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Heavy Metal Contamination in the Kali River: Irrigation Unsuitability and its Adverse Effects on Human Health

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ABSTRACT

This study evaluates the concentration of heavy metals in the Kali River, Uttar Pradesh (from Bhavanpur, Saharanpur to Pithlokhar, Meerut). Some heavy metals (HMs) (Cr 10.3-479.6 µg/l, Mn (128.3-9054.5 µg/l), Fe (0-14534 µg/l), Ni (0-789.7 µg/l), Cu (57.2-32720.1 µg/l), Zn (89.7-6487.8 µg/l), As (17.3-90 µg/l), Cd (7.8-184.7 µg/l), and Pb (57.3-1860.1 µg/l) were among the HMs that exceeded allowable limits. Few risk assessment metrics (Degree of Contamination (Cd), Hazard Quotient (HQ), Carcinogenic Risk (CR), Heavy Metal Evaluation Index (HEI), and Total Hazard Index (THI)) were applied to check the hazardous effect. However, the S2 sampling location had the greatest HPI indices, whereas Dable village (S19) had the highest values of Cd, HEI, and THI. Health risks are more likely to affect adults and children, especially in rural locations. The pollution also seriously impairs the water's suitability for irrigation, which affects the quality of the crops and the health of the soil. To protect agricultural and human populations, immediate regulatory actions and routine water quality monitoring are required.

Keywords HPI, THI, Kali river, Health risk, Heavy metal.

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INTRODUCTION

Water is an essential natural resource for all life forms and has multiple uses in every sector such as agriculture, industries, hydropower production, and so on. However, rivers are the most important freshwater sources for human habitation (Khan *et al.* 2021). The increasing rate of urbanization and growth, along with the discharge of municipal and industrial effluents that threaten the survival of aquatic and human populations, has resulted in an excessive amount of stress being placed on rivers (Singh *et al.* 2020). More than 700 chemical contaminants are in the waters and the discharge of industrial and municipal wastewater has led to heavy metal contamination in the rivers that run through urban agglomerations, resulting in a decline in water quality (Ustaoglu & Aydın 2020). Heavy metals are the most toxic substances to human life forms and nature because of their toxic and carcinogenic nature (Shankar 2019). Natural activity such as soil leaching and the chemical weathering of rocks are the two primary sources of heavy metals in water (Ali and Khan 2018). Anthropogenic activity results from the use of chemical fertilizers (zinc and copper), phosphate fertilizers (cadmium), and atmospheric deposition (especially lead from car fuels). These accumulating metals will eventually leach into surface waters and groundwater (Mukherjee *et al.* 2021). Toxic metals have accumulated in the natural environment as a result of human activity. Because of their persistence for a long-term and biological half-life inside the human system, the presence of heavy metals in and near urban areas has been a major source of cancer. These substances bioaccumulate (build up in the tissues of living things) and bio-magnify (move from lower to higher trophic levels) when their concentrations rise (Ali *et al.* 2022, Ali and Khan 2018). In terms of toxicity, metals like Hg, Cd, Pd, and As are toxic elements, while Cu and Zn are categorized under trace elements. Several health problems occur due to toxic HM concentration and its oxidation state which determines the bioavailability of the metals (Morais *et al.* 2012). Meanwhile. This polluted water is also used for irrigation purposes which suppresses the growth of crops and their production (Mukherjee *et al.* 2021).

In the current investigation, the prominence of HMs, possible health hazards, and contaminant sources was calculated using the Heavy metal evaluation index (HEI), Heavy metal pollution index (HPI), and Degree of Contamination (Cd) in Kali River (west). In addition, hazard quotient (HQ), carcinogenic risk (CR), and hazard index (HI) were calculated and their potential impacts on irrigation water quality. The Kali River contains many non-point and point sources of pollution. The study highlights the unsuitability of the river water for irrigation due to high heavy metal content, which threatens both agricultural productivity and public health.

