Contamination and ecological risk assessment of Cr, As, Cd and Pb in water and sediment of an urban river in a developing country

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Tables 1 to 4 are available in the Supplementary Files section.
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Abstract
Safe levels of heavy metals in the surface water and sediment of the Kirtankhola River watershed have not been universally established. Current study characterized heavy metals such as arsenic (As), chromium (Cr), cadmium (Cd) and lead (Pb) in surface water and sediments of the most important fishing resource at the coastal area of Bangladesh. Considering both of the season, the mean concentration of Cr, As, Cd and Pb in water sample was 33.25, 8.14, 0.48 and 21.14 µg/L, respectively and in sediment was 30.47, 4.48, 0.20 and 19.98 mg/kg, respectively. Heavy metals concentration in water samples surpassed the acceptable limits of drinking water quality, indicating that water from this river is not safe for drinking and cooking. Enrichment factors also directed minor enrichment of heavy metals in sediments of the watershed. Other indexes for ecological risk assessment such as pollution load index (PLI), contamination factor (CF), geoaccumulation index ($I_{geo}$), modified contamination degree (mCd) and potential ecological risk index (PERI) also indicated that the sediment of the study river was low contamination. Taking into account, water and sediment of the study river, in-depth inventoring of heavy metals and holistic ecological risk assessments are required to determine river health.

Keywords: Ecological Risk, Heavy metals, Sediment, fish resource river, Water.

1. Introduction
Heavy metals pollution in the aquatic environment of developing countries especially in Bangladesh are increasing due to expanding urbanization, industrialization, technical innovation and dangerous farming methods (Ahmed et al., 2021; Rakib et al., 2022a,b). Due to the long-term abundance (Kumar et al., 2021), persistence (Rani et al., 2021), environmental toxicity (Jolly et al., 2021) and high bioaccumulation potential to the biota, heavy metals in the aquatic ecosystem poses a significant global crisis (Yüksel et al., 2021;
Ali et al., 2021a,b). Long persistence, non-biodegradable nature and accumulation tendencies of them in the riverine ecosystems can produce an enduring negative impact to the watershed ecosphere (Ali et al. 2021a,b; Hoque et al. 2021; Ustaoğlu et al. 2022a). In any riverine ecosystem, heavy metal is the most harmful toxins and they have consistently harmed the entire ecosystems (Hossain et al., 2020; Kahal et al., 2020; Proshad et al., 2021a,b). Excess amount of toxic trace elements like Cr, As, Cd and Pb can harm to human health and aquatic ecosystem (Ahmed et al. 2020). Due to the bio-magnification nature of toxic metals in the food chains, marine habitats are natural hotspots for their contamination, which can have serious environmental consequences (Jolly et al.; 2021; Hoque et al., 2021). Previous studies reported that toxic elements enriched aquatic biota induce nephritis, kidney lesions, hypertension, liver damage, renal failure and hepatic dysfunction in human body (Ali et al., 2022). Therefore, it is important to assess the levels of toxic elements in the aquatic compartment like water and sediment to evaluate their levels of contamination and potentiality of harmful effects to the riverine ecosystem in Bangladesh.

Natural and human activities have contributed to the accumulation of heavy metals (around 85 percent) to in the surface water and sediments of the aquatic ecosystem (Okro et al., 2020; Ezewudo et al., 2021; Mutlu et al., 2023; Kubra et al., 2023). In recent decades, rapid unplanned industrialization and urbanization (Ustaoğlu and Islam, 2020; Proshad et al., 2021c,d), agricultural runoff (Islam et al., 2023), usage of fertilizers and pesticides in an offensive way (Kahal et al., 2020), and municipal waste disposal (Asomba et al., 2023; Islam et al., 2022) to the riverine ecosystem have evolved heavy metals accumulation. As a result, excess loads of heavy metals in the aquatic environment can cause an acute risk to the biota, invertebrates and fishes (Rajeshkumar et al., 2018; Rajeshkumar and Li, 2018; Yang et al., 2020), increase toxicity to the environment (Kormoker et al., 2019a,2020a), and possible danger to the aquatic species (Shaheen et al., 2019) and human health (Kormoker et al.,
2020b; Kubra et al., 2023). Therefore, it is very important to know the status of heavy metals in the riverine ecosystem for sustainable management of heavy metals in any riverine environment.

