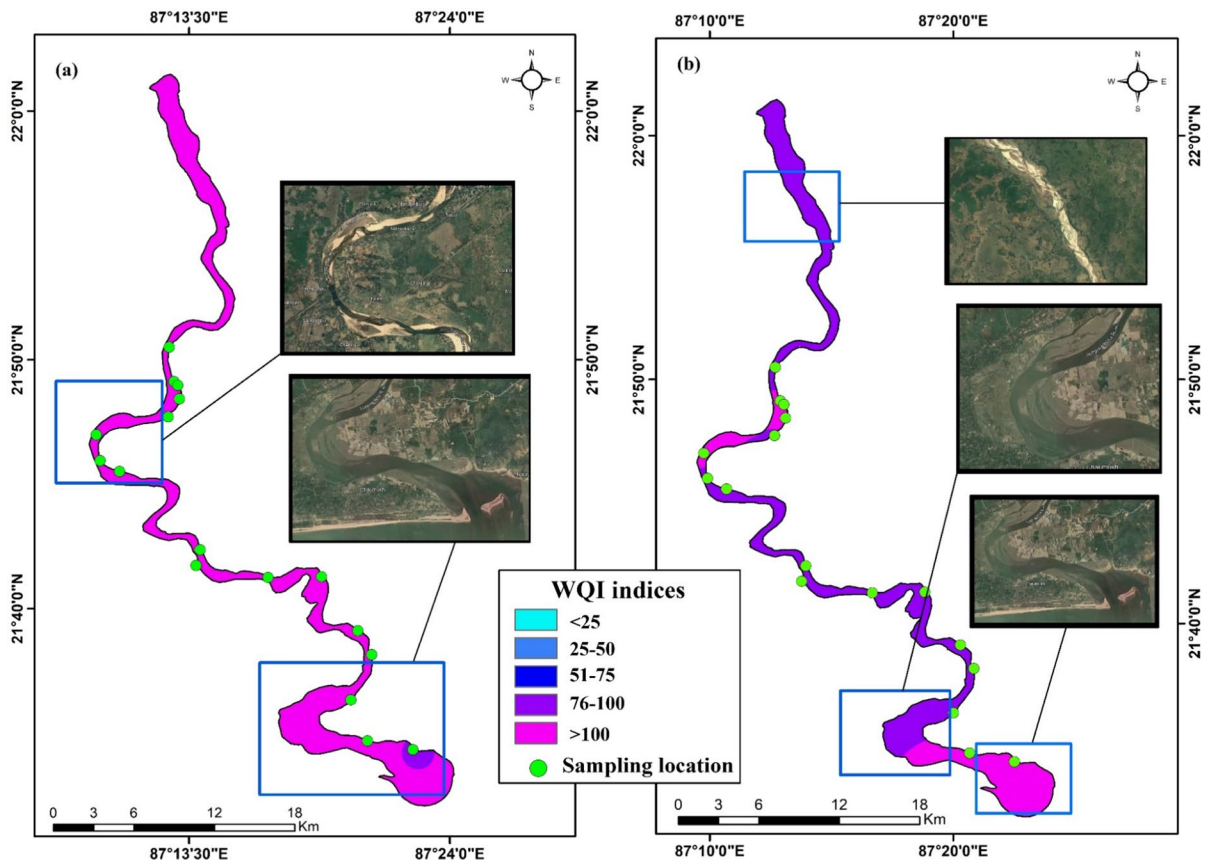
Nonetheless, the majority of the river water samples based on WQI value also revealed that 64.70% of sampling location are under “poor” water category during pre-monsoon, while in post-monsoon, 76.47% of sampling locations lie under “moderate” water category (Fig. 2). The result suggests the river water is not suitable for domestic uses without proper treatment. The deterioration of water quality can be attributed to significant industrialization in river banks along with various anthropogenic activities such as the inflow of direct sewerage discharges from residential and commercial establishments, surface runoff from agricultural cropland, and solid waste dumping. Therefore, kind attention from government authorities is sought to take proper management for restoration of river water quality.

#### Quantification of PTEs contamination

In this study, the level of metal pollution in Subarnarekha River is evaluated by using three pollution indices such as degree of contamination ( $C_d$ ), heavy metal pollution index (HPI), and heavy metal evaluation index (HEI) with the reference guideline obtained from Indian standards for drinking water (BIS, 2012). The outcomes of calculated aforementioned pollution indices and their modified classification are described in Table 3.

#### Degree of contamination index ( $C_d$ )

The estimated values of degree of contamination reflect the combined effects of metal pollution in riverine system, while contamination factor ( $C_f$ ) highlights the influence of individual metals on total contamination. The calculated  $C_f$  values of PTEs in sampled water are represented in Table 4. The  $C_f$  values of PTEs in river water are Pb (0.6–2.9), Cu (–0.99 to –0.97), Ni (–0.1 to 2.55), Cd (–1 to nil), Fe (0.31–2.22) Cr (–0.16 to 0.84) and Pb (0.1–2.9), Cu (–0.99 to –0.96), Ni (–0.45 to 0.55), Cd (–1 to nil), Fe (–0.25 to 0.87), and Cr (–0.48 to 0.3) in pre- and post-monsoon seasons, respectively. According to mean  $C_f$  values, PTEs in the river water are in the sequence of  $\text{Pb}(1.78) > \text{Ni}(1.08) > \text{Fe}(0.97) > \text{Cr}(0.35) > \text{Cd}(-0.73) > \text{Cu}(-0.98)$  in the pre-monsoon and  $\text{Pb}(0.97) > \text{Fe}(0.11) > \text{Ni}(-0.06) > \text{Cr}(-0.25) > \text{Cd}(-0.86) > \text{Cu}(-0.98)$  during the post-monsoon season, respectively.



**Fig. 2** WQI of Subarnarekha River during **a** pre-monsoon and **b** post-monsoon seasons

During the pre-monsoon season, the calculated  $C_d$  values in river water ranged from 1.52 to 7.96. Approximately, 23.5% of the sampling sites are moderately contaminated, and the remaining 76.5% have low contamination level. Whereas in the post-monsoon season,  $C_d$  values ranged from 0.1 to 4.16, and all examined sites (100%) were identified as having low contamination in terms of PTEs (Table 3).

