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RESEARCH PAPER



## Assessing heavy metal index referencing health risk in Ganga River System

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### ABSTRACT

River Ganga, one of the largest perennial rivers, conserves the cultural heritage of the Indian sub-continent, supporting as the nectar of life to millions residing on the banks of the river basin. With unlimited use, the river also receives a large amount of untreated wastewater discharged from different industrial, commercial and residential complexes, unbalancing the nutrient concentration at many points along the stretch. The current study assesses water samples collected from 20 monitoring locations and the Ganga River System in the Himalayan region, evaluating the potential risk of heavy metal pollution. The concentration of Zn, Pb, Mn, Fe, Cu, Al, Ni, Cd, Mg and Co is determined by atomic absorption spectrophotometer (AAS). Fe, Cd and Mg's observed values exceeded various standards (WHO, BIS and USEPA) for drinking water. The pollution assessment index (heavy metal pollution index: HPI) and multivariate analysis (principal component analysis: PCA and cluster analysis: CA) were implemented to identify the intensity of pollution and its sources. The seasonal values of HPI were found 88.69, 90.32, 88.53 and 84.96 in winter, summer, monsoon and post-monsoon seasons. The index value on all monitoring locations varied between the range of PCA outcomes for three factors and explained 72.1% of the variance, indicating natural and man-made activities as responsible metal abundance factors in the river system. The hazard quotient (HQ) and hazard index (HI) are used to assess non-cancer health risks to humans. The seasonal evaluation recorded  $HQ < 1$  for all the metals and  $HI > 1$  was found for the entire study period. This study contributes to various conservation initiatives for the River Ganga System with factual datasets and characterization of various sampling locations using heavy metal indexing while sharing common masses' findings for people participation at the regional level.

### ARTICLE HISTORY

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### KEYWORDS

Ganga River System; water quality; heavy metal pollution index; health risk assessment; multivariate statistical analysis

### Significance statements

1. Long stretch (around 320 km) of the Ganga River System was assessed in terms of heavy metal toxicity to check the suitability for drinking and other purposes.
2. The comparison of observed data elicits the concentration of Fe, Cd and Mg higher than the proposed drinking water standards.
3. Seasonal heavy metal pollution index (HPI) values were found below the critical pollution index value (100), indicating river water quality requires immediate and improved remedial measures.
4. Study includes the integrated approach of indexing and multivariate analysis to evaluate the most significant polluted sites and similarities between relative sites and identify the most polluted sites with pollution sources.
5. Study helps maintain data set for the future providing sufficient information for policymakers, environment conservators and water resource managers.

### 1. Introduction

River Ganga basin is one of the largest in the Indian sub-continent, and by length (2525 km) it is the 30th longest river globally, covering an area of 8,61,404 km<sup>2</sup> (Ahmad et al., 2010). India's Himalayan region possesses abundant river

resources, including some of the gradual tributaries, hosting demographic culture and modern societies, inevitably increasing commercial, agricultural and domestic freshwater needs (Ramesh et al., 2000). The river water quality in the Himalayan region is under the influence of climate change on the glacier melting, which affects the water chemistry and the seasonal discharge of river runoff (Matta et al., 2020). Across the Himalayan region, the glaciers are the headwaters of many prominent Asian rivers, experiencing intensive shrinkage characterized by a significant reduction in glacial area (Singh, 2010).

Heavy metals pollution in the surface water is one of the most significant quality issues in various metropolitan cities in developing countries, due to the open discharge of chemicals from industrial and commercial complexes and agricultural runoff into freshwater bodies without any treatment process (Ezemonye et al., 2019; Karbassi et al., 2007; Matta & Uniyal, 2017). Heavy metals could be introduced into the river from various sources, either natural or anthropogenic (Maigari et al., 2016; Matta, Kumar, et al., 2018; Matta et al., 2015; Matta, Gjyli, et al., 2018). Many important pollutants are found in water like biodegradable and volatile organic compounds, and toxic metals (cadmium, lead, zinc, iron, nickel, copper, cobalt, etc.). Amid the pollutants, all the heavy metals are harmful to aquatic biota because they accrete through the food chain and create many hazardous compounds harmful to living organisms' biological activity

(Ezeonyejiaku et al., 2014; Ogbomida et al., 2018; Paul, 2017). With continued increasing population, urbanization and industrialization, the rivers and the streams are often being treated as detriment disposal sites for various municipal and industrial wastes, causing the most significant detriment to the various rivers' health (Matta, Dhingra, et al., 2018; Matta & Kumar, 2017).

Various studies in the literature have focused on heavy metal contamination in water resources worldwide (Manoj et al., 2012; Matta et al., 2016; Matta & Kumar, 2017; Reddy et al., 2012; Reza & Singh, 2010). Due to industrialization, there has been a tremendous amount of waste materials, waste effluents and sewage entering the water bodies, which is the main source of environmental pollution, increasing the environment's toxicity (Reddy, 1995). Different type of toxic and heavy metals plays an essential role in environmental pollution. The river system provides factual records of heavy metal pollution. Rivers in populated areas passing through industrial areas are associated with water-related problems because of untreated discharge of waste effluents and sewage water into water bodies, which increased heavy metal levels in the rivers (Mohan et al., 1996). Monitoring and assessment are the major components for all freshwater bodies, especially those that nourish millions of people and provide water for agricultural, commercial, and industrial uses and are simultaneously threatened by various anthropogenic activities along the river course causing pollution (Ahmad et al., 2010; Amadi, 2011). The metals like Zn, Fe, Cu, Ni, Mn, Al and Mg are essential micronutrients for the growth of any plant, animal and other life forms, whereas some of the metals like Cd, Pb and Co have rarely have known physiological role (Aktar et al., 2010; Kar et al., 2008). Generally, most heavy metals enter the river from different sources; it can be either natural by erosion or weathering, or anthropogenic (Sheykhi & Moore, 2016). In comparing anthropogenic activities, natural sources of heavy metals like weathering of rocks and leaching contribute little to the environment (Dixit et al., 2015). Ingestion of potentially toxic river water above recommended oral reference doses may cause individuals to experience harmful health problems. For that reason, reporting and monitoring river water quality for drinking purposes is a high priority. Considering the above facts, this study was taken up to monitor the River Ganga's quality status with emphasis on heavy metals pollution and their seasonal variations and source identification. Very few studies conducted on heavy metal pollution and health risk assessments covered that much longer stretch of River Ganga using various integrated statistical techniques and HPI. This study will make it possible to evaluate the present pollution level and management strategy accordingly for the future.

