Comprehensive Spatio-temporal Benchmarking of Surface Water Quality of Hindon River, India– a Tributary of River Yamuna, India

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Comprehensive spatio-temporal benchmarking of surface water quality of Hindon River, India– a tributary of river Yamuna, India

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Abstract

The quality of Hindon River, western Uttar Pradesh, India was benchmarked with 19 sampling sites by analysing seventeen water quality parameters and eight heavy metals for pre and post-monsoon seasons to assess the existing quality of water which is a milestone for preparing roadmap for its betterment. Indices associated with water quality and heavy metals were computed to scale the accurate state of risk associated to its use for drinking and irrigation. During the pre and post-monsoon seasons, only four and five sites were found having safe water quality index (WQI) values respectively. The average WQI (2015–2019) for pre and post-monsoon seasons ranged between 8.69–706.47 and 7.20–341.56 respectively. During pre-monsoon and post-monsoon seasons *w.r.t.* drinking purpose, heavy metal pollution index ranged between 0.76–4470.78 and 0–1425.31 respectively; heavy metal evaluation index ranged between 0.21–163.11 and 0.00–57.70 respectively; contamination evaluation index ranged between -7.79–155.11 and -8.00 to 49.70 respectively. During pre-monsoon and post-monsoon seasons *w.r.t.* irrigation purpose, heavy metal pollution index ranged between 0.82–1492.71 and 0.00–300.06 respectively; heavy metal evaluation index

ranged between 0.10–20.44 and 0.00–5.66 respectively; contamination evaluation index ranged between -15.97–10.03 and -17.00 to -6.08 respectively. The heavy metals were positively correlated where highest value observed between Cu and Mn (correlation coefficient value 0.95). For physico-chemical parameters, observed adj- R^2 value ranged from 0.50 for pH to 0.98 for total hardness and calcium. PCA analysis achieves three principle components (PCs) for physico-chemical and three PCs for heavy metals that explained 88.67% and 89.68% variability of the original data set, respectively.

Keywords Benchmarking, GIS, Pollution indices, Hierarchical cluster analysis, Principal component analysis

Introduction

Water being an essential commodity for human life, its availability in superior quality *w.r.t.* its use in drinking, irrigation, cultural has become one of the greatest challenges of the present world. The concern for sustainable water availability in terms of quality and quantity lies in building basic provision of water supply to meet this basic need for human life, more so in the rural areas of Indian sub-continent. Out of the available sources, only few sources of surface and ground water are safe for human health due to various point and non-point sources of pollution. The rivers and surface water plays an essential role especially in agriculture and drinking water in rural areas of world. The situation has worsened over time due to a rapid increase in disposal of agriculture, industrial and domestic waste into the water bodies without any treatment. The increase in population also accelerated the use and pollution of surface water significantly. Unequal access to poor quality water by different user groups, economic strata, and regions, as well as a steady deterioration of water quality compound this untoward condition of water scarcity. The river catchments are facing huge crisis of untreated wastewater disposal from industries, rural and urban areas (Phiri et al. 2005). Developing country like India, it is a major challenge to maintain the water quality of

its water bodies. The indiscriminate development in the form of urbanization, industrialization has significantly influenced the river water quality (Singh and Singh 2007).

Benchmarking of water sources using primary dataset helps in improving performance qualitatively for human health by providing accurate and authentic information of quality of water available. It also ensures judicious use of water resources and also identifies quantum of unaccounted discharge of wastewater. Inefficiency in the use of good quality water results in worsening of already difficult situations and further pollutes our food upon irrigation through poor quality water. Geochemical processes to understand the path and its impact on environment are gaining wide attention in the present world. Riverine systems are key link in the geological processes. In the modern world, there has been a vast surge of identifying the sources and the impact of heavy metals in the riverine environment. The providence of heavy metals present in the river systems is of immense significance. In the past few decades, the global interest on heavy metal contamination of hydrosphere has been magnified due to its damaging impacts on the ecosystem. In freshwater ecosystems, heavy metals enter through natural weathering and atmospheric precipitation as well as anthropogenic activities in which later are more perilous (Kumar et al. 2019). Noxious heavy metals are judged as severe ecological pollutants in the fresh water environment. These heavy metals have potential to bio-accumulate in the biological systems and they persist and cause toxicity even at very low amount (Wang et al. 2017). The anthropogenic sources of heavy metal pollution pose more health risks to human and environment (Benson et al. 2018). The degree of heavy metal pollution has been amplified significantly with hasty industrialization (Vu et al. 2017). These heavy metals can be relocated to human body through the food chain and cause health issues (Jiang et al. 2008). Drinking water intake and irrigation through the contaminated water are the most common pathways for the entry of heavy metals in human body. The heavy metals are potent carcinogens *w.r.t.* risk associated to human health (Kai et

al. 2018; Smith et al. 1992). Furthermore, long stretch exposure of heavy metals even at low concentrations can be a persuasive health hazard (Jiang et al. 2008).

The evaluation of surface water quality of some past studies was mainly focussed on few physico-chemical parameters that can only reproduce an inequitable information about the actual quality of water (Xia et al. 2018; Nong et al. 2020). For a holistic quantification of water class, an extensive long term data is required over space and time. With the ease of selection of variables for developing a quality or pollution index, one can effortlessly devise a method to represent the qualitative status water in a single unit. Moreover, a model or index is very useful for specific research information (Avigliano and Schenone 2016). The distribution pattern of water quality variables and heavy metals for characterizing the potential ecological risk in surface water has always been a very important concern for policymakers and scientific community globally.

In order to sustain the water in terms of its quality, it is utmost imperative to benchmark current status of surface quality and rank them accordingly. Keeping this in view, the present study was conducted to determine the impact of various anthropogenic actions on riverine system water quality and establish the link between different exhaustive water quality parameters including toxic heavy metals in Hindon River, western U. P., India. The results of this study will be definitely helpful for the stakeholder agency, policy makers to devise instantaneous measures to mitigate the surface water pollution and restoring the natural water bodies. Further, our study would contribute in achieving goals 3, 6, 12, 14, 15 and 17 of United Nations' sustainable development goals (SDGs) and contribute to prepare a roadmap for inclusive appraisal of water contamination in surface waters globally.

Materials and Methods

Study vicinity

100 Hindon River originates in close proximity to rural area Saharanpur district, upper Shivalik
101 hills range of western part of Uttar Pradesh, India which lies under Doon valley having geo-
102 coordinates 30.073814 N to 28.41205N and 77.745586 E to 77.49230E. The catchment area
103 of Hindon River is 7082 km² and it travels a distance of 400 km (approximately) before
104 joining the River Yamuna near Tilwara village, Gautam Buddha Nagar, Uttar Pradesh, India.
105 In this study, we covered a catchment area of 4141.64 sq km and a length of 305 km which
106 covers 75% length of the river. The study lies between 30.073814N to 29.051591N and
107 77.745586E to 77.4538188E. In our study area, two tributaries of Hindon viz. Kali and
108 Krishni Rivers also contribute to water quality of Hindon. The climatic condition of the area
109 is characterized as a moderate subtropical monsoon. The chief land uses include agriculture
110 in the riparian areas of the river in which the farmers cultivate vegetables, sugarcane, cereal
111 crops etc. Mostly the soil of this area is silty loam. During the monsoon season, the river flow
112 increases to a level approx. 10 to 15 times higher than the lean season flow and flooding also
113 occurs in the adjacent areas. A general plan for sampling locations of Main River with respect
114 to its quality is illustrated in Fig. 1.

Fig. 1 Sampling locations of the study area

Table 1 Sampling locations with geo-coordinates and possible source of pollution.