During pre-monsoon studies, the variation of HEI values is 5.27–12.98 with a mean of 8.48 (i.e. moderately contaminated), while in post-monsoon studies, HEI values range from 3.54 to 9.19 with a mean value of 4.92 (i.e. <8, low contamination). The investigation reveals that 52.94% of sampling sites are moderately contaminated, and 47.06% of sampling sites have a low contamination level in pre-monsoon with respect to PTEs (Table 3). However, estimated HEI values in post-monsoon studies demonstrate that the majority of sampling sites (94.12%)

have low contamination levels with respect to PTEs, with the exception of sampling site S16 (moderately contaminated).

According to the HPI assessment (Fig. 3, Table 5), the range of this index is 58.34–185 (mean value 105.04) during the pre-monsoon and 36.07–167.89 (mean value 64.15) in the post-monsoon season, respectively. However, 64.71% and 35.29% of sampling locations were moderately and highly contaminated with PTEs during the pre-monsoon. The high HPI value in river water is mainly associated with discharges of wastewater and dumping of solid waste, agricultural, and other anthropogenic activities in river basin areas. Contradictorily, the majority of sampling sites (58.82%) are low contaminated with PTEs in post-monsoon season, which reveal good similarities with HEI and  $C_d$  values, whereas 29.41% sampling locations are moderately contaminated and only 11.77% of sampling locations are highly

**Table 3** Heavy metal pollution index (HPI), heavy metal evaluation index (HEI), and degree of contamination ( $C_d$ ) of Subarnarekha River in pre- and post-monsoon

Pollution indices	Post-monsoon									
	Pre-monsoon					Post-monsoon				
	Classification	Degree of pollution	No. of samples	% of Samples	Sampling sites	Classification	Degree of pollution	No. of samples	% of samples	Sampling sites
HPI	< 55	Low	Nil	Nil	Nil	< 55	Low	10	58.82	S13, S14, S1, S2, S12, S8, S3, S7, S11, S9
	55–110	Medium	11	64.71	S1, S13, S3, S2, S12, S8, S6, S14, S5, S7, S4	55–110	Medium	5	29.41	S10, S5, S4, S15, S6
	> 110	High	6	35.29	S11, S9, S10, S15, S17, S16	> 110	High	2	11.77	S17, S16
HEI	< 8	Low	8	47.06	S1, S13, S12, S14, S5, S4, S11, S6	< 8	Low	16	94.12	S13, S1, S14, S12, S11, S8, S7, S9, S2, S3, S4, S10, S15, S5, S6, S7
	8–15	Medium	9	52.94	S3, S2, S9, S8, S15, S10, S7, S17, S16	8–15	Medium	1	5.88	S16
	> 15	High	Nil	Nil	Nil	> 15	High	Nil	Nil	Nil
$C_d$	< 5	Low	13	76.5	S1, S14, S13, S5, S12, S4, S11, S6, S3, S15, S2, S9, S8	< 5	Low	17	100	S13, S14, S1, S12, S2, S8, S11, S15, S7, S4, S3, S9, S10, S5, S6, S17, S16
	5–10	Medium	4	23.5	S10, S7, S17, S16	5–10	Medium	Nil	Nil	Nil
	> 10	High	Nil	Nil	Nil	> 10	High	Nil	Nil	Nil

**Table 4** Site-wise contamination factor ( $C_f$ ) values of potentially toxic elements in Subarnarekha River

Sampling location	$C_f$											
	Pb		Cu		Ni		Cd		Fe		Cr	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
S1	1.10	0.40	-0.99	-0.99	-0.10	-0.45	-1.00	-1.00	0.42	0.09	-0.16	-0.48
S2	1.40	0.20	-0.98	-0.97	0.60	0.05	-1.00	-1.00	1.48	0.38	0.84	-0.10
S3	1.50	0.50	-0.98	-0.98	0.30	-0.10	-1.00	-1.00	1.52	0.46	0.76	-0.22
S4	2.20	0.90	-0.98	-0.99	0.40	-0.20	-0.67	-0.67	0.52	0.05	0.28	-0.32
S5	1.80	1.40	-0.99	-0.99	0.60	0.00	-0.67	-1.00	0.32	-0.06	0.08	-0.38
S6	2.20	1.80	-0.98	-0.99	0.70	0.10	-1.00	-1.00	0.37	-0.25	0.64	0.30
S7	2.40	0.90	-0.98	-0.98	1.20	-0.35	-1.00	-1.00	1.42	0.02	0.56	-0.26
S8	1.60	0.60	-0.97	-0.99	1.40	-0.25	-1.00	-1.00	1.56	0.22	0.30	-0.32
S9	1.80	1.00	-0.98	-0.99	1.45	-0.10	-0.67	-1.00	1.02	0.06	0.08	-0.46
S10	2.10	1.20	-0.98	-0.99	2.55	0.10	-0.67	-1.00	0.58	-0.08	-0.04	-0.42
S11	1.90	0.80	-0.99	-0.99	1.10	0.05	-0.67	-1.00	0.31	-0.20	0.16	-0.48
S12	1.50	0.50	-0.98	-0.99	0.75	-0.15	-1.00	-1.00	0.47	-0.09	0.16	-0.42
S13	0.80	0.10	-0.98	-0.99	0.70	-0.10	-1.00	-1.00	0.83	-0.11	0.26	-0.36
S14	0.60	0.20	-0.98	-0.99	0.85	-0.20	-0.33	-1.00	0.55	-0.09	0.30	-0.32
S15	1.80	0.90	-0.98	-0.99	1.20	-0.10	-0.33	-0.67	0.98	-0.03	0.24	-0.22
S16	2.70	2.90	-0.97	-0.96	2.20	0.55	0.00	0.00	2.22	0.55	0.84	0.16
S17	2.90	2.20	-0.97	-0.97	2.40	0.15	-0.33	-0.33	1.92	0.87	0.72	0.04
Min	0.60	0.10	-0.99	-0.99	-0.10	-0.45	-1.00	-1.00	0.31	-0.25	-0.16	-0.48
Max	2.90	2.90	-0.97	-0.96	2.55	0.55	0.00	0.00	2.22	0.87	0.84	0.30
Mean	1.78	0.97	-0.98	-0.98	1.08	-0.06	-0.73	-0.86	0.97	0.11	0.35	-0.25
SD	0.60	0.73	0.00	0.01	0.72	0.22	0.31	0.28	0.59	0.29	0.30	0.22

contaminated with PTEs during the post-monsoon. However, relatively low contamination level of PTEs in the majority of sampling locations during post-monsoon for all estimated indices (Table 3) because of the dilution effects of river water.