## 2. Materials and methods

### 2.1. Study area

The Ganga originates from the Gangotri glacier in the Himalayan region at an altitude of about 7010 m in the Uttarkashi district of the Uttarakhand Region. The selected river stretch covers around 315 km of distance from Gangotri to Roorkee. The research area lies between the coordinates from 30°49' N and 79°10' E to 29°51' N and 77°53' E. The area's climatic condition varies from cold at the upstream location to

very warm towards downstream sites. The temperature variation can touch the sub-zero level by covering the land area with snow up to 10 ft at the upstream site during winters whereas at downstream sites temperature reaches up to 45 °C during the summer season (CWC, 2012). The study was conducted at specified sampling points illustrative of the River Ganga in the Uttarakhand stretch. A total of 20 sampling sites were selected, which receive municipal and domestic waste and other hazardous materials from various point and non-point sources (Sharma et al., 2015). Table 1 gives locational details of the study area and provides the geographical setting and description of sampling areas, whereas Figure 1 gives the locational detail of sampling sites. Most of these sampling sites are known for their religious importance, attractive tourist destination and fastest industrial growing sites.

### 2.2. Sample collection and analysis

The fieldwork was carried out in winter (November–February), summer (March–June), monsoon (July–August) and post-monsoon (September–October) in the years 2014–2015. All the samples were collected fortnightly each month in different seasons since the level and fate of the pollutants in river water get affected by seasons to a great extent. The grab sampling method was used for sample collection in the triplicate manner from a depth of about 0.3 m in 1 L acid-washed (10% HNO<sub>3</sub>) wide-mouth bottle of Nalgene Natural HDPE polypropylene. The collected unfiltered samples were preserved by adding 2 mL of conc. HNO<sub>3</sub> to 1 L of the sample to prevent precipitation of heavy metals. All the samples were stored at 4 °C to avoid evaporation. For heavy metal analysis, 10 mL of HNO<sub>3</sub> was mixed with 50 mL of preserved samples and digested at 90 °C to reduce the volume up to 10–20 mL. Whatman filtered final volume No. 42 filter paper after making up the volume to 50 mL by adding de-ionized water. The concentrations of individual heavy metals were determined using a flame atomic

**Table 1.** Details of monitoring locations with their geo-coordinates.

S.No.	Sampling site	Type of system	Latitude	Longitude
1.	Gangotri	30.993877	78.941364	River System
2.	Uttarkashi	30.73	78.45	River System
3.	Badrinath	30.742603	79.491568	River System
4.	Tehri Dam	30.373331	78.474997	River System
5.	Koteshwar	30.26027	78.49805	River System
6.	Rudraprayag	30.28	78.98	River System
7.	Srinagar	30.221397	78.780044	River System
8.	Devprayag	30.146144	78.598586	River System
9.	Byasi, Rishikesh	30.064861	78.472622	River System
10.	LakshmanZhoola, Rishikesh	30.126331	78.329681	River System
11.	TriveniGhat, Rishikesh	30.103028	78.298611	River System
12.	Pashulok Barrage, Rishikesh	30.074956	78.287403	River System
13.	Chilla Power House, Rishikesh	29.976764	78.202233	River System
14.	Bhimgoda Barrage, Haridwar	29.956472	78.182853	River /Canal System
15.	Har-Ki-Pauri, Haridwar	29.955231	78.170683	Canal System
16.	Mayapur, Haridwar	29.942097	78.155736	Canal System
17.	Jatwara Bridge, Haridwar	29.919372	78.103564	Canal System
18.	Missarpur Village, Haridwar	29.895167	78.146367	River System
19.	Bahadradab, Haridwar	29.919922	78.040686	Canal System
20.	Roorkee	29.856636	77.883453	Canal System