S.No	Location	Symbol	Latitude	Longitude	Source of pollution	Landuse
1	Mandowala Village	H1	30.0738140	77.7455860	NP	R
2	Nagdehi	H2	30.1215188	77.6829048	NP	R
3	Gagalheri	H3	29.9759000	77.6554000	NP	R
4	Paragpur	H4	29.9243198	77.5903906	NP	R
5	Naklaur village	H5	29.9016736	77.5955900	P; NP	R
6	Nandi Firozpur	H6	29.8690500	77.5729019	P; NP	R
7	Maheshpur	H7	29.7048670	77.561390	P; NP	R
8	Kutvi village	H8	29.4210858	77.5123445	NP	R

9	Charthawal	H9	29.5540761	77.5476463	NP	R
10	Nasirpur	H10	29.4917490	77.5233520	NP	R
11	Titavi	H11	29.4784876	77.5180580	P; NP	R+U
12	Savtoo village	H12	29.4210858	77.5123445	NP	R
13	Budhana Village	H13	29.2945831	77.4842398	P; NP	R+U
14	Chandheri	H14	29.2693266	77.4914197	P; NP	R
15	Kutubpur	H15	29.2225740	77.526296	NP	R
16	Atali	H16	29.2115368	77.5215919	NP	R
17	Khiyai	H17	29.1132310	77.4402220	NP	R
18	Barnawa	H18	29.1014850	77.4311322	NP	R
19	Kinauni	H19	29.0515910	77.4538188	NP+P	R+U

(NP: Non-point source pollution, P: Point source pollution, R: Rural, U: Urban)

Water sampling and preservation

Water samples from 19 different locations of mainstream covering upper, middle and downstream regions were collected (Table 1) with information on possible sources of pollution. All these samples were representative of the actual condition of Hindon River. The water samplings for physico-chemical variables were conducted during 2015 to 2019 for two seasons *i.e.* pre monsoon (February to May) and post-monsoon (October to January) making a total of 10 sampling seasons. The water samples for heavy metals analysis were collected using collection vessel immersion technique at approximately 15 cm below the water surface using high-density polyethylene bottles having capacity 1000 ml (CETESB 2001) during pre and post-monsoon of 2019 making it two sampling seasons. The samples were collected and preserved in ice box and transported to the laboratory.

Water quality variables analysed

Water samples collected and preserved were analyzed according to the standards procedures (APHA 2005; 2012) and standard procedures as per manuals of different instruments. Methods of analysis and preservation of water samples are represented in Table 2. Each water sampling was done with three replications. pH, electrical conductivity, turbidity, and dissolved oxygen was analyzed using pH Meter (model: systronics μ pH system 361, India), conductivity meter (model: systronics–306), turbidity meter (model: Extech TB–400, United States) and dissolved oxygen meter (model: Extech DO–210, United States) respectively. Spectrophotometric and flame photometer analysis were conducted using double beam UV-visible spectrophotometer (model: Systronics–2701, India) and flame photometer (model: Systronics–128, India). Heavy metals were analysed using an atomic absorption spectrophotometer (Analytikjena contrAA 300, Germany) after acid digestion with concentrated HNO₃.

Table 2 Analytical methods for physico-chemical variables and heavy metals.

S. No.	Parameter	Unit	Method Used	Preservation	Analysis Location
1	pH	NA	pH meter	NA	On Site
2	EC	μ S/cm	EC meter	NA	On Site
3	TDS	ppm	Filtration and Oven dry @ 105°C	Cool @ 4°C	Laboratory
4	Turbidity	NTU	portable turbidity meter	NA	On site
5	DO	ppm	portable DO meter	Cool @ 4°C	On Site
6	BOD	ppm	Azide fixation at 20°C (5 Days test)	Cool @ 4°C	Laboratory
7	K ⁺	ppm	Flame Photometer	Cool @ 4°C	Laboratory
8	Na ⁺	ppm	Flame Photometer	Cool @ 4°C	Laboratory

9	Total Hardness	ppm as CaCO_3	Titration with EDTA-2Na and EBT as an indicator	Cool @ 4°C	Laboratory
10	Ca^{2+}	ppm	EDTA Titration	Cool @ 4°C	Laboratory
11	Mg^{2+}	ppm	EDTA titration method	Cool @ 4°C	Laboratory
12	Cl^-	ppm	Silver nitrate titration method	Cool @ 4°C	Laboratory
13	SO_4^{2-}	ppm	Turbidimetric	Cool @ 4°C	Laboratory
14	NO_3^-	ppm	Cadmium reduction method	Cool @ 4°C	Laboratory
15	PO_4^{2-}	$\mu\text{g/L}$	Molybdate ascorbic acid method	Cool @ 4°C	Laboratory
16	Total Alkalinity	ppm	H_2SO_4 titration method	Cool @ 4°C	Laboratory
17	HCO_3^-	ppm	Acid titration with phenolphthalein indicator	Cool @ 4°C	Laboratory
18	Cd	$\mu\text{g/L}$	Acid digestion followed by		
19	Cr	$\mu\text{g/L}$	Atomic Absorption		
20	Pb	$\mu\text{g/L}$	Spectrophotometry		
21	Zn	$\mu\text{g/L}$		2 ml conc.	
22	Mn	$\mu\text{g/L}$		nitric acid/L	Laboratory
23	Cu	$\mu\text{g/L}$		sample	
24	Fe	$\mu\text{g/L}$			
25	Ni	$\mu\text{g/L}$			

144 (ppm: Parts per million; NA: Not applicable; $\mu\text{S/cm}$: Micro Siemens centimetre⁻¹, NTU:

145 Nephelometric turbidity unit, $\mu\text{g/L}$: Micrograms per litre; EC: Electrical Conductivity, TDS:

146 Total dissolved solids, DO: Dissolved Oxygen, BOD: Biochemical oxygen demand, Ca^{2+} :

Calcium, Mg^{2+} , Magnesium, TH: Total hardness, TA: Total alkalinity, Na^+ : Sodium, K^+ : Potassium, Cl^- : Chloride, NO_3^- : Nitrate, PO_4^{2-} : Phosphate, SO_4^{2-} : Sulphate)

Computation of Water Pollution Indices

Four nos. of water pollution indices *viz.* water quality index, heavy metal pollution index, heavy metal evaluation index and contamination index were computed using the measured value of variable and standard permissible limit of the variable.

Water quality index (WQI)

The WQI was computed on weighted arithmetic mean method (Brown et al. 1970; Cude 2001). The WQI corresponds to a single numeric value which reflects the authentic value for the quality of water and it is cumulative indicator of environmental variables. The 15 physico-chemical variables (pH, EC, TDS, turbidity, DO, BOD, Na, TH, Ca, Mg, Cl^- , SO_4^{2-} , NO_3^- , PO_4^{2-} and TA) were used for the computation of WQI as follows:

$$Q_i = (O_i - I_i) / \{(S_i - I_i) \times 100\}$$

Where, Q_i : sub-index of individual (ith) parameter, O_i : Observed/ analysed value, I_i : Ideal value, S_i : Standard value for ith parameter. For most of the parameters, the value of ideal value is zero ($I_i = 0$) but for pH and dissolved oxygen (DO), it is not zero ($I_i \neq 0$). The I_i value for pH and DO is 7 and 14.6 respectively.

$$W_i = k / S_i$$

Where, W_i : unit weightage of ith parameter, k: proportionality constant, S_i : standard value for i^{th} parameter and, $W_i = 1 / (\sum_{i=1}^n 1/S_i)$. The numeric vales of S_i , I_i and permissible limits for water quality variables are given in Table 3. WQI is computed by following equation and according to WQI, suitability of water for consumption is judged:

$$WQI = \sum_{i=1}^n W_i Q_i / \sum_{i=1}^n W_i$$

170 Where, W_i : unit weightage of i^{th} parameter, Q_i : sub-index of individual (i^{th}) parameter and n :
 171 total number of variables. The computed values of WQI are categorized as excellent (WQI:
 172 0–25), good (WQI: 26–50), poor (WQI: 51–75), very poor (WQI: 76–100) and unsuitable
 173 (WQI >100).

174 **Table 3** Permissible limits prescribed by different National and International agencies and
 175 standard (Si) and ideal values (Ii) for i^{th} parameters.