MATERIALS AND METHODS

Area of study

The Kali River originates from the Upper Shivalik range in Uttarakhand, close to Rajaji National Park. The river runs for 150 kilometers in its entire course before joining the Hindon River near Pithlokhar, Meerut, in western Uttar Pradesh. Geographically, the 750 km^2 Kali River basin is located between 29° 13’ 30” N and 77° 32’ 45” E. The research area has high to moderate monsoon rainfall throughout the monsoon season and a humid subtropical climate. There is not enough forest cover in the area, and agriculture occupies the majority of the land. The soil type in the area is silty-loamy without carbonate (Maurya and Malik 2016, Singh *et al.* 2020).

Collection of samples and their examination

27 samples were gathered for the current study along 150 km of the Kali River west in UP, from Bhavanpur (Saharanpur) to Pithlokhar (Meerut) Table1 and Fig.1. Samples were gathered in bottles that had been prewashed with high-density polyethylene (HDPE). To stop metal precipitation, nitric acid (65%) was applied (APHA 2017). After acid digestion, heavy metals were analyzed using an Inductive Couple Plasma mass spectroscopy (ICP-MS) model-ICAPRQ (RQ01013). Throughout the procedure, method validation and quality control were carried out using the multi-element standard solution VI (Merk, Germany). Every sample and standard were examined in triplicate.

Degree of contamination

Degree of contamination (Cd) represents of effects of HMs on surface water quality (Khan *et al.* 2021) and their calculation has been done on the basis of Edet and Offiong (2002) research article. The brief calculation formula is explained in the supplementary file.

Potential human health risk assessment

Utilizing the hazardous quotients (HQ) and total

Table 1. Concentration of heavy metals in sample locations (μg/L).

Site	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
S1	34.2±3	**508±50**	**2891.9±295**	**69.9±7**	142.6±15	2612.1±262	20.4±2	**25.4±3**	**187.6±20**
S2	24.8±3	**379.5±40**	0	0	166.4±18	582.2±60	28.5±3	**36±4**	**172.7±20**
S3	10.3±1	128.3±15	**521.3±55**	10.9±1	57.2±6	89.7±10	19.8±2	**7.8±.8**	**57.3±6**
S4	**137.3±6**	**397.9±42**	**6611.4±670**	**186.9±20**	112.5±12	2590.6±270	17.3±2	**35.3±4**	**151±17**
S5	**125±10**	298±30	**4932±500**	**189±20**	116±12	2932±295	34±4	**23±3**	**189±20**
S6	41.7±5	**454.6±50**	**5758.2±580**	**26±2**	167.1±18	5630.8±565	**64.7±7**	**13.7±2**	**204.2±22**