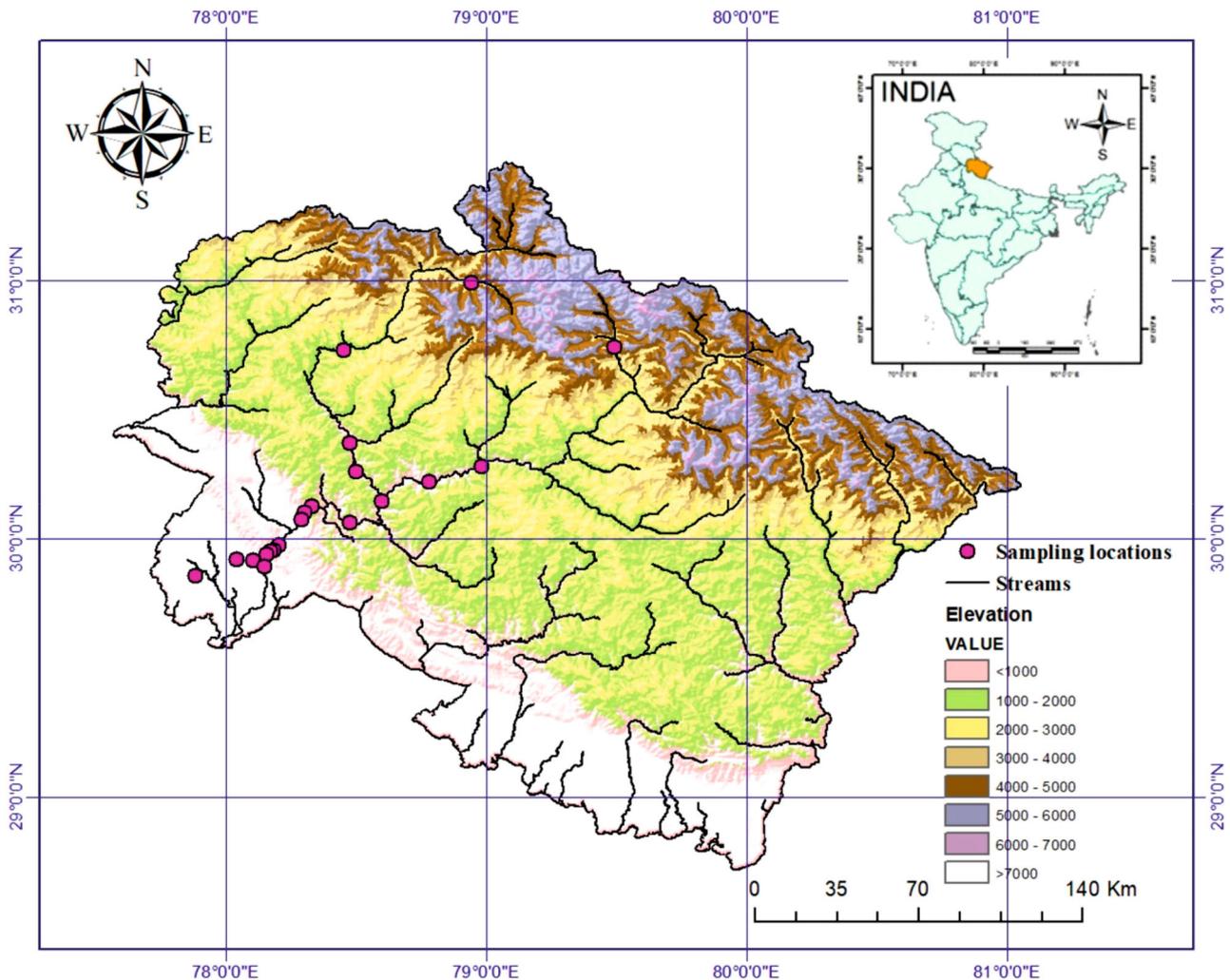


Figure 1. Location map of study area with monitoring station of Ganga River System.

absorption spectrophotometer (FAAS) using the model: ECIL AAS4129 (PC-based) (APHA, 2012; USEPA, 1999).

### 2.3. Multivariate statistical analysis

Various researchers have applied multivariate statistical methods to characterize and determine water quality (Lin et al., 2003; Reghunath et al., 2002). Environ metrics, also called multivariate statistical techniques, such as PCA and CA, were occupied to group the sampling locations according to water quality characteristics and determine the probable factors influencing the water chemistry.

### 2.4. Principal component analysis

PCA is the very extensively used quantitatively involved technique for transforming a given set of interrelated variables into a new set of variables called the principal components (PCs). This technique distinguishes the different heavy metals that correlate with similar behaviour and common origin (Tahri et al., 2005). In this technique, the entire PCs produced are unrelated to each other; hence, the correlation between them is zero.

The PCA is a beneficial technique to explain the variance of a huge dataset of inter-correlated variables with a smaller set of independent variables (Simeonov et al., 2003). PCA method extracts the eigenvalues and eigenvectors from the

covariance matrix of the real variables. The PCs are the unrelated variables derived by multiplying the original correlated variables with the eigenvector, a coefficients list (loadings or weightings). Thus, the PCs are weighted linear integrations of the original variables. PC gives all the information on the most significant parameters, representing the entire dataset while affording data reduction with a minor loss of original information. Factor analysis further diminishes the contribution of less important variables produced from PCA and the new group of variables known as varifactors (VF) is extracted by rotating the axis defined by PCA (Wunderlin et al., 2001). PCA with varimax rotation of standardized component loadings was conducted for amplifying the variation among the variables under each factor, and those PCs with eigenvalue > 1 were retained (Singh et al., 2004).

### 2.5. Cluster analysis

This environmetrics technique is used to categorize and identify groups or clusters of similar sampling locations based on similarities within a class and dissimilarities between different classes. The grouping of similar sampling stations occurs first and eventually, as the similarity decreases, all subgroups of sampling stations are merged into a single cluster (Birth, 2003). In this research paper,

the hierarchical cluster analysis (HCA) based on the ward method was performed to analyse the similarities.

**2.6. Heavy metal pollution index**

The HPI represents the overall quality of water concerning heavy metals. The HPI is based on the weighted arithmetic quality average method and developed in two steps: (1) establishing a rating system for every selected parameter giving weightage and (2) selecting the pollution parameter on which the index-based. The rating scale is an arbitrary value between 0 and 1. Its selection depends upon the importance of individual quality considerations comparatively or determined by making values inversely proportional to the corresponding selected parameter’s recommended standard. In computing, the HPI, considered unit weightage ( $W_i$ ) as a value inversely proportional to the recommended standard ( $S_i$ ) of the corresponding parameters proposed.

The HPI model (Mohan et al., 1996) is given by the following equation:

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i}, \tag{1}$$

where  $Q_i$  is the sub-index of the  $i$ th parameter,  $W_i$  is the unit weightage of the  $i$ th parameter and  $n$  is the number of parameters considered. The sub-index ( $Q_i$ ) of the parameter is analysed by the following equation:

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \times 100, \tag{2}$$

where  $M_i$  is the monitored value of the heavy metal of  $i$ th parameter,  $I_i$  is the ideal value of the  $i$ th parameter, and  $S_i$  is the expected value of the  $i$ th parameter. The critical pollution index of HPI value for drinking water (Prasad & Bose, 2001) is 100. However, a modified scale using three classes has been used in the present study (Edet & Offiong, 2002).