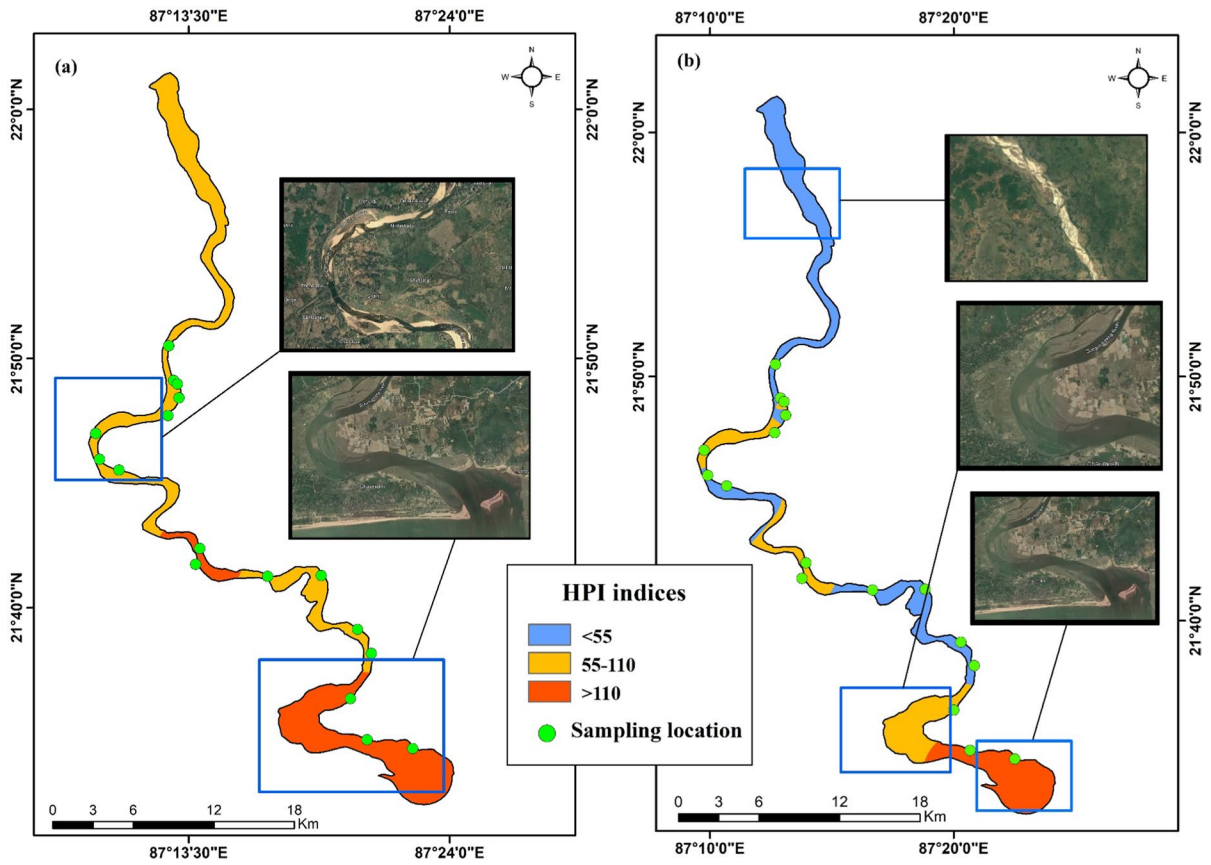
Source identification of pollutants using multivariate statistical analysis

#### Principal component analysis (PCA)

Table 6 shows the principal component analysis's findings. It demonstrates that only five components have been extracted with eigenvalues greater than 1 for post-monsoon season, while for pre-monsoon season, only four components have been disclosed. This is based on the premise made by Chatfield and Collin (1980) that components with eigenvalues less than 1 should be removed. In order to facilitate knowledge and highlight the basic importance of the extracted

components to the water quality state of the selected study area, the extracted components were subsequently rotated in accordance with the varimax rotation. The rotation's outcome also showed that the percentages of the cumulative variances of the four extracted components in pre-monsoon season and five extracted components in post-monsoon season, account for a total 80.0% and 89.5% of the overall variance of the observed variables, respectively (Table 6). This shows that these extracted components in both seasons had successfully accounted for the variation of the observed variables.

In pre-monsoon season, the first component, i.e. PC1, accounted for 37% of total variation and showed a strong loading of Fe, Cu, COD, and  $\text{NO}_3^-$  and moderate loading of Cr,  $\text{Cl}^-$ , and TH. The significant positive ion loadings in PC1 pointed out to anthropogenic activities occurring in the basin (Gupta et al., 2016; Gyimah et al., 2021). In post-monsoon season, PC1 has accounted for 42.3% of total variation



**Fig. 3** HPI of Subarnarekha River during **a** pre-monsoon and **b** post-monsoon seasons

**Table 5** Weightage and sub-index of PTEs for HPI calculation of river Subarnarekha during pre-monsoon and post-monsoon

PTEs	Mean concentration (µg/L)		Highest permitted values for drinking water ( $S_i$ ) (µg/L)	Unit weight-age ( $W_i$ )	Sub-index ( $Q_i$ )		$W_i * Q_i$	
	Pre-monsoon	Post-monsoon			Pre-monsoon	Post-monsoon	Pre-monsoon	Post-monsoon
Pb	27.82	19.71	10	0.100	278.24	197.06	27.82	19.71
Cu	30.59	22.94	1500	0.001	46.94	47.71	0.05	0.05
Ni	41.53	18.82	20	0.05	207.65	94.12	10.38	4.71
Cd	0.82	0.41	3	0.30	27.45	13.73	8.24	4.12
Fe	590.71	331.76	300	0.003	196.90	110.59	0.59	0.33
Cr	67.71	37.47	50	0.02	135.41	74.94	2.71	1.50

Mean HPI = 105.04 (pre-monsoon) and 64.15 (post-monsoon)

and exhibited strong loading of COD,  $Cl^-$ , TH, with moderate loading of Cu, Fe, pH, and  $NO_3^-$ . Owing to these results, PC1 can be linked to anthropogenic sources such as urban waste disposal and industrial

wastewater discharges. Hamed (2019) also reported industrial activities due to the strong loading of Fe.