S. No.	Parameter	Unit	WHO	USEPA	BIS	CPCB	CCME	Drinking	
								Si	Ii
1	pH	–	6.5– 8.5	6.5–8.5	6.5– 8.5	5.5–9.0	6.5–9.0	7.5	7
2	EC	$\mu\text{S cm}^{-1}$	1500	–	–	–	–	250	0
3	Turbidity	NTU	5	–	1	–	–	5	0
4	TDS	ppm	1000	500	500	–	–	1000	0
5	DO	ppm	–	–	–	–	5.5–9.5	5	14.6
6	BOD	ppm	–	–	–	30	–	5	0
7	Ca	ppm	200	–	75	–	–	75	0
8	Mg	ppm	150	–	30	–	–	30	0
9	TH	ppm as CaCO ₃	500	–	200	–	–	500	0
10	HCO ₃ [–]	ppm	–	–	–	–	–	–	–
11	TA	ppm	–	–	200	–	–	200	0
12	Na	ppm	200	–	–	–	–	200	0
13	K	ppm	–	–	–	–	–	–	–
14	Cl [–]	ppm	250	250	250	–	120	250	0
15	NO ₃ [–]	ppm	45	45	45	16	2.9	45	0

16	PO ₄ ²⁻	µg L ⁻¹	0.3	—	—	5	—	5	0
17	SO ₄ ²⁻	ppm	500	500	200	—	—	500	0

Heavy metal pollution index (HPI)

The HPI represents the superiority and suitability of water for drinking purpose pertaining to the heavy metals (Prasad and Bose 2001). The values of heavy metals analysed during pre and post-monsoon seasons are used in calculating HPI. It is computed by weighted arithmetic mean technique as follows (Mohan et al. 1996):

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

Where, HPI: Heavy metal pollution index, Qi: Quality rating of individual ith metal, Wi: Weightage unit of individual variable, Qi: Quality rating of individual ith metal and was computed as follows: $Q_i = (M_i / S_i) \times 100$, where, M_i : Monitored/ analysed value of the individual ith metal, S_i : Standard permissible value of individual metal, W_i (weight unit) is inversely proportional to recommended permissible upper limit and given by the expression as follows: $W_i = 1 / S_i$, where, S_i : Standard permissible value of individual metal. S_i and W_i values for each heavy metals selected for HPI computation were given in Table 4 (WHO 2011). Prasad and Bose (2001) have articulated that the critical pollution index score for drinking water is 100. Table 4 represents the permissible limits of heavy metals *w.r.t.* drinking (WHO 2011; BIS 2012; EWQS, 2007; CCME 2014) and irrigation (Ayers and Westcot 1994) purpose, standard values (S_i) and weightage unit (W_i) values *w.r.t.* drinking as well as irrigation water.

Table 4 Permissible limits of heavy metals, standard values (S_i) and weightage unit (W_i) values *w.r.t.* drinking and irrigation water.

S. No.	Heavy Metals	WHO (2011)	BIS (2012)	EWQS (2007)	CCME (2014)	Ayers and (Drin)	S_i (Drin)	W_i (Drin)	S_i (Irri)	W_i (Irri)
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Westcot (1994)										
1	Cd	3	3	3	0.18	10	3	0.3333	10	0.1
2	Cr	50	50	–	–	100	50	0.0200	100	0.01
3	Pb	10	10	10	2	5000	10	0.1000	5000	0.0002
4	Zn	4000	5000	3000	30	2000	5000	0.0002	2000	0.0005
5	Mn	400	100	100	–	200	100	0.0100	200	0.005
6	Cu	2000	50	2000	2	200	50	0.0200	200	0.005
7	Fe	1000	300	300	300	5000	300	0.0033	5000	0.0002
8	Ni	70	20	20	65	200	20	0.0500	200	0.005
								$\sum W_i = 0.537$ $\sum W_i = 0.126$		

(Drin: Drinking; Irri: Irrigation)

Heavy metal evaluation index (HEI)

The HEI method gives the overall quality of the water with respect to heavy metals contamination. For the computation of HEI, the monitored numeric values of heavy metals in the present study were used. This index classify into three categories, which include low (HEI < 10), medium (HEI = 10–20) and high (HEI > 20). The index is computed using the following equation (Edet and Offiong 2002; Prasanna et al. 2012):

$$HEI = \sum_{i=1}^n Mc/M_{max} ,$$

Where, Mc: monitored value of the parameter, M_{max} : the maximum permissible concentration of the ith parameter, n: total number of variables.

Contamination index (CI)

The contamination index measures the relative contamination of different metals separately and manifests the combined effects of all metals. It was computed as follows (Backman et al. 1998): $Cd = \sum_{i=1}^n Cfi$, where Cfi was calculated as the following equation: $Cfi = CAi/CNi-1$,

where, C_{fi} : Contamination factor for i^{th} metal, CA_i : Measured value for i^{th} metal, CNi : upper allowable limit of i^{th} metal. (Same as S_i in HPI), N refers to the normative value. The resultant Cd values are grouped into three classes: high ($CI > 3$); medium ($CI = 1-3$) and low ($CI < 1$).

Spatial analysis

Geographical information system (GIS) is one of the finest and authenticated tools used in statistical interpolation of diverse research field data to create spatial maps and thematic layers. This tool was used to establish relationship among variables to summarize the river water quality in a simple image format. In the present study, to generate spatial distribution maps of all the indexed parameters the inverse distance weighted (IDW); interpolation method was performed using QGIS 3.20 Odense software. The IDW technique was employed for the deterministic model approach and calculating the unknown values based on the nearness by points other than values far off. This interpolation technique is widely accepted and used in the field of spatial distribution analysis for describing the contaminants distribution patterns in space and time (Tiwari et al. 2016; Vaiphei et al. 2020).

Statistical Analysis

The central tendency and dispersion of all the parameters were performed using descriptive analysis of the Hindon river dataset. The data of physico-chemical variables and heavy metals were analysed using factorial analysis of variance (ANOVA) and further post-hoc test were performed for pair-wise comparison by tukey's honest significant difference (HSD) test at p -value=0.05. Pearson's correlation coefficient analysis was done to measure the linear bivariate relationship between all the 25 variables (17 physico-chemical and 8 heavy metals) at p -value =0.05 and 0.01. To analyse the high dimension data in better way, multivariate techniques viz. principle component analysis (PCA) and hierarchical cluster analysis (HCA) were performed. Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy and Bartlett's

test of sphericity were done prior to PCA to ensure application adequacy of PCA. KMO closer to 1 and Bartlett's test with p-values <0.05 were both essential criteria to carry out PCA. PCA was done to rank sites and to find their sources of origin of metals. HCA was done adopting Euclidean distance method on 17 physico-chemical parameters and 8 heavy metals to identify different physico-chemical and heavy metal group and clustering the sites with similar physicochemical and heavy metal load independently. Following the approach of the Wang and Xing (2017), PCA results were extendedly used to rank the sampling sites of Hindon river by evaluation score (ES), calculated by the formula:

$$ES_{n \times 1} = \mathbf{Y}_{n \times p} \mathbf{e}_{p \times m} \boldsymbol{\lambda}_{m \times 1}; m \leq p$$

where, $\mathbf{Y}_{n \times p}$ is a matrix of order $n \times p$, that contains normalized observed value, where n is the number of sites and p is the number of parameters, $\mathbf{e}_{p \times m}$ a matrix of order $p \times m$, contains m eigen vectors of length p . $\boldsymbol{\lambda}_{m \times 1}$ is a $m \times 1$ vector of eigen value. All the statistical analyses were performed through open source software RStudio desktop (R version 4.0.2).

Results and Discussion

Spatio-temporal variation of physico-chemical properties of Hindon River

The spatial (19 locations) and temporal (average of pre and post-monsoon seasons from 2015 to 2019) distribution of water quality parameters of Hindon River is illustrated in Fig. 2(A–Q) *w.r.t.* variables analysed. The water quality variables were compared with WHO (2011) and BIS (2012).

pH is the strength of acidity or alkalinity of a liquid which shows the hydrogen ions concentration of any liquid. It is a key parameter for reaction equilibrium and chemical solubility of a liquid (Al-Saffawi. and Al-Shanona 2013). In the present study, pH ranged from 6.28 to 8.17 in pre monsoon (mean 7.03 ± 0.31 SD) and 6.66 to 7.43 in post-monsoon (mean 7.43 ± 0.28 SD) (Fig. 2A). In pre monsoon season, reasonably low pH was recorded as

compared to post-monsoon. There is significantly difference in seasons and sampling sites ($p < 0.05$). The variation in pH is due to different activities of domestic and industrial inflow. The acidic nature of river water can cause the fatality of several aquatic lives while alkaline nature can lead to precipitation reactions as well as the death of aquatic organisms.