S7	**250.3±20**	**763.8±80**	**9401.6±950**	**23.3±3**	186.1±19	1604.7±170	**90±10**	**34.7±4**	**265.5±30**
S8	**221±19**	**652±70**	**9880±990**	**27±3**	134±15	1543±160	**89±10**	**53±6**	**232±25**
S9	**132±11**	**721±75**	**7643±780**	**113±12**	434±45	842±90	**59±6**	**34±4**	**431±45**
S10	**86.1±9**	**544±56**	**6647.8±680**	**154.8±16**	581.9±60	716.7±80	**63±7**	**29.3±3**	**322.8±33**
S11	**65±8**	**611±62**	**7533±780**	**189±19**	612±60	981±100	**68±7**	**14±2**	**412±40**
S12	**70.1±8**	**412.8±45**	**7897.6±790**	**176.2±190**	642.2±62	1019.5±105	**68.5±7**	**9.3±1**	**288.7±30**
S13	**156.6±16**	**1502.6±160**	**9136.7±920**	**296.8±35**	302.1±30	2696.3±270	**79.7±10**	**19.7±2**	**327.8±35**
S14	**474.4±42**	**1286.1±135**	**9320.8±940**	**151.3±17**	434.5±50	1922.9±200	**65.9±8**	**65.8±7**	**797.4±85**
S15	**246.1±22**	**2667.5±275**	**9870.3±995**	**62.7±7**	310.9±35	1677.8±170	**68.5±8**	**68.4±7**	**1860.1±190**
S16	**316.4±30**	**9054.5±950**	**9420.3±950**	**789.7±85**	1040.3±110	6487.8±650	**87.4±9**	**69.4±7**	**777.7±80**
S17	**174.1±18**	**4219.3±430**	**9388.2±945**	**84.1±9**	415.9±45	1431.3±150	32.5±4	**44.1±5**	**596.6±60**
S18	**243±21**	**4523±460**	**14534±1490**	**87±9**	534±51	2391±240	**57±7**	**56±6**	**845±85**
S19	**479.6±50**	**7524.4±760**	**1808.4±190**	**159.2±17**	**3272.1±310**	5828.5±590	**68.5±9**	**184.7±20**	**1842.7±190**
S20	**193.2±20**	**4464.3±450**	**9824.2±990**	**79.4±8**	647.2±70	1940.8±195	44±7	**53.1±6**	**692.5±70**
S21	**215±20**	**4945±501**	**8945±890**	**69±7**	645±65	2134±218	**54±6**	**34±4**	**745.6±80**
S22	**121.7±10**	**4746.7±480**	**6815±690**	**49.7±5**	327.9±33	2259.4±230	36.2±4	**25.1±3**	**439±45**
S23	**107.6±10**	**3658.8±380**	**7988.3±801**	**64.7±7**	227.6±23	1906.8±200	29.4±3	**38.2±4**	**372.6±40**
S24	**84±9**	**2523.4±260**	**5662.1±580**	20.7±3	316.3±35	1856.1±190	36.8±5	**16.7±2**	**174.9±20**
S25	**96±10**	**2689±275**	**6719±680**	**34.5±4**	431±44	1934.3±200	45.6±6	**18.9±2**	**265.4±30**
S26	**123±11**	**2445±250**	**9043±905**	15.6±2	316±32	2014±200	23±3	**32.1±4**	**312.3±35**
S27	**173.9±16**	**2630.9±270**	**8233.5±830**	**24.6±3**	218±22	1953±201	35±4	**24.7±3**	**314.2±32**
Min	10.3	128.3	0	0	57.2	89.7	17.3	7.8	57.3
Max	479.6	9054.5	14534	789.7	32720.1	6487.8	90	184.7	1860.1
Mean	163.05	2398.2	7275.059	116.85	1564.40	2206.60	51.322	39.49	491.76
BIS	50	300	300	20	1500	15000	50	3	10