**2.7. Health risk assessment**

The health risk to humans by heavy metals could occur through direct ingestion, inhalation and dermal contact; however, ingestion is the main significant way of exposure (Giri & Singh, 2015; USEPA, 2004). The risk posed through direct ingestion of Ganga River water was assessed for the study region as per the guidelines of USEPA (2004). It is conducted as the following equation:

$$ADD_{\text{ingestion}} = \frac{C_i \times IR \times EF \times ED}{BW \times AT}, \tag{3}$$

where  $ADD_{\text{ingestion}}$  is the average daily dose;  $C_i$  is the mean concentration ( $\mu\text{g/L}$ ) of  $i$ th trace metal; IR is the water intake rate (2 L/day for adults and 0.64 L/day for children) (Xiao et al., 2019); EF, exposure frequency (350 days/year) (USEPA, 2004); ED, exposure duration (70 years for adults and 6 years for children); BW, average body weight for Indian adult is 52 kg (Mishra et al., 2014) and 15 kg for children (Njuguna et al., 2020); AT, average exposure time (365 days/year  $\times$  70 or 6 years).

The non-carcinogenic risk from individual metals is characterized by the hazard quotient (HQ), which is the ratio of ADD and  $R_f D_i$  (reference dose for ingestion) proposed by USEPA from the dose–response experiment. The

**Table 2.** Descriptive statistical analysis of various heavy metals in Ganga River water during different seasons ( $\mu\text{g/L}$ ).

Heavy metals	Winter			Summer			Monsoon			Post-monsoon			WHO (2017)	BIS (2012)	USEPA (2009)
	Min	Max	Mean $\pm$ SD	Min	Max	Mean $\pm$ SD	min	Max	Mean $\pm$ SD	Min	Max	Mean $\pm$ SD			
Zn	18.40	59.30	32.69 $\pm$ 9.95	12.00	52.30	34.38 $\pm$ 11.28	14.60	49.70	30.53 $\pm$ 10.09	17.60	49.60	32.33 $\pm$ 8.45	4000	5000	5000
Pb	1.00	8.90	5.09 $\pm$ 2.48	0.90	10.10	4.55 $\pm$ 2.57	1.30	9.10	4.60 $\pm$ 2.35	1.30	8.80	4.75 $\pm$ 2.37	50	10	-
Mn	2.60	15.10	4.83 $\pm$ 3.45	2.50	9.80	4.26 $\pm$ 1.63	2.10	6.10	3.70 $\pm$ 1.19	1.80	10.10	8.75 $\pm$ 21.76	100	100	50
Fe	4894.60	6123.50	5158.58 $\pm$ 298.14	4101.30	6320.40	5417.00 $\pm$ 433.66	4764.20	5898.10	5475.93 $\pm$ 299.65	4934.10	6562.10	5367.31 $\pm$ 440.79	300	300	300
Cu	1.80	9.90	4.23 $\pm$ 2.18	1.90	7.90	4.32 $\pm$ 1.67	2.20	9.20	3.85 $\pm$ 1.69	1.90	9.50	3.68 $\pm$ 1.60	2000	50	1,300
Al	0.70	2.70	1.52 $\pm$ 0.56	0.70	2.00	1.42 $\pm$ 0.52	0.70	2.60	2.01 $\pm$ 2.06	0.70	2.20	1.40 $\pm$ 0.47	100–200	30	50–200
Ni	1.30	3.90	2.58 $\pm$ 0.723	1.50	4.10	2.72 $\pm$ 0.76	1.90	4.20	2.66 $\pm$ 0.73	1.70	4.20	2.62 $\pm$ 0.73	20	20	-
Cd	1.90	4.80	2.86 $\pm$ 0.77	1.90	4.60	2.99 $\pm$ 0.79	1.20	4.30	2.90 $\pm$ 0.76	1.70	4.70	2.74 $\pm$ 0.76	-	3	-
Mg	1872.80	4425.40	3431.81 $\pm$ 877.06	1798.50	4812.00	3406.23 $\pm$ 886.41	1460.00	4364.20	3438.40 $\pm$ 982.38	1998.60	4368.50	3337.08 $\pm$ 823.77	-	30	-
Co	2.20	9.80	4.29 $\pm$ 2.16	2.00	12.10	4.46 $\pm$ 2.31	1.60	8.90	3.70 $\pm$ 1.66	1.90	8.80	3.95 $\pm$ 1.68	-	-	-

HQ > 1 indicates the increased health risk to exposed masses from contaminants (Njuguna et al., 2020)

$$HQ = \frac{ADD_{\text{ingestion}}}{R_f D_i}, \quad (4)$$

where the  $R_f D_i$  ( $\mu\text{g}/\text{kg}\cdot\text{day}$ ) values for Zn, Pb, Mn, Fe, Cu, Al, Ni and Cd are 300, 14, 24, 300, 40, 1000, 20 and 0.5, respectively (USEPA, 1994).

To pose the overall non-carcinogenic risk through ingestion of individual metals, HQ accumulation was employed and expressed as a hazard index (HI). The equation for the calculation of HI is as follows:

$$HI = \sum_{i=1}^n HQ_i. \quad (5)$$

### 3. Results and discussions

Contamination of heavy metals in the river is one of the biggest and emerging issues. Ten heavy metals were analysed, and average concentrations, standard deviation and other standard values are given in Table 2. Significant variations of heavy metal concentration in the river are mainly due to the geological conditions, natural resource input and anthropogenic interference at different monitoring stations during different seasons. The presence of heavy metal was recorded in the entire sample throughout the sampling period along the River Ganga stretch in Uttarakhand Region. The mean concentration of Zn, Pb, Mn, Fe, Cu, Al, Ni, Cd, Mg and Co during the summer, winter, monsoon and post-monsoon seasons was found to be 32.69, 5.09, 4.83, 5158.58, 4.23, 1.52, 2.58, 2.86, 3431.81 and 4.29  $\mu\text{g}/\text{L}$  and 34.38, 4.55, 4.26, 5417.52, 4.32, 1.42, 2.72, 2.99, 3406.23 and 4.46  $\mu\text{g}/\text{L}$  and 30.53, 4.60, 5475.93, 3.85, 2.01, 2.66, 2.90, 3438.40 and 3.70  $\mu\text{g}/\text{L}$ , respectively. The average concentration of Zn, Pb, Mn, Fe, Cu, Al, Ni, Cd, Mg and Co in the post-monsoon season samples was 32.33, 4.75, 8.75, 5367.31, 3.68, 1.40, 2.62, 2.74, 3337.08 and 3.95  $\mu\text{g}/\text{L}$ , respectively. All the metal concentrations showed a seasonal variation throughout the study period.