PC2 in pre-monsoon season has accounted for 25.3% of total variation and pointed out towards



**Table 6** Principal component analysis (PCA) of water quality parameters along with PTEs for Subarnarekha River

Variables	Components								
	PC1		PC2		PC3		PC4		PC5
	Pre-	Post-	Pre-	Post-	Pre-	Post-	Pre-	Post-	Post-
pH	-0.005	0.700	0.597	0.564	0.024	0.238	-0.020	-0.051	0.083
EC	-0.022	-0.039	0.615	-0.022	0.513	0.001	0.096	0.071	0.990
TSS	-0.289	-0.060	0.798	-0.838	0.004	0.311	0.162	0.119	0.053
TDS	0.338	0.208	0.108	0.118	0.734	-0.019	-0.048	0.945	0.078
TA	0.304	0.210	-0.562	0.656	0.601	0.452	0.057	0.299	0.006
TH	0.671	0.881	-0.116	0.194	0.414	0.128	-0.464	0.178	-0.129
DO	0.244	0.214	-0.664	0.801	0.568	0.175	-0.065	0.191	0.023
BOD	0.217	0.165	0.804	-0.881	-0.067	0.319	0.398	0.219	0.056
COD	0.861	0.933	-0.089	0.161	0.456	0.259	0.117	0.105	0.041
Cl <sup>-</sup>	0.777	0.928	0.406	-0.069	0.110	0.289	0.383	-0.039	-0.009
SO <sub>4</sub> <sup>2-</sup>	0.132	-0.021	0.829	-0.934	-0.374	0.147	0.204	-0.203	0.027
NO <sub>3</sub> <sup>-</sup>	0.855	0.548	-0.235	0.739	0.036	-0.115	0.118	-0.056	-0.032
PO <sub>4</sub> <sup>3-</sup>	0.208	0.239	-0.221	0.693	0.871	0.461	0.165	0.407	0.265
Pb	0.079	0.164	-0.056	-0.071	0.536	0.929	0.755	0.076	-0.052
Cu	0.939	0.796	0.011	0.117	0.018	0.516	0.205	0.235	0.063
Ni	0.267	0.340	0.206	-0.272	-0.048	0.771	0.846	-0.234	0.243
Cd	0.232	0.420	0.378	-0.328	-0.004	0.669	0.667	0.398	-0.120
Fe	0.886	0.783	-0.093	0.075	0.238	0.243	0.292	0.460	0.016
Cr	0.745	0.393	0.080	0.067	0.497	0.754	-0.021	-0.002	-0.026
% of Variance	37.0	42.3	25.3	25.9	9.8	8.3	7.9	7.4	5.7
Cumulative %	37.0	42.3	62.3	68.2	72.1	76.5	80.0	83.8	89.5
Eigen values	7.02	8.03	4.81	4.92	1.87	1.57	1.50	1.40	1.08

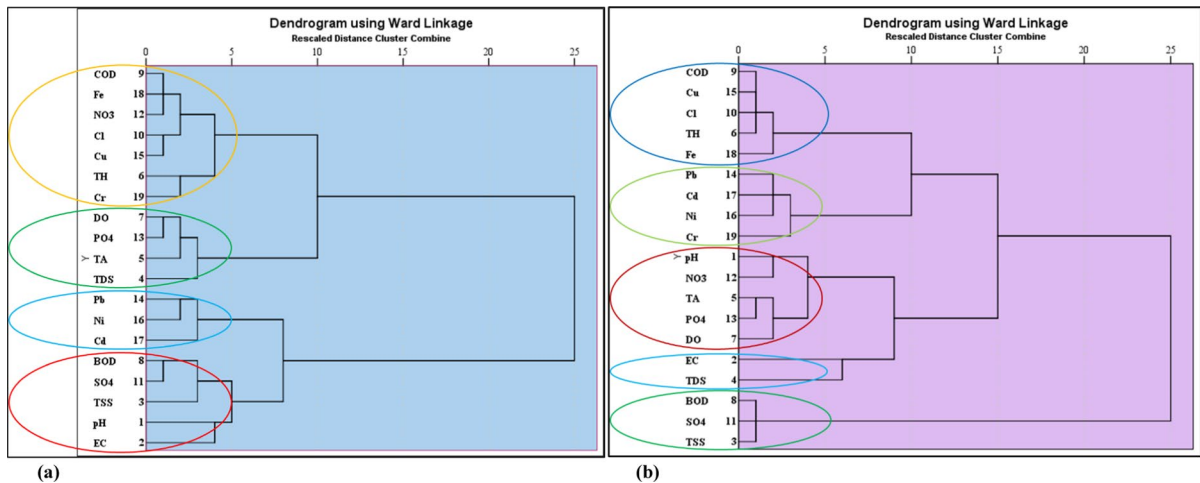
Rotation method: varimax with Kaiser normalization

strong loadings of BOD and SO<sub>4</sub>, while moderate loadings of TSS, EC, and pH. PC2 components are derived from mixed sources of organic wastes from adjacent human settlements, agricultural fields, forest dominated areas, and geogenic attributes (Gupta et al., 2016). While in post-monsoon season (accounted for 25.9%), a strong negative loading has been seen for BOD, SO<sub>4</sub><sup>2-</sup>, and TSS, whereas positive strong loading of DO along with positive moderate loading of NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup>, TA, and pH have been observed. The positive loadings indicated organic waste disposal from domestic, agricultural fields, and fish processing industries, while negative loading pointed out towards geogenic sources.

In pre-monsoon season, the third component (PC3) accounted for 9.8% of total variance, while 8.3% in post-monsoon season. The positive loading of PO<sub>4</sub>, TDS, DO, and TA has been observed in pre-monsoon

season due to poor agricultural practices, discharges from fisheries industries, and sewage treatment plants (Roy and Bickerton, 2014). In post-monsoon studies, PC3 has executed positive loadings for Pb, Ni, Cr, and Cd, which can be attributed to fertilizer and pesticide residues in adjacent agricultural fields as well as discharges from the fisheries industry (Githaiga et al., 2021).

PC4 has accounted for 7.9% and 7.4% of total variance in pre-monsoon and post-monsoon, respectively. In pre-monsoon PC4 have shown strong positive loadings for Pb, Cd, and Ni). The findings ascribe that these toxic metals could have originated from fertilizers and pesticide residues in agricultural fields and can be associated with harbour and dockyards, as well as paints used in boats (Githaiga et al., 2021). However, in post-monsoon, PC4 explained positive loading of TDS only, which



**Fig. 4** Dendrogram of the analysed parameters for **a** pre-monsoon and **b** post-monsoon seasons

can be attributed to weathering and erosion and influx of domestic wastewater and runoff water.