Bold caption denoted as standard exceeded values.
All the values are the mean of three replicates ± standard deviation.

hazard index (THI), the amount of heavy metal pollution associated with possible non-carcinogenic health effects resulting from oral ingestion has been estimated. The Environmental Protection Agency's recommended equation has been used to calculate the chronic daily intake (CDI) obtained by drinking water in a supplementary section (USEPA 1989, Mohammadi *et al.* 2019, Khan *et al.* 2021). However, the hazard quotient (HQ) (Liang *et al.* 2011, Mohammadi *et al*. 2019, Khan *et al.* 2021) and THI (Total Hazard Index) index of Several HMs were also calculated in the supplementary section (Ali and Khan 2018).

Index for the evaluation of HMs

The evaluation index for the HMs describes the wa-

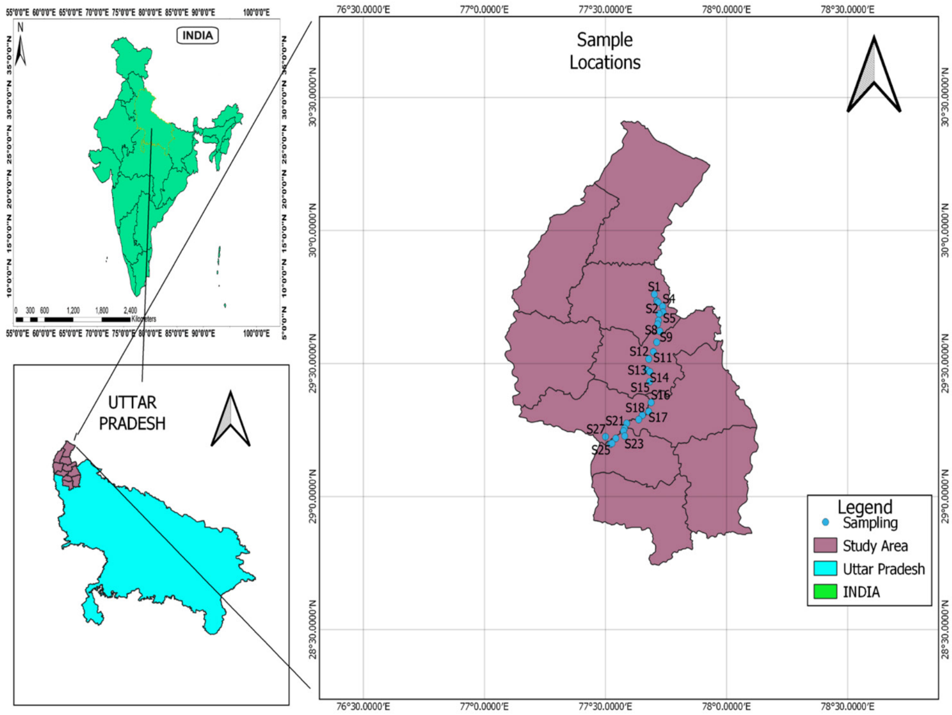

Fig. 1. Sampling locations of River Kali in western Uttar Pradesh, India

ter's overall tendency which, in terms of heavy metal pollution, is equivalent to the HPI level. As a result, it is simple to evaluate water quality using this contamination level (Mokarram *et al.* 2020). HEI is calculated by following the equation presented in Prasanna *et al.* (2012) and Liang *et al.* (2011) research article.

Carcinogenic health risks

In drinking water, a specific dose of heavy metals determines the possible risk of cancer, and carcinogenic risk refers to the chance of developing cancer as a result of lifetime exposure to carcinogens (Mohammadi *et al.* 2019).

$$CR = Cdi \times Csf \qquad \ldots\ldots (1)$$

Where, Cdi= Cronic daily intake.
Csf= Cancer slope factor.

Heavy metal pollution index (HPI)

HPI indexing is a technique to understand the valuation of water quality concerning heavy metal concentration. It is a scaling parameter that illustrates the complete impact of each HM on the whole water quality (Goher *et al.* 2014). HPI is calculated using the following formula (2, 3).

$$HPI = \frac{\sum WiQi}{\sum Wi} \qquad \ldots\ldots (2)$$

$$Qi = \frac{\sum Mi - Ii}{\sum Si - Ii} \times 100 \qquad \ldots\ldots (3)$$

Where Qi= Sub-index of the parameter,
Wi= Unit weight.

However, an HPI less than 100 showed a very low level of HM contamination and an HPI value is equal to 100 reflects that the limit may adversely affect human health and less than 100 indicates a higher level of HM contamination which not safe for drinking purposes (Liang *et al.* 2011, Ustaoglu and Aydın 2020).

RESULTS AND DISCUSSION

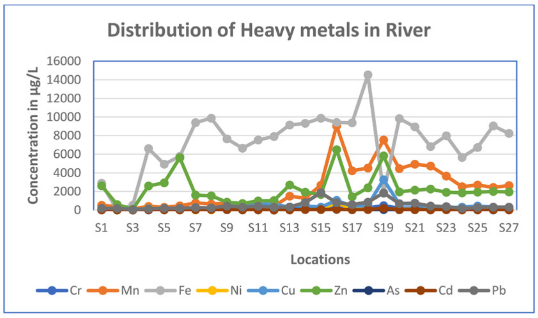

Fig. 2. Distribution of heavy metals in river.

Heavy metal concentration and suitability for irrigation

The concentration of metals analyzed viz., Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb ranged between 10.3-479.6, 128.3-9054.5, 0-41420.3, 0-789.7, 57.2-32720.1, 89.7-6487.8, 17.3-90, 7.8-184.7 and 57.3-1860.1 µg/L. According to BIS (2012), all sample locations contain total metal concentrations above allowable limits. Individual metal concentrations varied among the sampling locations. Zinc concentration is within permissible bounds at all stations. However, chromium concentration at locations S1, S2, S3, and S6 and manganese concentration at S3 and S5 fall under acceptable limits. For Cu, the values are within acceptable bounds at all sampling stations except the S19 location. Findings also revealed that Cd and Pb concentrations are higher than the BIS (2012) permissible level at all locations indicating potential hazard association with the consumption of untreated river. The mean of the all-sampling station showed that Mn, Fe, Ni, Zn and Pb are in higher concentration (Table 1) and above the permissible limit as the BIS report.