Electrical conductivity (EC) is a measure of electric current movement in water. Chemically pure water does not conduct electric current. EC can be affected by many factors such temperature, precipitation and geology of a certain area. Total Dissolved Solids (TDS) is the measure of different kinds of salts dissolved in natural water. A high amount of dissolved solids in the river water affects the specific mass of water, regulation of osmotic pressure in freshwater fishes, gas solubility, and use of water for a variety of purposes. EC ranged from 1014.36 to 3837.55 $\mu\text{S cm}^{-1}$ in pre monsoon (mean 2176.70 ± 561.87 SD) and 215.04 to 2954.13 $\mu\text{S cm}^{-1}$ (mean 1539.49 ± 504.5 SD) (Fig. 2B) in post-monsoon as compared to permissible limit of 1500 $\mu\text{S cm}^{-1}$ (WHO 2011). As a thumb rule, high values of EC represent the greater concentration of dissolved ions in the water. TDS ranged from 771.48 to 2580.40 ppm (mean 1642.05 ± 429.46 SD) in pre monsoon and 345.20 to 1872.97 (mean 1038.56 ± 339.64 SD) ppm in post-monsoon (Fig. 2C) as compared to permissible limit of 1000 ppm (WHO 2011). The significant difference ($p < 0.05$) in EC and TDS is consequence of unmanaged disposal of domestic, agricultural and industrial wastewater in fresh water. The high values of EC and TDS in water result in making water unsuitable for irrigational and drinking purposes. High concentrations of TDS and EC in drinking water can cause several health problems such as abortion, cancer, and disorders of alimentary canal, respiratory system, nervous system, coronary systems.

Turbidity is associated to the presence of suspended particles of organic and inorganic origin. It is the ability of water molecules for penetration of light. It affects the aquatic photosynthesis due to the penetration of sunlight into the water bodies (Romero-Rodríguez et

al. 2020). Turbidity values varied from 2.07 to 59.73 NTU and 1.15 to 44.40 NTU in pre and post-monsoon respectively (average 36.69 ± 15.13 SD and 18.50 ± 11.56 SD in pre and post-monsoon seasons respectively) as compared to the criterion limit of 5 NTU (BIS 2012). Higher value of turbidity was recorded in pre monsoon as compared to post-monsoon at all the locations (Fig. 2D). The maximum turbidity was recorded in 2019 pre monsoon season at site H19. This was because of the addition of pollution load from domestic and industrial drains Meerut district and also due to load of Krishni River.

Dissolved oxygen (DO) is essential for the survival of aquatic life. It is consumed by the aquatic living beings including plants, animals, algae, and bacteria in the water column and sediments. The DO value ranged from 0.00 to 8.42 ppm (mean 3.28 ± 1.53 SD) and 2.69 to 8.75 (mean 5.91 ± 1.39 SD) in pre and post-monsoon respectively (Fig. 2E). The elevated load of organic stuff in the water is responsible for disturbing the natural oxygen budget of a water body which directly affects the quality of water as well aquatic environment. The maximum DO was observed during post-monsoon season due to dilution effect on pollutants and low temperature.

BOD is a very crucial parameter of organic pollution in water which further affects the other variables of water (Ali et al. 2014). It is defined as the oxygen content used by the microorganisms at the time they decompose organic matter at a specific temperature. The value varied from 1.29 to 87.83 ppm (mean 31.06 ± 13.38 SD) and 0.49 to 34.84 (mean 12.31 ± 8.28 SD) in pre and post-monsoon respectively (Fig. 2F). The lowest value of DO was found at H14 which is due to the addition of high organic load of domestic and industrial discharge. But the maximum BOD was recorded at H19 which is due to the addition of high organic load of industrial and municipal effluents from Budhana.

Potassium (K) is the key plant nutrient which affects growth and productivity of the crop directly. During the literature survey, it was found that the permissible or desirable value

of K is not set by WHO (2011) and BIS (2012). The value of K ranged from 2.64 to 37.84 (mean 24.36 ± 9.58 SD) and 1.62 to 33.45 (mean 16.56 ± 8.06 SD) during pre and post-monsoon (Fig. 2G). The nutrient salt concentration in water depends on the pollution sources and types (Gohar et al. 2015).

Sodium (Na) is often found in the natural environment and in water bodies. High Na causes hypernatremia in humans and irrigation with high Na water adversely affect the soil physical and chemical properties which adversely affect the plant growth and productivity. Na varied from 19.94 to 210.52 ppm (mean 131.66 ± 48.15 SD) and 17.86 to 190.02 (mean 86.93 ± 41.70 SD) ppm during pre and post-monsoon respectively (Fig. 2H). The concentration of Na is closely associated with urban land cover and density of population, while the concentration of potassium is associated with anthropogenic activities including discharge of untreated wastewater and agricultural land use. Elevated concentrations of Na and K indicate the presence of natural and industrial brines and sewage.

The hardness of water is governed by the kind of parent material of rock and minerals in the ambient environment, the hydrological features of the region and the anthropogenic sources from an area. High amount of hardness in surface water affects the aquatic organisms by the accumulation of several minerals and economic loss (Selvam et al. 2013). During the study, total harness (TH) is ranged from 108.84 to 412.08 (mean 240.13 ± 64.73 SD) ppm and 86.96 to 315.35 ppm (mean 176.14 ± 57.41 SD) during pre and post-monsoon (Fig. 2I).

The calcium (Ca^{2+}) and magnesium (Mg^{2+}) constitute the main portion of hardness in the natural water. Ca^{2+} is present in surface water at varying amounts naturally. Ca^{2+} is a nutritional mineral but at higher concentration its causes detrimental to environmental machinery. Ca^{2+} varied from 16.60 to 100.64 ppm (mean 55.73 ± 19.03 SD) and 13.74 to 74.42 ppm (mean 41.04 ± 15.66 SD) during pre and post-monsoon (Fig. 2J). Mg^{2+} varied from

10.70 to 39.14 ppm (mean 24.59 ± 5.23 SD) and 7.38 to 31.62 ppm (mean 17.93 ± 5.21 SD) during pre and post-monsoon (Fig. 2K).

Chlorides (Cl^-) are a naturally occurring element and also a contaminant. A major anthropogenic source of Cl^- is water softeners utilized for industrial/commercial purposes. Chloride is not toxic to humans but increased concentration makes water unpotable due to the saltiness. Severely increased concentration of chloride is harmful to aquatic organisms and can increase the mobility of metals (WHO 2002; Rupal et al. 2012). Due to the corrosive nature and salty flavour, increased chloride concentration in drinking water supplies may lead to elevated treatment costs. Cl^- ranged from 18.54 to 465.70 (mean 231.10 ± 90.87 SD) and 13.96 to 309.27 ppm (mean 139.91 ± 71.10 SD) during pre and post-monsoon (Fig. 2L). The data confirmed that there is an amplification of Cl^- concentrations from upstream to downstream due to point and non-point sources adjoining the river at various locations.

The sources of sulphates (SO_4^{2-}) can be natural or anthropogenic. SO_4^{2-} and NO_3^- are vital parameters for representation of surface water quality, which designate the status of anthropogenic pollution in the fresh water (Suthar et al. 2010). SO_4^{2-} varied from 34.74 to 383.38 (mean 163.91 ± 69.43 SD) and 26.20 to 272.52 ppm (mean 58.33 SD) during pre and post-monsoon (Fig. 2M). The variations in the SO_4^{2-} values are consequence of untreated sewage discharge, industrial effluent release and agrochemicals use.