PC5 in post-monsoon season has accounted for 5.7% and indicated the positive loading of only EC. EC demonstrates the presence of dissolved salts and ions in river water. PC5 represents the geogenic sources and describe natural mechanisms such as geochemical weathering and mineral dissolution which are the major contributors to dissolved salts and ions in river water.

*Hierarchical cluster analysis (HCA)*

In order to identify clusters, hierarchical cluster analysis (HCA) was used. In this analysis, the Wards method and squared Euclidean distance method using Z-scores standardization were employed. The numerous clusters have been represented by a dendrogram. Four groups were established in accordance with the HCA results in pre-monsoon season (Fig. 4). The results showed similar outcomes as PCA. Cluster 1 comprises of COD, Fe, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Cu, TH, and Cr which directed towards anthropogenic activities. The loading of parameters in each PC was similar with each cluster in pre-monsoon season. Therefore, the sources are also analogous.

In post-monsoon season, the HCA have shown five clusters (Fig. 4), and the output was relatively similar to the PCA results (Table 6). The basic grouping of the parameters in cluster and PCA was identical except two or three deviations. pH and

NO<sub>3</sub><sup>-</sup> were absent in Cluster 1, while both were loaded in PC1 in post-monsoon season. TDS and EC were independently loaded in PC4 and PC5, respectively; however, their grouping was observed in Cluster 4. So, weathering of rocks and dissolution of salts were the main reasons behind this. Only BOD, SO<sub>4</sub>, and TSS, which were independently grouped in cluster 5, showed negative loading in PCA. Cluster 5 was found in a separate branch of the dendrogram, indicating that its sources were distinct from those of other parameters and were clearly geogenic.

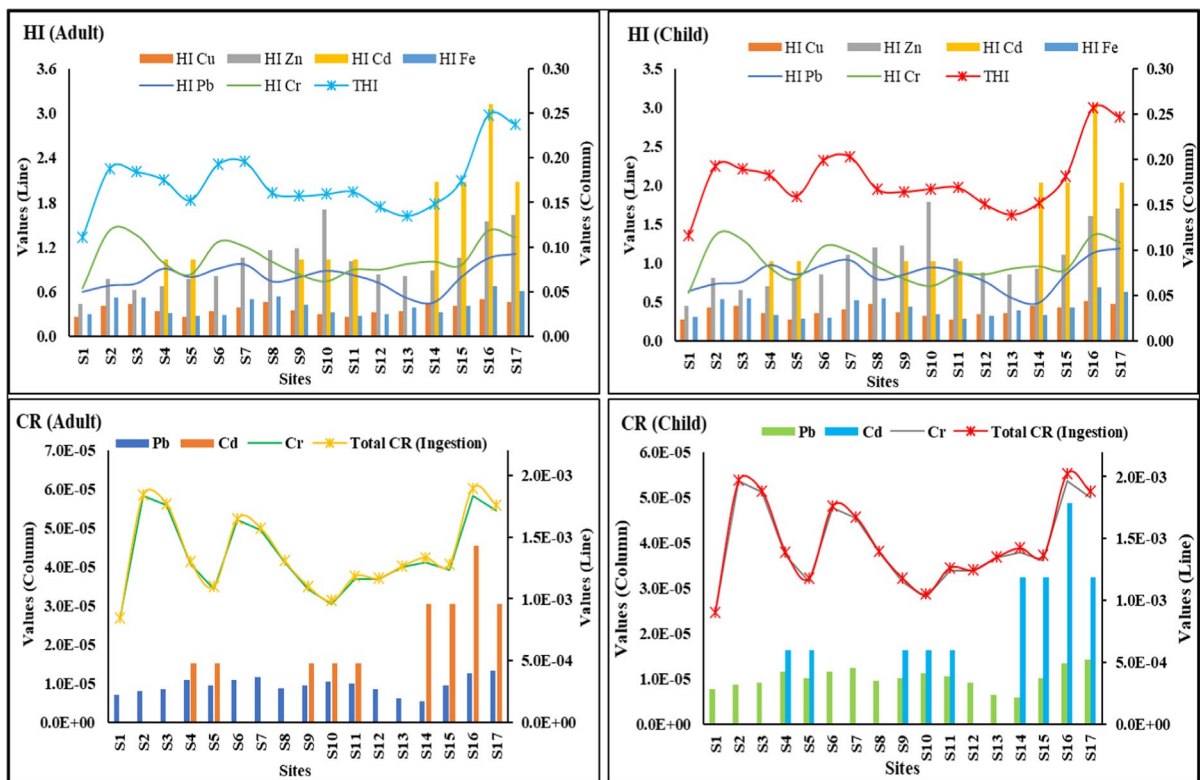
*Health risk assessment*

Supplementary Table 3 (a) and (b) displays the results of the evaluation of oral and dermal pathways for the health risk assessment of contaminants (Fe, Ni, Cu, Cr, Cd, and Pb) in water samples from the Subarnarekha River. The results for the dermal absorption hazard quotients (HQ<sub>derm</sub>) also indicated values < 1 for all the elements examined at all the sites in both pre- and post-monsoon seasons for both adults and children. De Carvalho et al. (2021) also reported similar findings in Joanes River, Brazil. The ingestion hazard quotients (HQ<sub>ing</sub>) values for both adults and children in both the seasons showed values < 1 for every element inspected except Cr and Pb. In pre-monsoon season, Site 16, 17, and 7 showed HQ values > 1 for children, while for adults, only Site 16 and 17 showed HQ values above 1 for Pb. Site 2, 3, 6, 7,

16, and 17 showed  $HQ_{ing}$  values  $> 1$  for both adults and children for Cr. This displayed that the Cr and Pb posed potential harm over the course of a lifetime exposure at those particular sites in pre-monsoon. In post-monsoon season, only site 16 has shown  $HQ_{ing}$  values above 1 for Pb for adults and children both. Therefore, in post-monsoon season, Pb posed the potential threat for the lifetime exposure at site 16. In comparison with adult values, it was found that children's HQ and HI values were higher. Children may be more prone to being harmed by these harmful contaminants, according to the health risk assessment. Njuguna et al. (2020) and De Carvalho et al. (2021) also reported identical findings. Except for few sites, the HI values in both the season of all the elements (except Cr and Pb) for both adults and children in the basin are generally below the recommended limits ( $< 1$ ) (Fig. 5a, b), indicating that the surface water from these basins clearly offered no possible health concern. Eight sites (Site 2, 3, 6, 7, 8, 14, 16,