Table 1 displays the findings of HMs concentration and their statistical analysis (Min, Max, Mean, and SD). The individual HM concentration varied in the order, Fe > Mn > Zn > Cu > Pb > Cr > Ni > As > Cd. Fig. 2 depicts the HMs distribution in the Kali River. The findings showed that all sampling sites' values of Cd and Pb were higher than the BIS (2012) permissible level.

However, certain HMs (like mercury, arsenic, cadmium, and lead) are toxic and have negative short- and long-term impacts on human health by influencing human organs such as the skin, respiratory system, immune system, reproduction, neurological system, lung cancer, and mutagenic, among others (Shankar 2019). In addition, the concentration of heavy metals was compared to the BIS standard. It was found that the overuse of fertilizers, the discharge of effluents from industries (such as battery manufacture, refineries, and tanneries), and factories enhance the contamination rate in the river water (Paul 2017, Ali *et al.* 2022).

According to the study, the Kali River was significantly contaminated with heavy metals such as Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb, much beyond the levels that are permitted by international regulations for irrigation water (BIS, FAO). Metals repeatedly detected beyond safe criteria, like lead and cadmium, seriously affect crop quality and agricultural output. Over time, these metals can build up in the soil, decreasing its fertility and causing crops to absorb poisons that then make their way into the human food chain (Shil and Singh 2019).

Degree of contamination (Cd)

In Kali River, the average computed value of Cd was determined to be 132.83. Water quality falls into the highly polluted category. According to the Cd value rating, S3/S2/S1/S6/S24/S5/S12/S25/S4/S11/S10/S26/S22/S9/S8/S23/S13/S27/S21/S17/S20/S14/S18/S15/S16/S19 were in the range of 4.94, 44.10, 49.92, 50.12, 54.37,62.00,66.56, 70.93, 76.00,83.52,85.14, 98.54, 102.91, 103.30, 107.97, 109.68, 121.84, 147.19, 153.54, 160.35, 168.42, 204.32, 324.29,356.00 and 486.70 which arranged from lowest to highest values, as shown in Fig. 3a and Table1. In the Kali River, HMs contamination occurs through the discharge of industrial effluents, such as chemical fertilizers, pharmaceuticals, textiles, electroplating, and trash from sugar mills (Mishra *et al*. 2015). Human activity may have had an impact because the village's drainage runs into the Kali River, close to Dable Village.

Health hazard assessment

The specific heavy metal contamination of the water was estimated using HPI. The HPI range values were

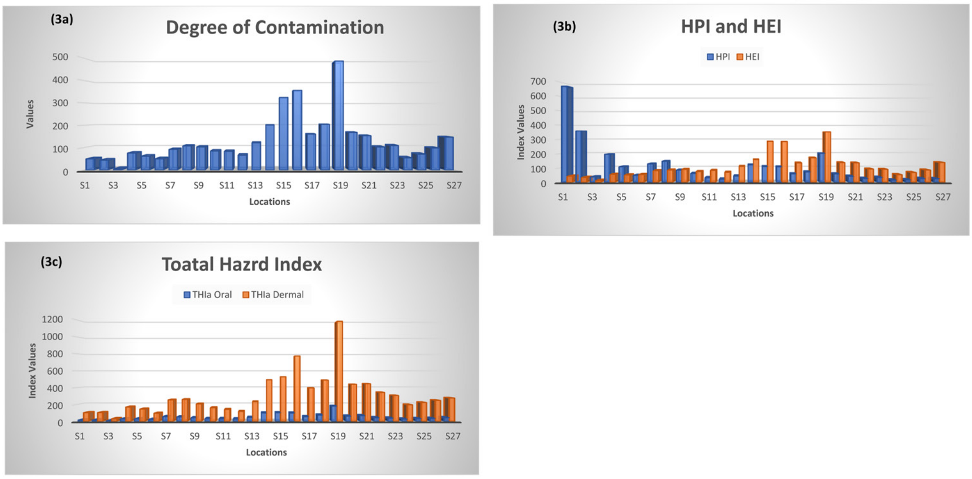

Fig. 3. Degree of contamination (a) Total hazard index for adults (Oral and Dermal), (b) HPI & HEI values (c) and Concerning heavy metals at all sampling stations.