The highest average Zn concentration was found at 34.38  $\mu\text{g}/\text{L}$  in summer, followed by 32.69  $\mu\text{g}/\text{L}$  in winter, 32.33  $\mu\text{g}/\text{L}$  in monsoon and 30.53  $\mu\text{g}/\text{L}$  in post-monsoon, respectively. The maximum Fe concentration was found at 6562.1  $\mu\text{g}/\text{L}$  in the post-monsoon season, followed by 6320.4  $\mu\text{g}/\text{L}$  in summer, 6123.5  $\mu\text{g}/\text{L}$  in winter and 5898.1  $\mu\text{g}/\text{L}$  in monsoon. The Fe concentration in this river system is higher because of urban-industrial waste, municipal solid waste, construction waste, agricultural runoff, iron

**Table 4.** Observed HPI values for Ganga River water during various seasons.

Serial No.	Seasons	HPI	Mean HPI value throughout study period
1	Winter	88.69	88.12
2	summer	90.32	
3	Monsoon	88.53	
4	Post-monsoon	84.96	

ore cluster, oxidation and a decrease in pH (Giri & Singh, 2015; Matta et al., 2022; WHO, 2003).

The maximum Pb concentration was detected at 10.1  $\mu\text{g}/\text{L}$  in summer, followed by 9.1  $\mu\text{g}/\text{L}$  in monsoon, 8.9  $\mu\text{g}/\text{L}$  during winter and 8.8  $\mu\text{g}/\text{L}$  in the post-monsoon season. Domestic sewage, industrial effluents and vehicular emissions are the primary anthropogenic sources of Pb (Kara et al., 2017; Matta, Nayak, Kumar, Kumar, et al., 2020; Matta & Gjyli, 2016). The maximum Mn concentration was recorded at 15.1  $\mu\text{g}/\text{L}$  in winter, whereas 10.1  $\mu\text{g}/\text{L}$  in post-monsoon, 6.1  $\mu\text{g}/\text{L}$  in monsoon and 9.8  $\mu\text{g}/\text{L}$  in summer, respectively. Mn's primary industrial sources can attribute to iron and steel-related industries, paper mills, commercial refrigeration instruments, equipment and welding industries (USEPA, 2003). Mn may also be entering the environment by using methylcyclopentadienyl manganese tricarbonyl (MMT) as a gasoline additive (ATSDR, 2008).

The highest Cu value was observed at 9.9  $\mu\text{g}/\text{L}$  in winter followed by 7.9  $\mu\text{g}/\text{L}$  in summer, 9.2  $\mu\text{g}/\text{L}$  in monsoon and 9.5  $\mu\text{g}/\text{L}$  in post-monsoon, respectively. Copper is commonly used in electrical wiring and the production of alloys, pigments and piping. Furthermore, the input of pesticides enhances copper in agricultural and metropolitan's areas. Cu is an essential element of pesticides entering the river by agricultural runoff (Kansal et al., 2013 Pandey & Singh, 2017). The maximum Al concentration was found at 2.7  $\mu\text{g}/\text{L}$  in winter, 2.6  $\mu\text{g}/\text{L}$  in monsoon, 2.0  $\mu\text{g}/\text{L}$  in summer and 2.2  $\mu\text{g}/\text{L}$  in the post-monsoon season. The maximum concentration of Ni was near about ( $\sim 3.9$ ) all over the study period. Ni is mostly used in household products such as stainless steel, electroplating and Ni-Cd batteries; there is a good chance of enhanced Ni in metropolitan areas.

The maximum concentration of Cd was detected at 4.8  $\mu\text{g}/\text{L}$  in winter, 4.7  $\mu\text{g}/\text{L}$  in post-monsoon, 4.6  $\mu\text{g}/\text{L}$  in summer and 4.3  $\mu\text{g}/\text{L}$  in monsoon season. Various industries such as alloys and paints are the primary source of cadmium in the environment and are linked with particles and bottom sediments (Lydersen et al., 2002). Rivers continuously receive a minimal quantity of heavy metals from erogenous sources such as weathering of rocks. Continuous but relatively higher input of heavy metals to rivers and streams is linked to anthropogenic sources such as urban, agricultural and industrial wastewater and atmospheric deposition

**Table 3.** Calculation process of HPI for Ganga River water during winter season.

Heavy metals ( $\mu\text{g}/\text{L}$ )	Mean concentration ( $V_i$ )	Highest permissible value ( $S_i$ )	Unit weight ( $W_i$ )	Sub-index ( $Q_i$ )	$W_i^*q_i$
Zn	32.69	15000	0.0001	49.67	0.006
Pb	5.09	10	0.2017	50.95	10.277
Mn	4.83	300	0.0067	47.58	0.319
Fe	5158.58	300	0.0067	1861.19	12.514
Cu	4.23	1500	0.0013	3.156	0.004
Al	1.52	200	0.0101	16.75	0.168
Ni	2.58	20	0.1008	12.9	1.301
Cd	2.86	3	0.6723	95.33	64.756
Mg	3431.81	10000	0.0002	38.115	0.001
			$\sum W_i = 1.002$		$\sum W_i \times Q_i = 88.69$

**Table 5.** The variation in HPI values for Ganga River water samples at all sampling stations.

Sampling site No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
HPI values	83.68	97.78	67.78	75.76	92.87	86.85	75.84	70.51	84.98	78.59	77.26	84.44	70.93	76.51	68.74	79.73	88.19	76.65	74.77	77.31
Mean HPI value	79.45																			

(Sekabira et al., 2010). The highest Mg concentration was recorded at 4425.4  $\mu\text{g/L}$  in winter, 4812  $\mu\text{g/L}$  in summer, 4364.2  $\mu\text{g/L}$  in monsoon and 4368.5  $\mu\text{g/L}$  in post-monsoon. Magnesium and other alkali metals are mostly responsible for water hardness. A high dose of magnesium can cause several human body problems like muscle slackening, nerve problems and other personality changes.