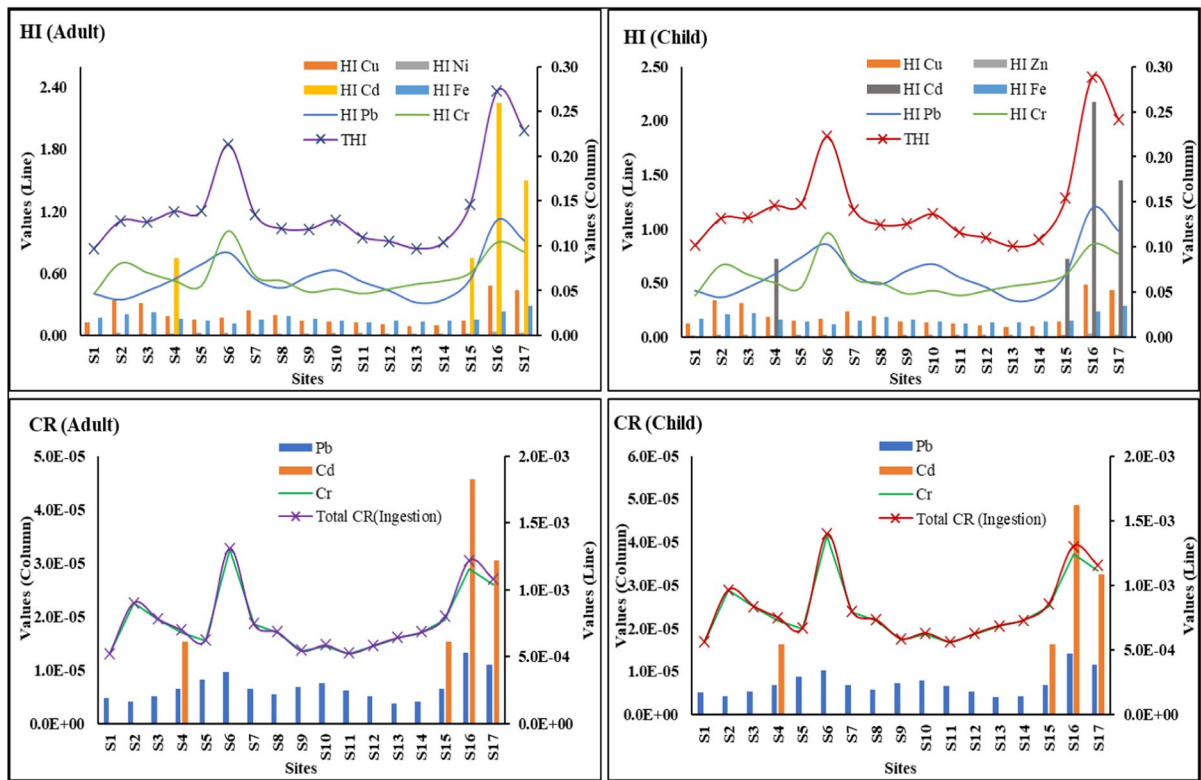
and 17) and six sites (Site 2, 3, 6, 7, 16, and 17) in pre-monsoon season for adult and children, respectively, indicated possible health concern for Cr as the HI values found above 1. Site 16 and 17 and site 7, 16, and 17 for adult and children, respectively, have shown HI values  $> 1$  indicating health concerns for Pb in pre-monsoon season. In post-monsoon season, site 6 has shown  $HI > 1$  in case of Cr for adults only, while site 16 has revealed HI above 1 in case of Pb for both adults and children indicating the presence of non-carcinogenic health risk at these sites.

According to the present study, the ILCR values indicated that children are more prone to cancer risk from Pb, Cd, and Cr compared to adults. The cancer risks for Cd and Pb were between  $10^{-5}$  and  $10^{-6}$  at all the sites of Subarnarekha River for both adults and children. All the sites in pre-monsoon as well as post-monsoon season have showed the chance of occurrence of carcinogenic risk from Pb in nearby future as all the values indicated  $> 10^{-6}$  for both child and



(a)

**Fig. 5** a, b Spatial distribution of the hazard index (HI) and carcinogenic risk (CR) values of PTEs for adults and children during a pre- and b post-monsoon season in the study area



(b)