15.01 to 671.17. Of the samples, 44.4% had an HPI value above the permissible limit (<100). The location S1 had the highest HPI value (671). According to Shil and Singh (2019) elevated HPI values signify the risk anthropogenic activities pose to river water quality. Additionally, the HMs Evaluation Index (HEI) was computed to quantify the pollution load in the river. HEI and HPI differed significantly varied from one location to another (Fig. 3b) and Table S4). The range of HEI values was 12.58 to 352.11, with 96.29% of the samples above values of 20. The overall result of the current investigation reflects the hazardous conditions of the Kali River as a result of heavy metals inputs at several points.

Oral and dermal total hazard index values ranged from 6.5 to 180.66 and 131.34 to 1183.20, respectively. The maximum adult hazard index (180.66 and 1183.20) for oral and dermal exposure was discovered at sampling station S19, demonstrating the higher percent of HM contamination in the area around Dable village. Table 1 and Fig. 3c present the THI (oral and cutaneous) results. In all the sampling stations, the calculated values of THI (oral and dermal) in adults surpass the permissible limit. The following sample stations throughout this study region have varying levels of adult (dermal) human health risk: S19 >S15 > S14 > S16 > S18 > S21 > S20 > S7 > S17 > S8 > S13 > S27 > S22 > S9 > S23 > S26 > S10 > S25 > S11 > S5 > S12 > S4 > S24 > S6 > S1 > S2 > 53**.**

Hazard quotient (HQ)

Figure 4(a) shows the values of HQ for each metal at each sampling station. Cr > As > Pb > Mn > Cd > Cu >Fe>Zn> Ni was the order in which the average value of HQ was discovered. Adults had HQ ranges of 1.32 to 61.48, 2.21 to 11.53, 1.58 to 8.24, 0.20 to 14.51, 0.6 to 14.20, 0.055 to 1.00, 0.00 to 2.27, 0.011 to 0.74, and 0 to 1.51, respectively, for Cr, As, Pb, Mn, Cd, Cu, Fe, Zn, and Ni. Adults who breathe in lead dust are at risk for disorders relating to the neurological, reproductive, nephrological, and cardiovascular systems (Mishra *et al*. 2018). The kidneys and lungs of humans suffer greatly when they consume cadmium (Cd).

Based on the oral intake of HMs (Cr, Ni, As, Cd, and Pb) from contaminated water, that can provide a carcinogenic risk to health depending on exposure level, the carcinogenic risk was assessed. Fig. 4(b) and 4(c) displays the sample station-wise representation of metal CR. It was discovered that As had very little contribution to CR. According to the observed value, Ni contributed most to the carcinogenic hazards. The order of carcinogenic risk is Pb < As < Cr < Cd < Ni. Research has shown that vulnerable health risks occur in children because they eat and drink more