Nitrate (NO_3^-) is the end product of organic matter degradation. Presence of high concentrations in drinking water cause lethal methemoglobinemia in infants. Further the high concentration in water bodies can lead to eutrophication in combination with PO_4^{2-} . NO_3^- varied from 2.51 to 72.58 ppm (mean 40.47 ± 16.44 SD) and 1.75 to 57.10 ppm (mean 22.15 ± 13.23 SD) during pre and post-monsoon (Fig. 2N). All the samples were found within permissible limit for NO_3^- during post-monsoon season due to dilution of water flow.

Phosphates (PO_4^{2-}): At lower concentrations, PO_4^{2-} is non-toxic to humans and animals. Phosphate (PO_4^{2-}) present in extremely high amount may cause digestive (Verma and Kumar 2014). High level of PO_4^{2-} may interfere with the health of natural ecosystems and can lead to algal growth. PO_4^{2-} ranged from 346.06 to 5018.96 ppb (mean 2071.54 ± 924.35 SD) and 204.32 to 2632.57 ppb (mean 1054.22 ± 550.37 SD) during pre and post-monsoon (Fig. 2O).

Alkalinity determines the buffering competence of the water against changes in pH. Total alkalinity ranged from 65.31 to 326.49 ppm (mean 166.41 ± 57.64 SD) and 44.01 to 194.99 ppm (mean 94.21 ± 36.77 SD) during pre and post-monsoon (Fig. 2P). Bicarbonates (HCO_3^-) of Ca and Mg are responsible for temporary hardness of water which causes crustations in water pipelines. HCO_3^- produces carbon di oxide in vapour form of water and corrodes the condensate lines. HCO_3^- is major contributor to the alkalinity drinking and irrigation water (Qaderi et al. 2017). HCO_3^- varied from 194.42 to 1030.77 ppm (mean 479.76 ± 176.38 SD) and 159.23 to 700.84 ppm (mean $315.79 \pm 12.6.84$ SD) during pre and post-monsoon (Fig. 2Q).

To recapitulate the differences in different variables of water quality for Hindon River, statistical difference were evaluated at 95% confidence level.

Comparing the concentration pattern of ions as a whole followed the order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$.

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Fig. 2 Spatio-temporal variation of Hindon river water physiochemical parameters of (A–Q). Boxes show the 25th and 75th percentiles. Lines in the boxes show the median values. Data are the means of five years, fifteen replications and two sampling seasons (pre and post-monsoon). Vertical bar with same letter(/s) are not significantly different according to Tukey's Honest test ($P=0.05$).

Heavy Metal status

Heavy metal concentrations in surface water environment are depending on various natural and anthropogenic activities. Hindon River water samples were analysed for 08 heavy metals *viz.* Cd, Cr, Pb, Zn, Mn, Cu, Fe and Ni for pre and post-monsoon seasons. The arithmetic mean concentrations with standard error are represented in Fig. 3.

Cadmium (Cd) is present in the environment at low concentrations. Cd is used comprehensively in fertilizers, pigments, batteries and galvanization. High concentration of Cd is acute and chronic to human and aquatic life. The concentration of Cd varied between BDL to 186.89 $\mu\text{g/L}$ (mean 38.51 ± 54.92 SD) and BDL to 36.85 $\mu\text{g/L}$ (mean 5.97 ± 7.42 SD) in pre and post-monsoon seasons respectively (Fig. 3A).

Chromium (Cr) is one of the most abundant heavy metals, polluting ground and surface water due to its recurrent anthropogenic activities. High dosage of Cr has detrimental

effects like cancer, skin disease and birth defects. In our study Cr ranged from BDL to 166.47 $\mu\text{g/L}$ (mean 74.70 ± 43.22 SD) and BDL to 58.45 $\mu\text{g/L}$ (mean $29.397.17 \pm 15.73$ SD) in pre and post seasons respectively (Fig. 3B).

Lead (Pb) enters in water bodies through industrial discharge or urban runoff. It is also shifted from the atmosphere to hydrosphere through precipitation. It is lethal to flora and fauna which affects the nephrological, vascular and nervous systems in humans (Gowd and Govil 2008). Pb concentration varied between BDL to 985.92 $\mu\text{g/L}$ (mean 187.77 ± 222.73 SD) and BDL to 348.65 $\mu\text{g/L}$ (mean 65.55 ± 79.24 SD) in pre and post seasons respectively (Fig. 3C).

Zinc (Zn) comes from unscientific discharge from brass and zinc containing fittings galvanized pipes and some other industrial processes. Zinc present in water gives an objectionable astringent taste and if present in higher amount can cause damaging effect on flora and fauna (Duruibe et al. 2007). Zn is a noteworthy metal in biological system but excess amount can. In the analysed water samples, Zn concentration was found between BDL to 1510.49 $\mu\text{g/L}$ (mean $625.50 \pm 450.55.13$ SD) and BDL to 641.14 $\mu\text{g/L}$ (mean 233.51 ± 181.13 SD) in pre and post seasons respectively (Fig. 3D).

Manganese (Mn) is a major component of enzymes in biological system but higher concentrations can affect the natural taste of water in households (Postawa et al. 2013). The presence of high concentrations of Mn imparts undesirable flavour to the drinking water, beverage and incrustation in pipelines. Mn ranged from BDL to 36.18 $\mu\text{g/L}$ (mean 16.86 ± 9.03 SD) and BDL to 11.75 $\mu\text{g/L}$ (mean 5.51 ± 3.06 SD) in pre and post seasons respectively (Fig. 3E).

Copper (Cu) is an essential element for human metabolism at low concentrations. However, high concentration may lead to severe hepatic and renal damage, central nervous system damage, irritation followed by depression. In the present study, Cu concentrations

varied between BDL to 292.09 $\mu\text{g/L}$ (mean 103.47 ± 74.64 SD) and BDL to 122.11 $\mu\text{g/L}$ (mean 36.43 ± 28.52 SD) in the pre and post seasons respectively (Fig. 3F).

Iron (Fe) is a very important metal for plants but when present in excess amount or exposed for longer time, it is toxic to the biological system (Duruibe et al. 2007). On precipitation, Fe discolours water; it is a source of deposits in boilers, municipal water supply etc. and it interferes with various industrial processes like pulp and paper, tanning, electroplating and dyeing. Fe concentrations varied between BDL to 3285.30 $\mu\text{g/L}$ (mean 498.47 ± 746.86 SD) and BDL to 19.71 $\mu\text{g/L}$ (mean 194.20 ± 430.84 SD) in pre and post-monsoon seasons respectively (Fig. 3G).

Nickel is used as an important constituent in some anthropogenic activities like metal plating, alloys manufacturing, batteries and as catalysts for some fungicides (Salt et al. 2000). In our study, Ni concentrations ranged from BDL to 89.10 $\mu\text{g/L}$ (mean 34.22 ± 24.85 SD) and BDL to 20.91 $\mu\text{g/L}$ (mean 8.74 ± 5.85 SD) during pre and post-monsoon seasons respectively (Fig. 3H).

Fig. 3(A–H) Spatio-temporal variation of heavy metals of Hindon River using error-bar (mean±standard error) graph over the 19 sites for pre-monsoon and post-monsoon seasons using 5 years (2015 to 2019) average value. Vertical bar with same letter(/s) are not significantly different according to Turkey's Honest test ($P=0.05$).

3.3. Indices of water pollution w.r.t. quality of water

Water Quality Index (WQI)

WQI designate the quality of water *w.r.t.* its use in quantitative form which symbolize overall worth of water. It is distinct score reflecting the collective influence of various water quality variables taken into account for computation of WQI (Yadav et al. 2015). WQI is an efficient way to summarize the large datasets of water quality variables into simple form. It represents the overall quality of a water body such as river, lake or stream and potential threats related to its use. WQI of Hindon River was calculated for 19 sampling sites from H1 to H19 to observe the spatial as well as temporal (two seasons *viz.* pre and post-monsoon) variability studied over a period of 5 years (2015–2019). The computed average WQI obtained from weighted arithmetic mean of 15 water quality variables at different locations and time is shown in Fig. 4A. During the pre-monsoon, minimum and maximum WQI value was observed as 8.69 at

H1 site during the 2018 and 706.47 at H19 site during 2017 respectively (Table S1). During the post-monsoon season, minimum and maximum WQI value was computed as 7.20 at H1 site during the 2015 and 341.56 at H19 site during 2015 respectively (Table S2). WQI ranged from 8.69 to 706.47 in pre monsoon (mean 318.96 ± 124.03 SD) and 7.20 to 341.56 in post-monsoon (mean 154.27 ± 84.08 SD). Among the 19 sampling locations, only 04 sites (H1–H4) and 05 sites (H1–H5 and H8) were found in safe limit of WQI *i.e.* 100 during pre and post-monsoon seasons respectively as per the average data over the period of 2015 to 2019 (Fig. 4A). The higher WQI value (>100) corresponds to the poor quality water which is not suitable for drinking. The spatio-temporal distribution map of WQI is shown in Fig. 5A–B. The unscientific and untreated discharges of industries and population are responsible for the higher values of WQI.