Cobalt enters the aquatic environment from various sources like cobalt mining, sewage effluents, volcanic emissions, agricultural wastes and chemicals (Nagpal, 2004). The maximum Co concentration was detected at 12.1  $\mu\text{g/L}$  in summer, 9.8  $\mu\text{g/L}$  in winters, 8.8  $\mu\text{g/L}$  in monsoon and 8.8  $\mu\text{g/L}$  in post-monsoon, respectively. Rivers continuously receive a massive amount of heavy metals from erogenous sources such as weathering of rocks. Rapidly or intermittent but relatively maximum input of heavy metals to surface water and streams linked to human-made sources such as urban, industrial and domestic wastewater and atmospheric deposition. Comparing the observed data set showed that Fe, Cd and Mg's concentrations were higher than the standard limits of drinking water proposed by various governmental agencies (BIS, 2012; USEPA, 2009; WHO, 2017).

### 3.1. Heavy metal pollution index

HPI is a rating method that considers the composite influence of individual heavy metals on overall surface water quality. To determine the HPI of the river water sample, the average concentration of the nine selected metals Cd, Mg, Fe, Ni, Cu, Al and Pb have been in use. In the present study, Table 3 shows the HPI calculation process with mean values ( $M_i$ ), unit weight ( $W_i$ ) and standard permissible value ( $S_i$ ), and Table 4 represents the seasonal observation of HPI. The HPI values were also determined separately for every sampling site to compare the pollution load and determine the water quality for the selected locations and seasons (Table 5).

During the summer seasons, maximum heavy metal concentrations were found in the Ganga river water as compared to other seasons, and therefore, the maximum HPI values were calculated (90.33) for the summer seasons followed by during winter (88.69), monsoon (88.53) and in post-monsoon season (84.96). The HPI values for various monitoring stations varied from the range of 67.78–97.78 and are graphically presented in Figure 2. From the above results, site-2 and site-5 are attributed as prime sites responsible for substantial amounts of heavy metals in River Ganga water samples. The maximum HPI values were observed due to industrial effluents, domestic sewage and landfill leachate.

### 3.2. Principal component analysis

In accordance, with using varimax normalized rotation, the PCA was conducted for source identification. The rotated PC loadings are given in Table 6. Three PCs (eigenvalues >1) emerged with more than 72.1% of the cumulative variance (Figure 3). The first principal component (PC1) with 37.7% of variance comprises Cu, Ni and Co with high loadings. Immense Cu mining is associated with the area and may have led to Cu, Ni and Co concentration. Ni and Co have studied to relate between Cu mining and smelting

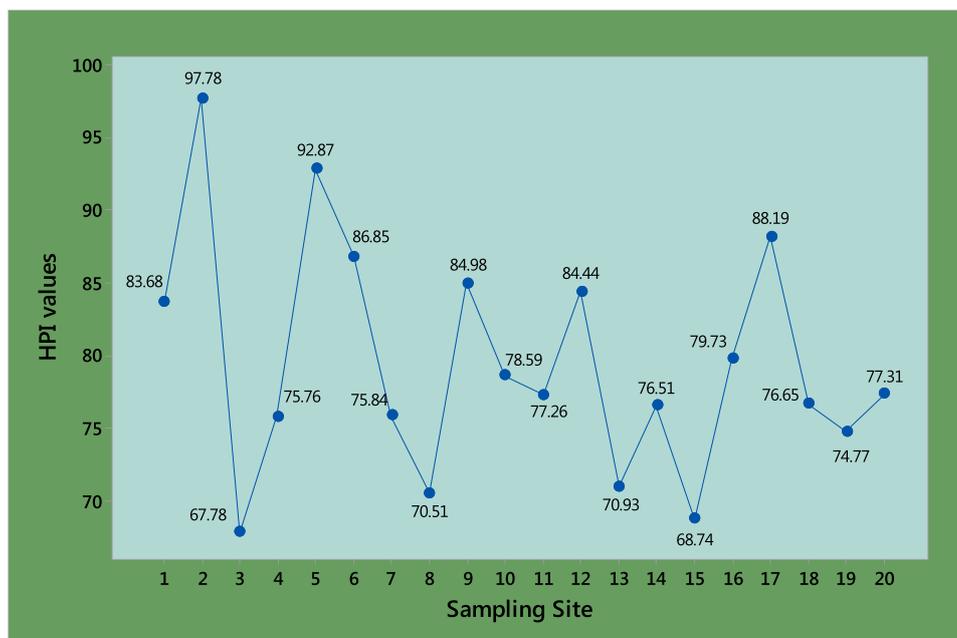


Figure 2. HPI values for Ganga River water samples at each monitoring station.

(Ikenaka et al., 2010). The second principal component (PC2) contributed Fe and Ni at 21.6%. The third component (PC3) explained 12.7% of our result's variance and was associated with Zn and Al. This PC2 seemed to have arisen from human-made sources, like industrial and vehicular pollution. Zn is mostly used as a vulcanization agent in vehicle tyres, and the maximum wearing rate at the high temperature in the area may contribute to the high Zn content in the environment Zn is used as lesser additives to gasoline and many auto-lubricants and is released during combustion and spillage process (Ipeaiyeda & Dawodu, 2008).