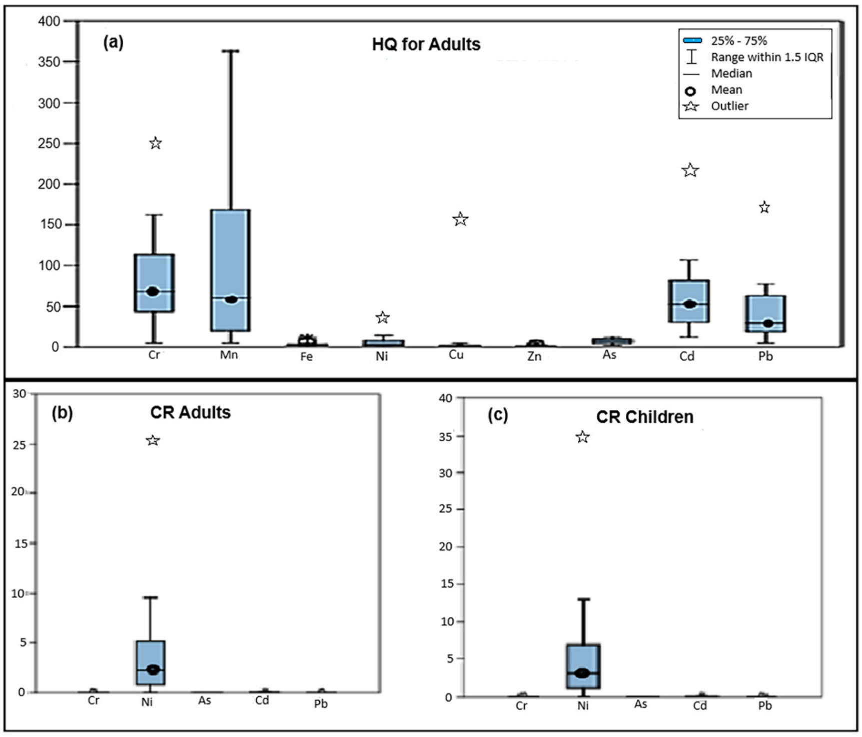

Fig. 4. Variation of the hazardous quotient (HQ) for adults (a) Carcinogenic risks for adults (b) Children (c) and Concerning Heavy metals.

about their body weight than adults do (Mishra *et al.* 2015). Meanwhile, the internal and external tissues, growing immune systems, and neurological systems are more susceptible to carcinogenic (Cancer-cell) and non-carcinogenic health concerns connected with HM exposure (Singh *et al.* 2021, Khan *et al.* 2021).

The study on heavy metal contamination in the Kali River reveals alarmingly high concentrations of toxic metals, significantly exceeding the permissible limits set by the World Health Organization (WHO 2011) and the Bureau of Indian Standards (BIS 2012). The degree of contamination (Cd), THI, HQ, and HPI all indicate the severe pollution levels. Specifically, the concentration of lead (Pb), cadmium (Cd), chromium (Cr), and arsenic (As) were found to be multiples of the permissible limits, with the degree of contamination reflecting a critical contamination state. The Heavy Metal Evaluation Index (HEI) and HPI values far surpass the critical threshold, underscoring the extreme pollution and posing serious health risks to local populations and also irrigational water quality. These findings necessitate immediate and stringent remedial actions to address the heavy metal contamination in the Kali River to protect public health and the environment. Subsequently, our study area highlighted the severe contamination of heavy metals which needs to be highly attention shortly. There are several reports available to validate the current results (Shankar 2019, Singh *et al.* 2021, Ali *et al.* 2022).

Among all sampling locations, site S19 along the Kali River exhibits an exceptionally high toxicity profile, characterized by elevated concentrations of heavy metals such as Fe, Zn, Cu, Ni, Pb, Cd, Cr, and As. Analysis reveals that the levels of these metals at S19 are significantly above the permissible limits set by the World Health Organization (WHO) and BIS report indicating severe contamination. For instance, Pb levels were found to be (49) times higher, Cd levels (13) times higher, Cr levels (3) times higher, and As levels (0.1) times higher than the safe thresholds. This site's Heavy Metal Pollution Index (HPI) and Heavy Metal Evaluation Index (HEI) values are alarmingly high, suggesting a critical health risk to the local population due to prolonged exposure and also affecting the irrigation water quality. Previous studies, such as those by (Mishra *et al*. 2015, Mishra *et al.* 2018, Singh *et al.* 2021) have documented similar contamination patterns in other regions, underscoring the pervasive issue of industrial discharge and inadequate waste management practices contributing to such toxic profiles.

CONCLUSION

The study has revealed elevated concentrations of metals in Kali River water samples collected from different locations, Health Hazard Assessment indices. The HQ and THI (Oral and Dermal) were found over and above acceptable limits, raising alarm for exposure of adults. The HPI values indicated the highest health risk at S1 and HEI, THI (Oral and Dermal), and Cd values indicated the highest health risk at S19, because of industrial and urban activities. The locations S27 were found worst condition of water quality when particularly Kali River merges with Hindon.

This study draws attention to the Kali River's extreme heavy metal pollution, which makes the water hazardous for drinking and agriculture. Because of the bioaccumulation of hazardous metals, using this water for agriculture will not only reduce the quality of the soil and crops, but it will also seriously endanger the health of farmers and the local populace. Controlling industrial discharge requires immediate regulatory actions, and to protect agricultural production, alternate irrigation water sources should be investigated. It is also advised to regularly check soil health and water quality to lessen long-term effects on the ecosystem and human health.

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