Fig. 4 Spatio-temporal variation of WQI (A); HPI *w.r.t.* drinking (B); HPI *w.r.t.* irrigation (C); HEI *w.r.t.* drinking (D); HEI *w.r.t.* irrigation (E); CI *w.r.t.* drinking (F); CI *w.r.t.* irrigation (G) using error-bar (mean $\pm$ standard error) graph over the 19 sites for pre-monsoon and post-monsoon seasons. Vertical bar with same letter (/s) are not significantly different according to Turkey's Honest test (P=0.05).

Heavy metal pollution index (HPI), Heavy metal evaluation index (HEI) and Contamination index (CI)

Heavy metal pollution indices are usually exercised to quantify potential injurious impact of noxious heavy metals on aquatic ecosystem and food chain (Prasad and Bose 2001). HPI is a practice of scoring the individual heavy metals into one single digit to provide the combined effect of unit heavy metal on the quality of water as a whole. The ranking of HPI values reflects the relative significance of individual heavy metals as per the standards (Prasad and Mondal 2008; Prasanna et al. 2012).

For irrigation purpose, among the 19 locations, lowest HPI (0.00), HEI (0.00) and CI (-17.0) values were observed at H1 site in both pre and post-monsoon seasons and highest HPI (1492.70), HEI (20.44) and CI (10.03) values were observed at H16 site in pre monsoon season, confirmed the evidence of spatial variations over the sites in Hindon River (Fig. 4B–G). With respect to drinking, among the 19 locations, lowest HPI (0.0), HEI (0.0) and CI (-8.0) values were observed at H1 site in pre and post-monsoon seasons and highest HPI (4470.78), HEI (163.11) and CI (155.11) value were observed at H7 site in pre monsoon season (Fig. 4B–G). Further during pre-monsoon, the value of HPI, HEI and CI *w.r.t.* irrigation were ranged between 0.81–1792.70 (average 315.10 $\pm$ 437.05 SD), 0.10–20.44 (average 5.83 $\pm$ 5.394 SD), -15.97–10.03 (average -4.32 $\pm$ 7.18 SD), respectively. In post-monsoon, the value of HPI, HEI and CI *w.r.t.* irrigation were ranged between 0.0–300.06 (average 50.84 $\pm$ 60.19 SD), 0–5.66 (average 1.31 $\pm$ 1.14 SD), -17.00 to -6.08 (average

1304±2.39 SD) respectively. The differences in ranges of values in between pre and post-monsoon seasons confirm the seasonal variation in heavy metal concentration (Table S2).

During pre-monsoon, the value of HPI, HEI and CI *w.r.t.* drinking purpose were ranged between 0.76–4470.78 (average 1167.83±1360.88 SD), 0.20–163.11 (average 38.87±37.99 SD), –7.79 to 155.11 (average 30.87±37.99 SD), respectively. In post-monsoon, the value of HPI, HEI and CI *w.r.t.* drinking purpose were ranged between 0.0–1425.31 (average 252.77±294.56 SD), 0–57.70 (average 11.05±12.25 SD), –8.00 to 49.70 (average 3.05±12.25 SD) respectively (Fig. 4B–G). The differences in ranges of values in between pre and post-monsoon seasons confirm the seasonal variation in heavy metal concentration.

For HPI *w.r.t.* drinking, in pre and post-monsoon seasons, only 03 sites (from H1 to H3) and 04 sites (from H1 to H4) are representing values below critical pollution index *i.e.* 100 (Milivojevic 2016) respectively (Table S3). For HPI *w.r.t.* irrigation, in pre and post-monsoon seasons, only 06 sites (from H1 to H4 and from H12 to H13) and 18 sites (except H7) are representing values below critical pollution index respectively (Table S4). The higher values of HPI indicate the input of high loads of heavy metal from industrial and municipal discharges. The spatio-temporal distribution map of HPI is shown in Fig. 5C–F.

For HEI *w.r.t.* drinking, in pre monsoon season, only 04 sites (H1–H4) are having low, 05 sites (H11–H13 and H18–19) are having medium and rest 10 sites are representing high values of HEI and during post-monsoon season, 13, 04 and 02 sites are having low, medium and high level of HEI. For HEI *w.r.t.* irrigation, in pre monsoon season, 16, 02 and 01 (H16) sites are found having low, medium and high level of HEI and during post-monsoon season, all the sampling sites are found having low level of HEI (Table S3). The higher values of HEI indicate the unauthorized and untreated release of heavy metal from industries and domestic uses. The spatio-temporal distribution map of HEI is shown in Fig. 5G–J.

For CI *w.r.t.* drinking, in pre and post-monsoon seasons, only 03 sites (from H1 to H4) and 13 sites are representing values in the safe limit of CI *i.e.* 3 respectively. For CI *w.r.t.* irrigation, in pre and post-monsoon seasons, 16 sites and all 19 sites (H1–H19) are representing values in the safe zone of CI respectively (Table S4). The spatio-temporal distribution map of CI is shown in Fig. 5K–N. The surface water is possibly affected by release of toxic heavy metal from the point and non-point sources.

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Fig. 5 Spatial and temporal variation maps of the WQI (A–B); HPI *w.r.t.* drinking purpose (C–D); HPI *w.r.t.* irrigation purpose (E–F); HEI *w.r.t.* drinking purpose (G–H); HEI *w.r.t.* irrigation purpose (I–J); CI *w.r.t.* drinking purpose (K–L); CI *w.r.t.* irrigation purpose (M–N)

Statistical Assessment

Correlation analysis

The linear association between each pair of 25 variables (17 physico-chemical variables and 8 heavy metals) was done. The correlation coefficients values were measured using Pearson's method of correlation coefficient (r) and t-test (p -value <0.05) were also done to test significance of the r values in Fig. 6. Among 17 physico-chemical variables, correlation coefficient was found highest between alkalinity and HCO_3^- . In the correlogram, most of the variables were positively correlated with few negatively correlated (pH and DO) and few non-significant (p value ≥ 0.05) pairs. The correlogram showed that 8 heavy metals were positively correlated where highest correlation coefficient value 0.95 observed between Cu and Mn whereas lowest value 0.34 observed between Cd and Cu.

Fig. 6 Upper triangular pie correlogram with heat map of 25 variables (17 physico-chemical and 8 heavy metals), ‘×’ indicate non-significant r value (p-value $\geq$ 0.05).

3.4.2 Regression analysis

The results of high correlation coefficient values provided scope of regression analysis. Multiple linear regression analysis (MLRA) was done (Table 5). In MLRA, model selection was done using stepwise regression method for best regression equation and criteria used for good fit was Adjusted- R^2 (adj- R^2). Among the physico-chemical parameters, observed adj- R^2 value ranged from 0.50 for pH to 0.98 for total hardness and Ca. Regression equations for heavy metals were also found good fit with Adj- $R^2\geq$ 0.70 except Cd (Adj- R^2 =0.32). The regression equations of WQI were found good fit using DO (adj- R^2 was 0.62) and BOD (Adj- R^2 was 0.86). The regression analysis for heavy metal indices viz. HPI, HEI and CI w.r.t. irrigation and drinking conditions were also found good fit with Adj- R^2 value more than 0.87 except, CI (irrigation).