### 3.3. Clustering of sampling sites

To make out the clusters of different sampling sites and to derive similar and dissimilar polluted locations, HCA was performed using the data sets of water quality parameters considered in our study for all seasons as shown in Figure 2. Many applications of CA to assess water quality have been reported (Singh et al., 2005; Zhao et al., 2012). The first cluster comprises 1, 11, 4, 7, 17 and 14 sites while the rest other sampling sites are constituted in the second (sites 3, 10, 20, 13, 19, 16) and third cluster (sites 2, 15, 8, 18, 5, 12, 6, 9) (Figure 4).

Table 6. PC2 loadings (varimax normalized) for the metals in the water of the Ganga River.

Variables	Components		
	PC1	PC2	PC3
Zn	0.254	-0.238	0.539
Pb	0.272	0.358	0.370
Mn	0.302	0.182	-0.291
Fe	0.271	0.457	-0.122
Cu	0.407	0.281	-0.140
Al	-0.188	0.240	0.647
Ni	-0.310	0.472	-0.067
Cd	-0.349	0.246	0.089
Mg	0.313	-0.360	0.057
Co	0.420	0.142	0.131
% of total variation	37.7	21.6	12.7
Cumulative %	37.7	59.4	72.1

### 3.4. Hazard quotient and index

Ganga River water is used for agriculture, commercial and domestic purposes. In the Himalayan region's hilly area, most people consume river water directly without any treatment for their daily purposes. Therefore, the determination of HQ and HI is significant to assess the health risk status. The seasonal value of HQ and HI was found higher for children than adults; consequently, children have a high risk of getting affected by heavy metal toxicity (Table 7). The HQ value for each metal was observed below 1 throughout the study period, which elicits minimal risk to human health (Kumar et al., 2021). The highest HQ was reported for Fe ( $7.47E-01$ ) during the monsoon season for the child, whereas Al ( $5.16E-05$ ) had the lowest HQ for adults during the post-monsoon season metals. The study area shows a huge variation in climatic conditions, from cold to hot summer and receiving heavy rainfall during the monsoon season. The rainfall-runoff brings lots of sedimentation, agricultural, industrial and domestic wastes into Ganga River water from the hilly area. Many tourist and developmental activities are going on in this region due to adventurous destinations and sacred places. The high contribution of Fe to posing health risks is due to geogenic processes. The highest HI values for children and adults were found at  $1.63E+00$  and  $1.47E+00$  respectively during the summer season. The lowest values were reported during the monsoon season for the child ( $1.52E+00$ ) and adults ( $1.37E+00$ ). The seasonal HI values for children and adults were presented graphically in Figure 5. The HI values were reported  $>1$  throughout the study period, indicating the potential health risk to children and adults for direct ingestion of Ganga River water.

## 4. Conclusion

Concentrations of heavy metals such as Al, Cr, Co, Cu, Fe, Mn, Ni, Pb and Zn in the Ganga River's water demonstrated great seasonality. Overall outcome of the results during the study defines that heavy metal concentration in the river is increasing with the metals, where Fe and Mg were found

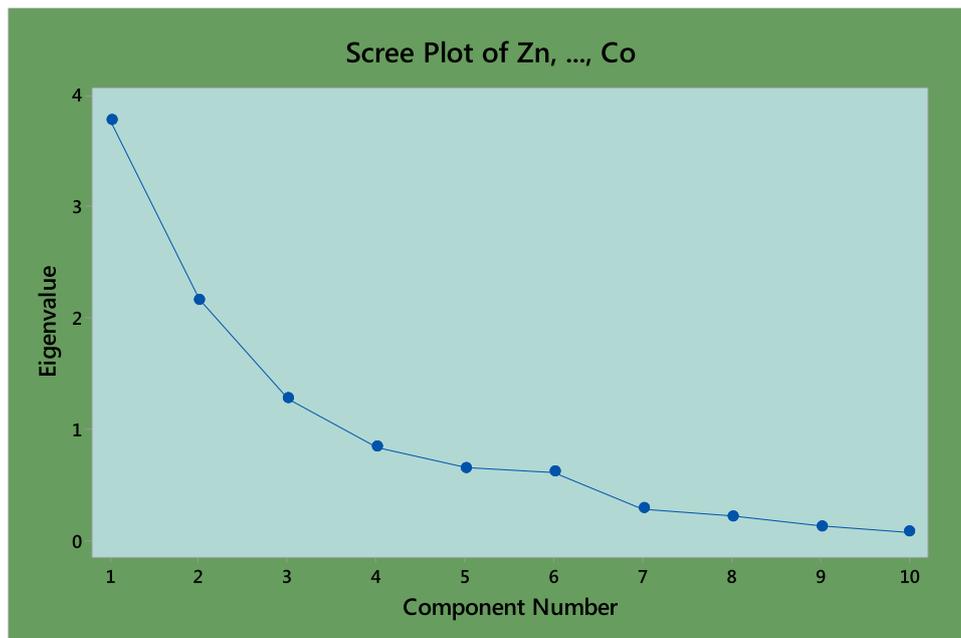


Figure 3. Screen plot of various PCs.