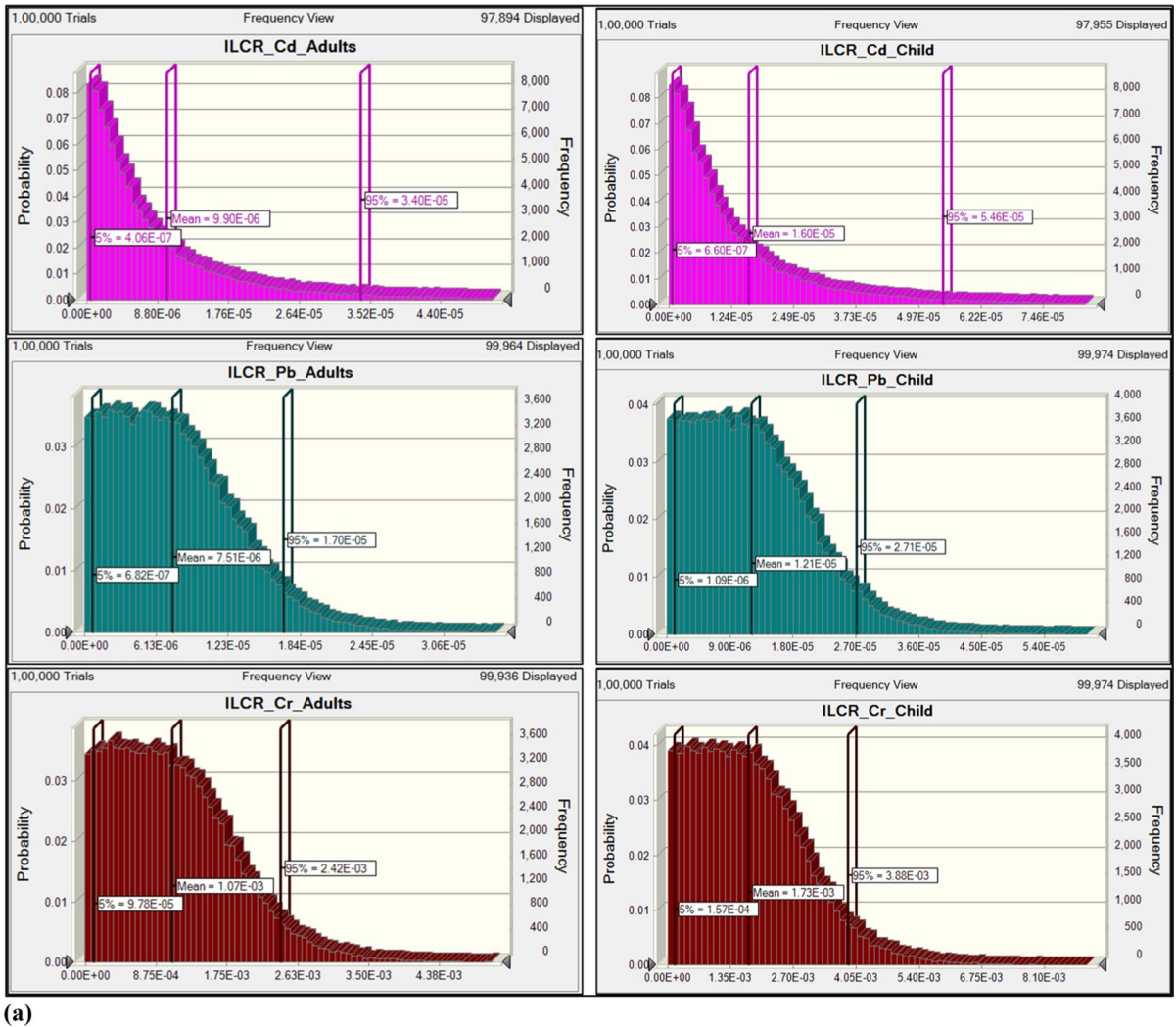
Fig. 5 (continued)

adults. In case of Cd, Site 4, 5, 9, 10, 11, 14, 15, 16, and 17 in pre-monsoon and Site 4, 15, 16, and 17 in post-monsoon have showed possibility of cancer risk in upcoming future for children and adults both as the ILCR values indicated  $>10^{-5}$ . ILCR values showed above  $10^{-4}$  for Cr in pre-monsoon and post-monsoon season at all the sites for both children and adults. Some sites (Site 6, 16, and 17 in post-monsoon and all the sites except Site 1 and 10 for adult and Site 1 for children in pre-monsoon season) also specified the ILCR values for Cr  $>10^{-3}$ . Therefore, these values clearly revealed the presence of carcinogenic risk not only in adjoining future, but in current time also. Yuan et al. (2020) also specified the worries regarding the cancer risk from Cr in river water from Jiangjin district, China.

Monte Carlo simulation for carcinogenic risk

The deterministic carcinogenic risk estimations technique's (conventional ILCR model) for adults

and child exposed to the ingestion pathways for Pb, Cr, and Cd were simulated using the MCS approach. The 5th mean and 95th percentile risk exposure in the current investigation are represented, where 5th and 95th percentile defines the low-end and the worst-case scenario. Histograms comparing the carcinogenic risk associated with exposure to Pb, Cd, and Cr in children and adults showed that the 95th percentile for children was greater than it was for adults for each investigated carcinogenic PTEs in both the season. The MCS has provided the probabilistic carcinogenic health risk by reducing the loop holes in input parameters by running the simulation for 100,000 iterations. The 95th percentile values of Cd are  $3.40E-05$  and  $5.46E-05$ , Pb are  $1.70E-05$  and  $2.71E-05$ , and Cr are  $2.42E-05$  and  $3.88E-05$ , respectively, for adult and child in pre-monsoon season. In post-monsoon season, the 95th percentile values have reduced for each investigated elements, and the values are  $1.92E-05$  and  $3.11E-05$  (Cd),  $1.27E-05$  and  $2.04E-05$  (Pb), and



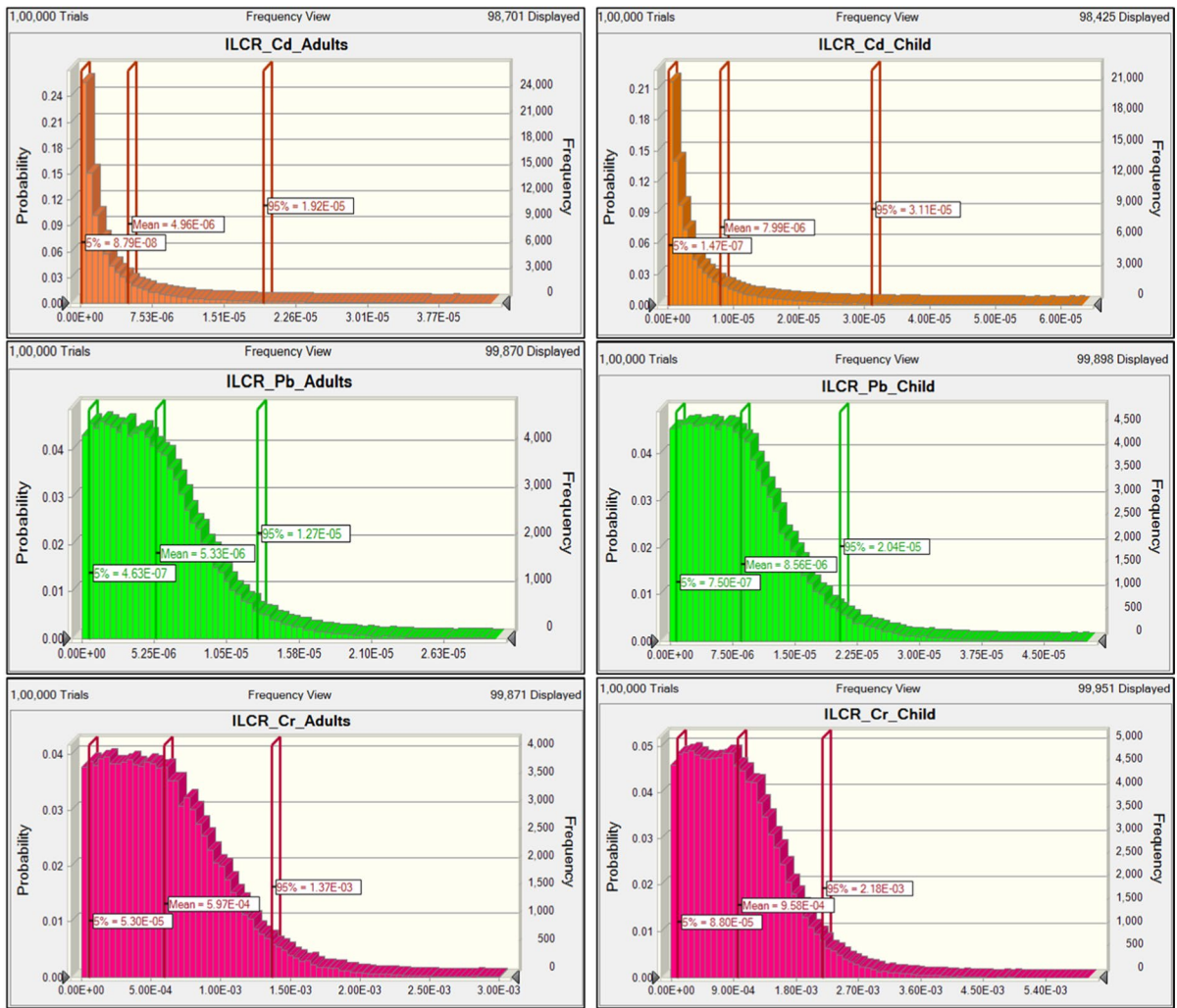
**Fig. 6** a, b Monte Carlo simulation approach for health risk assessment during a pre-monsoon and b post-monsoon seasons in study area