Table 5 Regression analysis of physico-chemical parameters, heavy metals, water quality index, and heavy metal indices

Regression equation	Adjusted- R^2
Physico-chemical parameters	
pH=6.74+0.11DO	0.50
TDS=757.22-143.21pH+0.59EC+24.13Mg	0.84
Tur=-48.775-9.103DO+16.07K	0.72
BOD =-4.66+0.004EC+0.62NO ₃ - 0.022Na	0.91
TH =0.00001+2.5Ca+4.1Mg	0.98
Ca=0.00002+0.4TH -1.64Mg	0.98
Mg=53.33-6.15pH+0.143Ca+0.055Na	0.82
Cl=499.68-66.64pH+0.54Na+0.74SO ₄	0.86
SO ₄ =-37.47+2.15Tur+0.49Na	0.74
NO ₃ =-2.33+0.18Cl	0.88
PO ₄ =-235.61+36.37Tur+0.41TDS+1.52Cl	0.73

$\text{Alk} = -34.37 + 0.58^{\text{TH}} + 0.222\text{Cl}$	0.88
$\text{HCO}_3 = -71.98 + 7.89\text{Ca} + 3.5\text{Tur}$	0.84
Water quality index	
$\text{WQI} = 459.48 - 54.77\text{DO}$	0.62
$\text{WQI} = 36.04 + 9.398\text{BOD}$	0.86
Heavy metals	
$\text{Cd} = -9.09 + 2.80\text{Mn}$	0.32
$\text{Cr} = -3.96 - 0.04\text{Cd} + 0.01\text{Zn} + 3.87\text{Mn}$	0.89
$\text{Pb} = -26.95 - 8.50\text{Mn} + 0.17\text{Fe}$	0.82
$\text{Zn} = -15.44 + 3.69\text{Cr} + 22.57\text{Mn}$	0.72
$\text{Mn} = 2.84 + 0.01\text{Zn} + 0.02\text{Pb}$	0.82
$\text{Cu} = 4.62 + 0.05\text{Pb} + 5.29\text{Mn}$	0.65
$\text{Fe} = 138.49 - 5.79\text{Cr} + 4.02\text{Pb}$	0.74
$\text{Ni} = -3.07 + 0.02\text{Pb} + 0.43\text{Cr}$	0.77
Heavy metal indices	
$\text{HEI(ir)} = 0.99 + 0.014\text{HPI(ir)}$	0.97
$\text{CI(ir)} = -11.67 + 0.02\text{HPI(ir)}$	0.64
$\text{CI(ir)} = -13.17 + 1.26\text{HEI(ir)}$	0.77
$\text{HEI(drink)} = 5.76 + 0.027\text{HPI(drink)}$	0.87
$\text{CI(drink)} = -2.24 + 0.023\text{HPI(drink)}$	0.87
$\text{CI(drink)} = -8.0 + 0.98\text{HEI(drink)}$	0.99

573 **Dendrogram analysis (DA)**

574 DA of Hierarchical cluster analysis (HCA) clustered in both space and time (season-year)
575 dimensions. DA over season-time clearly grouped the WQI value into two clusters, where
576 cluster1 contains pre-monsoon value for the five years data [with lowest (18.7) in 2016 at H1)
577 and highest value [(699.4) in 2017 at H19] and cluster2 contains post-monsoon value for the
578 five years data [with lowest (5.4) in 2015 at H1) and highest value [(335.2) in 2015 at H19]
579 **(Fig. 7).**

580 DA over the sampling sites clearly grouped the WQI value into three clusters, where cluster1
581 contains H1 site [with lowest (5.4) in post-monsoon 2015) and highest value [(37.4) in post-

monsoon 2017], cluster2 contains sites [H9, H10, H2, H4, H18, H19, H3 with lowest (16.7) in post-monsoon 2015) and highest value 699.4 in pre-monsoon2017] and cluster3 contains sites [H5, H12, H8, H16, H14, H6, H13, H7, H11, H17, H15 with lowest (70.1) in post-monsoon 2015) and highest value 491.0 in pre-monsoon 2016] (**Fig. 7**).

Fig. 7 Heatmap with dendrogram analysis representing variation in WQI values among sampling sites (H1–19), over the seasons (PrM: Pre-monsoon and PsM: Post-monsoon) and years (2015–2019).

Fig. 8 Heatmap with boxplot and dendrogram analysis of HPI, HEI and CI values among sampling sites (H1–19) in pre and post-monsoon season *w.r.t.* drinking purpose (A); irrigation purpose (B).

For drinking as well as irrigation water indices, the heatmap analysis portrayed the pre and post-monsoon variability row wise and site-specific variability column wise. Overall, the heatmap shows the spatio-temporal variability in a scale of 0 to 1500, 0 to 20 and -20 to 10 for HPI, HEI and CI respectively *w.r.t.* irrigation purposes. The heatmap shows the spatio-temporal variability of in a scale of 0 to 5000, 0 to 200 and -200 to 200 for HPI, HEI and CI *w.r.t.* drinking purposes (Fig. 8A–B).

Dendrogram analysis (DA) of Hierarchical cluster analysis (HCA) for clustering of sites and seasonal dimensions was conducted. DA clearly grouped pre and post season values of HPI, HEI, CI into separate clusters where pre-monsoon phased more heavy metal contamination than post-monsoon for both irrigation and drinking purpose (Fig. 3.4.2a-b).

Dendrogram analysis of HPI, HEI and CI for both irrigation and drinking purposes, portrayed 3 clusters where cluster1 for high, cluster2 for medium and cluster3 for low contamination sites. For HPI drinking, cluster1 contains sites H7, H16, H14, H17; cluster2 contains sites H5, H6, H8, H9, H15 and cluster3 contains sites H10, H19, H18, H11, H13, H12, H4, H3, H2, and H1. For HEI drinking, cluster1 contains sites H7; cluster2 contains sites H16, H14, H5, H6, H17, and cluster3 contains sites H8, H9, H10, H15, H19, H18, H13, H11, H12, H4, H3, H2, and H1. For CI drinking, cluster1 contains sites H7, cluster2 contains sites H16, H14, H5, H6, H17, and cluster3 contains sites H15, H19, H18, H9, H11, H8, H10, H13, H12, H4, H3, H2, and H1 (Fig. 3.4.2a). For HPI irrigation, cluster1 contains sites H16, H7, H14, H17; cluster2 contains sites H5, H15, H19, H18, H9, H11, H8, H6, H10, and cluster3 contains sites H13, H12, H4, H3, H2, and H1. For HEI irrigation, cluster1 contains sites H16, H7, H14, H17; cluster2 contains sites H5, H15, H19, H18, H9, H11, H8, H6, H10, H13, and cluster3 contains sites H12, H4, H3, H2, and H1. For CI irrigation, cluster1 contains sites H16, H7, H14, H17, H5, H15, H19, H18, H9; cluster2 contains sites H11, H8, H6, H10, H13, H12, H4, and cluster3 contains sites H3, H2, and H1 (Fig. 7A–B).

620 **Table 6** Results principal component analysis (PCA) showing principal components (PCs)
621 with their Eigen values and proportion of variance (in percent) explained, along with rotated
622 factor loadings and communalities of physico-chemical variables.

Physico-chemical variables	PC-1	PC-2	PC-3	Communalities
pH	-0.27	0.499	-0.059	0.325
EC	0.556	-0.352	0.71	0.937
Tur	0.618	-0.678	-0.287	0.924
DO	-0.569	0.744	0.184	0.911
Na	0.887	0.326	-0.158	0.918
K	0.766	0.286	-0.402	0.830
TDS	0.738	-0.193	0.541	0.875
TH	0.73	0.66	0.042	0.970
Ca	0.634	0.742	-0.029	0.953
Mg	0.857	0.42	0.186	0.945
Cl	0.94	-0.19	-0.162	0.946
SO4	0.946	-0.126	-0.04	0.912
BOD	0.884	-0.345	0.107	0.912
NO3	0.924	-0.304	-0.034	0.947
PO4	0.731	-0.501	-0.217	0.832
Alk	0.895	0.403	0.019	0.964
HCO3	0.883	0.436	0.021	0.970
Eigenvalues	10.203	3.641	1.229	
%variance	60.017	21.42	7.229	
%cumulative variance	60.017	81.437	88.67	

623 **Principal component analysis (PCA)**

The PCA was performed for 17 physico-chemical and 8 heavy metals, separately to find out variation in water quality parameters among the sampling sites and further to rank the sampling sites (H1–H19) according to the evaluation index scores (high to low) of each indices for heavy metal loadings.