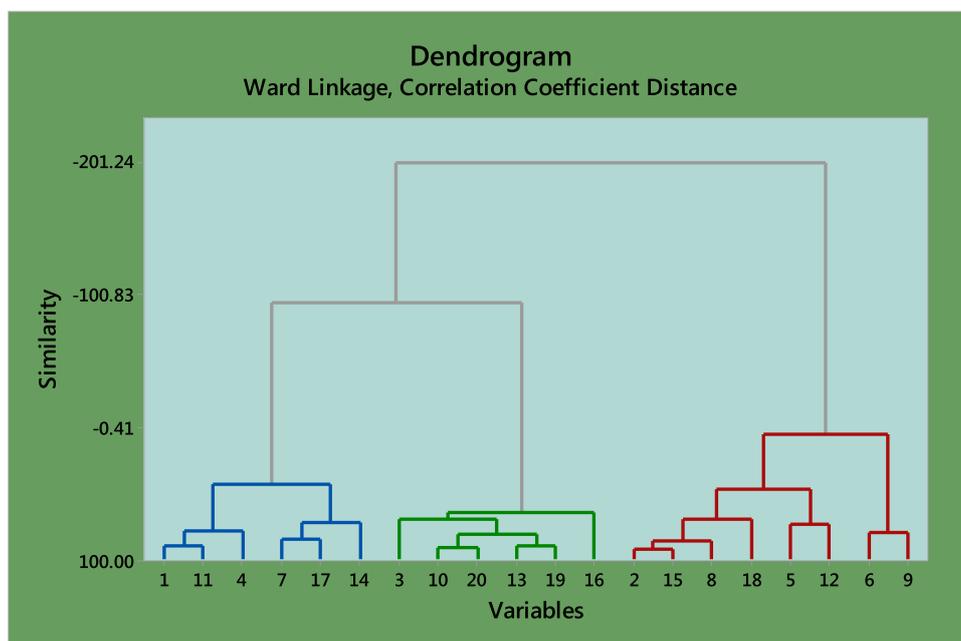
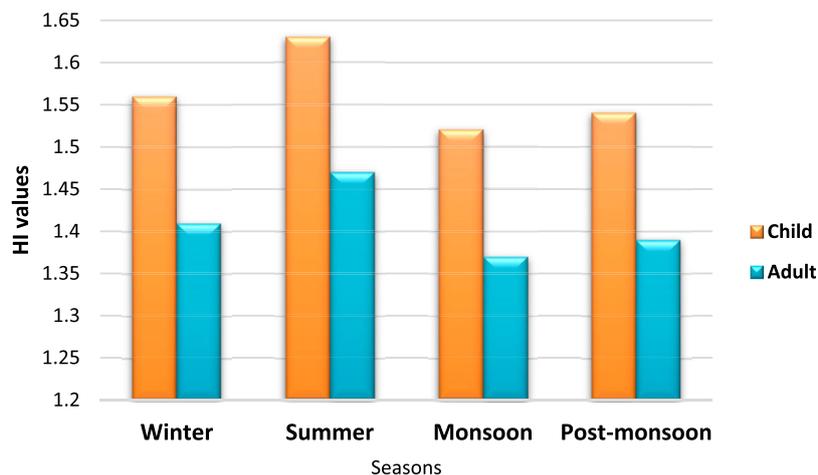


Figure 4. Hierarchical dendrogram of various sampling locations.

Table 7. The seasonally HQ and HI values of individual heavy metal for Ganga River water.

Heavy metals ( $\mu\text{g/L}$ )	$R_f D_{\text{ing}}$ ( $\mu\text{g/kg-day}$ )	Winters		Summer		Monsoon		Post-monsoon	
		$HQ_{\text{ing}}$		$HQ_{\text{ing}}$		$HQ_{\text{ing}}$		$HQ_{\text{ing}}$	
		Child	Adult	Child	Adult	Child	Adult	Child	Adult
Zn	300	4.46E-03	4.02E-03	4.69E-03	4.23E-03	4.16E-03	3.75E-03	4.41E-03	3.97E-03
Pb	14	1.49E-02	1.34E-02	1.33E-02	1.20E-02	1.34E-02	1.21E-02	1.39E-02	1.25E-02
Mn	20	9.88E-03	8.91E-03	8.71E-03	7.86E-03	7.57E-03	6.82E-03	1.79E-02	1.61E-02
Fe	300	7.04E-01	6.34E-01	7.39E-01	6.66E-01	7.47E-01	6.73E-01	7.32E-01	6.60E-01
Cu	40	4.33E-03	3.90E-03	4.42E-03	3.98E-03	3.94E-03	3.55E-03	3.76E-03	3.39E-03
Al	1000	6.22E-05	5.61E-05	5.81E-05	5.24E-05	8.22E-05	7.41E-05	5.73E-05	5.16E-05
Ni	20	5.28E-03	4.76E-03	5.56E-03	5.02E-03	5.44E-03	4.91E-03	5.36E-03	4.83E-03
Cd	0.5	2.34E-01	2.11E-01	2.45E-01	2.21E-01	2.37E-01	2.14E-01	2.24E-01	2.02E-01
Co	0.3	5.85E-01	5.27E-01	6.08E-01	5.48E-01	5.05E-01	4.55E-01	5.39E-01	4.86E-01
HI		1.56E+00	1.41E+00	1.63E+00	1.47E+00	1.52E+00	1.37E+00	1.54E+00	1.39E+00



**Figure 5.** Comparable seasonally HI values for children and adults.

to be higher than the standard limits for drinking water of various governmental agencies. The study provides important information for future studies and conservation plans and control of drainage in the basin under various initiatives like National Mission for Clean Ganga, Govt. of India. The seasonal HPI values indicated that the Ganga River water is very close to being highly contaminated by heavy metals. Hence, it is important to take precautions before the use of river water for drinking water. PCA analysis indicated three components responsible for the data set covering 72.1% of the total variance and grouped in three PCs. The highest weight factors of the element Zn, Fe, Cu, Al, Ni and Co lead to the formation of PCs. On the other hand, the CA was performed to identify the relative monitoring stations contributing to similar pollution sources. The CA results support the evaluation of pollution index values of grouped sampling locations. Fe contributes majorly to higher HQ while Al represents lower HQ during the study period. The HI for the complete study period was recorded  $>1$ , indicating potential non-carcinogenic health hazards through ingestion of river water. The assessment clearly defines the current condition while creating a big challenge for the government agencies and policymakers while planning for ecological conditions of River Ganga System in Uttarakhand. Thus, it is suggested that precautions should be taken while consumption of river water at certain locations and necessitate appropriate policies to control the heavy metal pollution in the Ganga River System. Furthermore, it is also suggested that while creating any management or conservation plan, mass awareness with people participation is suggested using tools of science communication for better approach.

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