1.37E-03 and 2.18E-05 (Cr) for adult and children, respectively. The overall carcinogenic risk levels Cr were greater than tolerable limits ( $1E-04$ ) in both the child and adult groups, indicating a very high chance of cancer hazards for people in the present time and future (Fig. 6a, b). The 95th percentile values of Pb and Cd indicated that the possibility of occurrence of cancer risk is in near future as the values are higher than the safe limit ( $1E-06$ ). MCS also revealed that the cancer risk for Cr, Pb, and Cd was found to be lower in post-monsoon compared to pre-monsoon, which is due to the dilution factor by rain.

## Conclusions

In the present investigation, the quality of Subarnarekha River water is slightly acidic to normal in nature. The physicochemical assessment of river water reveals that most of the parameters are well under the prescribed guidelines of BIS (2012), except TH which has significant seasonal variations. Pollution indices and statistical models such as WQI,  $C_d$ , HEI, HPI, HIs, HQs, ILCR, PCA, and HCA were used to appraise the level of PTEs contamination in river water and identify the possible contamination sources.





(b)

Fig. 6 (continued)

Pollution indices and statistical models such as WQI,  $C_d$ , HEI, HPI, HIs, HQs, ILCR, PCA, and HCA were used to appraise the level of PTEs pollution and determine the possible contamination sources. The mean abundance of PTE concentration of the Subarnarekha River water follows the order of  $Fe > Cr > Ni > Cu > Pb > Cd$  during the pre-monsoon and  $Fe > Cr > Cu > Pb > Ni > Cd$  in the post-monsoon season. Based on  $C_d$  values, 76.50% of sampling sites were low contaminated, and 23.5% of sampling sites were moderately contaminated during the pre-monsoon study. However, post-monsoon studies have shown all sampling stations

(100%) fall under the low contamination level. Pre-monsoon studies of HEI reveal that the river water has a moderate (52.94% sampling sites) to low level (47.06% sampling sites) of contamination with respect to PTEs, while in post-monsoon, the majority of sampling sites (94.12% sites) have low contamination level. Moreover, the estimated HPI of PTEs has a moderate-to-high level of contamination during the pre-monsoon season and a low to high level of contamination in the post-monsoon season. The descending trend of PTEs contamination in the post-monsoon season is because of dilution effects.

Non-carcinogenic and carcinogenic health risk assessments indicated the presence of health hazards in the Subarnarekha River. In the basin, the HI values for all the elements during both seasons are typically within the advised limits (except Cr and Pb), for both adults and children. Cr and Pb posed non-cancerous health concerns to both children and adults in some monitored sites of Subarnarekha River basin. Carcinogenic risk results distinctly demonstrate the presence of a cancer risk not only just in the near future, but also in the present. Cr emerged as the most hazardous element in terms of health risk in the Subarnarekha River basin. Children are more prone to cancer and non-cancer risks compared to adults in both seasons, but post-monsoon seasons have shown less risk compared to pre-monsoon seasons owing to the dilution factor due to rain. The findings of this study emphasize the necessity for well-informed policies to stop water quality degeneration and the accumulation of PTEs in order to protect human health. For the purpose of determining the risk levels, MCS projected the probability distribution of the carcinogenic risk. This method eliminates uncertainty, data measurement constraints, and other human errors. The likelihood of a few polluted samples tends to be on the higher end, which raises the mean value and, in turn, the danger for the entire region. To ascertain the severity or greatest risk for the region, however, assessing the risk for higher concentrations is also necessary.

**Acknowledgements** The authors wish to thank Amity University Kolkata, The University of Burdwan, and Asansol Engineering College to provide facilities and infrastructure to conduct this research work.

**Author contributions** Anup Pradhan: Conceptualization, Methodology, Validation, Data curation, Formal analysis, Visualization, Writing - original draft preparation. Manash Gope: Software, Formal analysis, Reviewing and Editing. Krishnendu Kumar Pobi: Methodology, Formal analysis, Software, Investigation, Writing - original draft preparation. Sucharita Saha Srimanta Gupta: Application of GIS Software, Formal Analysis, Data interpretation & representation. Srimanta Gupta: Application of GIS Software, Formal Analysis, Data interpretation & representation. Reviewing and Editing. Rama Ranjan Bhat-tacharjee: Software, Formal analysis. Reviewing and Editing. Sumanta Nayek: Supervision, Visualization, Investigation, Validation, Reviewing and Editing.

**Funding** Not applicable.

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

**Code availability** Not applicable.

**Declarations**

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

**Ethics approval** Not applicable.

**Consent to participate** Not applicable.

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

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