Under physico-chemical parameters, the PCA analysis achieves three principle components (PCs) with >1 eigen values and the three principle components PC1 (% variance explained 60.02%), PC2 (% variance explained 21.42%), and PC3 (% variance explained 7.23%) cumulatively explained 88.67% variability of original data set. Among the 17 physico-chemical parameters, under PC1, SO_4^{2-} was the highest contributing parameter with factor loadings 0.946, in PC2, DO was highest contributing parameter with factor loadings 0.744, and in PC3, EC being the highest contributing parameter with factor loadings 0.71. The three PCs explain the variability of each physico-chemical parameters with >0.8 communality values except for pH (communality value 0.325) (Table 6).

Further factor map analysis using PCs was done where PC1 included TH, Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , BOD, NO_3^- , PO_4^{2-} , Alk, TDS, and HCO_3^- , while PC2 was constituted by pH, Ca^{2+} , DO and Turbidity whereas PC3 included EC only (Fig. 9a–c).

Further, PCA was performed on 8 heavy metals, it produces three PCs that explained 89.68% variability of the original data set. In PC1 (% variance explained 71.185), Cr and Mn were the highest contributing heavy metals with factor loading more than 0.9. Under PC2 (% variance explained 10.175), Fe was the highest contributing heavy metal with factor loading 0.616. Under PC3 (% variance explained 8.323), Cd was the highest contributing heavy metal with factor loading 0.768 (Table 7). In addition, the heavy metals were patriated in three component models using factor map. In the factor map, PC1 included Cr, Pb, Zn, Mn, and Cu, while Fe was constituted by PC2, whereas Cd was included by PC3 (Fig. 10a–c).

648 **Table 7** Results of principal component analysis (PCA) showing principal component (PC)
 649 with their eigen values and proportion of variance (in percent) explained, along with rotated
 650 factor loadings and communalities of heavy metals.

Heavy metal	PC-1	PC-2	PC-3	Communalities
Cd	0.624	0.097	0.768	0.989
Cr	0.921	-0.194	-0.149	0.908
Pb	0.86	0.392	-0.163	0.920
Zn	0.821	-0.448	-0.064	0.879
Mn	0.927	-0.173	-0.064	0.893
Cu	0.872	-0.116	0.045	0.776
Fe	0.751	0.606	-0.126	0.947
Eigenvalue	5.695	0.814	0.666	
%variance	71.185	10.175	8.323	
Cumulative% variance	71.185	81.36	89.683	

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652

Fig. 9 PCA factor map of physico-chemical parameters representing contribution of all the 17 variables (a) on PC1 and PC2 (b) on PC1 and PC3, and (c) on PC2 and PC3.

658 **Fig. 10** PCA factor map of heavy metals representing contribution of all the 8 variables (a) on
659 PC1 and PC2 (b) on PC1 and PC3, and (c) on PC2 and PC3.

660 **Table 8** PCA evaluation score (ES) values of sampling sites (H1–19) and its corresponding
661 rank for physico-chemical parameters and heavy metals load.

Sites	Physico-chemical		Heavy metal	
	ES	Rank	ES	Rank
H1	-183.39	19	-47.52	19
H2	-151.21	18	-46.00	18
H3	-132.64	17	-43.20	17
H4	-93.66	16	-33.08	16
H5	206.84	2	21.11	3
H6	79.22	4	11.45	5
H7	55.10	5	91.77	1
H8	-6.77	11	14.52	4
H9	-8.68	12	4.79	8
H10	-38.92	13	-2.13	11
H11	44.03	6	-3.96	12
H12	-2.28	10	-7.58	14
H13	89.42	3	7.02	7
H14	216.00	1	43.63	2
H15	-50.11	15	4.48	9
H16	3.54	9	8.07	6
H17	-47.79	14	-1.82	10
H18	6.29	8	-14.41	15
H19	15.03	7	-7.12	13

Further, PCA was extended to rank the sampling sites by calculating evaluation score (ES) score (Eq. 1) for both physico-chemical parameters and heavy metals loads. The results observed that the site H14 has highest ES value 216.0 (rank 1) and the site H1 has lowest ES value -183.39 (rank 19) for physico-chemical parameters. Whereas, in case of heavy metals load, site H7 has highest ES value 91.77 (rank 1) and the site H1 has lowest ES value -47.52 (rank 19) (Table 8).

3.4.5. Hierarchical cluster analysis (HCA)

Clustering of homogeneous sites was done for both physico-chemical variables and heavy metals using HCA of PCs with highest inertia gain with the first three PCs of physico-chemical variables. The HCA was performed based on most popular Euclidean distance method. The factor map analysis was conducted for depicting, distances among multi-attribute sites into two dimensional models. Further, dendrogram analysis was done to find out at what distance measure, the clustering were done. First, HCA was done for physico-chemical variables that produced 3 clusters, where cluster1 contained sites (H1, H2, H3 and H4) characterised by low concentration, cluster2 contained sites (H6, H7, H8, H9, H10, H11, H12, H13, H15, H16, H17, H18, and H19) with moderate concentration and cluster3 (H5, H14) contained sites with high concentration (**Fig. 11a–b**). Further, HCA was performed for heavy metals that produced 3 clusters, where cluster1 contained sites (H1, H2, H3 and H4) characterised by low heavy metals load, cluster2 contained sites (H5, H6, H8, H9, H10, H11, H12, H13, H14, H15, H16, H17, H18, and H19) with moderate heavy metals load and cluster3 (H7) contained sites with high heavy metals load (**Fig. 12a–b**).

Fig. 11 (a) Individual factor map of different sites using principal component analysis (PCA) for physico-chemical variables content at different sites. (b) Dendrogram obtained by

687 hierarchical cluster analysis (HCA) of different sites using PCA for physico-chemical
688 variables content at different sites.

Fig. 12 (a) Individual factor map of different sites using principal component analysis (PCA) for heavy metals content at different sites. (b) Dendrogram obtained by hierarchical cluster analysis (HCA) of different sites using PCA for heavy metals content at different sites.

Conclusions

On the basis of the present study it can be concluded that there is urgent necessity to formulate a national plan to manage the level of pollution for improving the quality of Hindon River in long term aspiration. The point and non-point sources are deteriorating the quality of river. The river is subjected to various level of pollution caused by a range of untreated discharges of waste water and solid wastes from industrial, domestic and agricultural origin. Treatments plants for both municipal and industries waste water should be installed and maintained efficiently so that the treated effluents with permissible limits can be discharged directly into the river and an organized network can be established for the safe utilization of river water for drinking as well as irrigation purposes. It is suggested that there should be strict follow up for discharge of treated waste water quality from various sources. It is also advocated there should be restriction on the release of toxic chemicals before proper treatment under permissible limits.

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Author contribution Anand Kumar Gupta: Conceptualization, laboratory analysis, writing-original draft. Ambrish Kumar: Research formulation. Uma Kant Maurya: conceptualization, review and editing. Deepak Singh: GIS mapping. Sadikul Islam: Statistical analysis. Avinash

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Author contributions

1. Anand Kumar Gupta, Ambrish Kumar and Uma Kant Maurya conceptualized the research plan and supervised the project.
2. Anand Kumar Gupta, Rajesh Kaushal, Sadikul Islam and Sandeep Kumar conducted the experiments and analyzed the experimental results.
3. Anand Kumar Gupta and Ravish Singh collected water samples and analysed physico-chemical parameters of water.
4. Deepak Singh and Parmanand Kumar analysed samples for heavy metals and prepared GIS map.
5. A. C. Rathore organized data, including research literature and drawing.
6. Anand Kumar Gupta, Deepak Singh and Sadikul Islam wrote the manuscript.
7. All authors discussed the results and commented on the manuscript.

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☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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869

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875

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