As an environmental measure of metal toxicity, water and sediments have been commonly used in the aquatic environment (Raknuzzaman et al., 2016a,b; Islam et al., 2023; Asomba et al., 2023). The composition of suspended sediments may have significant influence on the behavior or function of heavy metals in its aquatic environment (Kahal et al., 2018). The dissolution, precipitation and sorption behavior of heavy metals can change during their transport in the riverine system (Rzetala et al., 2019), which affect their function, bioavailability and ecotoxicity (Haque et al., 2022; Islam et al., 2021c). Sediments play an important role in the riverine ecosystem to alter the bioavailability and toxicity function of heavy metals (Wei et al., 2019; Ustaoğlu et al., 2022b). The levels and distribution of heavy metals in water and sediments of the riverine environment is therefore significant impact to classify the anthropogenic and industrial effects and ecological risks (Proshad et al., 2021c,d; Shammi et al., 2022). In recent times, the indices of geoaccumulation index (\(I_{geo}\)), enrichment factor (EF), and contamination factor (CF) are single indices commonly used for contamination assessment of single element in sediments (Asomba et al. 2023). Meanwhile, pollution load index (PLI), degree of contamination (Cd), modified degree of contamination (mCd), and potential ecologically risk index (PERI) were developed to holistically evaluate the ecotoxicological risk assessment of heavy metals in surface sediments, thereby bridging the lapses in single risk assessment indices (Ustaoğlu and Islam 2020; Kumar et al. 2021; Ezewudo et al. 2021; Jolly et al. 2021).

Barishal is one of the largest coastal cities and the divisional headquarters located at the southern part of Bangladesh. The study river Kirtankhola is located in Barishal district which is one of the major hubs for Hilsa fishery resources in Bangladesh and source of fresh water.
supply. Hilsa (*Tenualosa ilisha*) is the national fish in Bangladesh and it is the largest single-species fishery in the world, supplying 11% of the total catch of fish in Bangladesh and employing 2.5 million people directly or indirectly on this sector (DoF, 2020). A large number of factories (jute, pharmaceutical, dying, cotton, textile, steel, oil and other industries) are situated adjacent to the Kirtankhola River to cause the pollution of heavy metals in this river system. In the one hand, heavy metals such as arsenic (As), chromium (Cr), cadmium (Cd) and lead (Pb) are releasing into the Kirtankhola River, on the other hand consumption of the water by restaurants and local residences for years, exposing people to heavy metals. Therefore, the consequences of heavy metals in water and sediments of this important river must be explored and managed (Kabir et al., 2020; Kubra et al., 2023). To date, no scientific research on the consequences of heavy metals in water and sediments of Kirtankhola River has been carried out so far. Therefore, the objective of this preliminary study is to assess the water quality parameters of the Kirtankhola River; to determine the levels of hazardous substances in water and sediments and to measure the toxicity of heavy metals in sediments using various indexes in respect of ecological view point. It is important to estimate the current contamination status of heavy metals in the hubs of fish resource riverine water and sediments, as it is essential to guide the plans of city development and plans of restoration for reclamation of this important river and thus, paramount for the advancement of the city's environment as well as future economy.

2. Materials and methods

2.1. Study area and sampling

The current study was conducted on the economically important coastal river, Kirtankhola which passes through Barisal divisional City and is connected to the Bay of Bengal, Bangladesh (Fig. 1). During the summer season, the study river has a strong current, whereas, in winter, the water flow is reduced. The river is about 16 kilometers in length, 600 meters in
width, and 15 meters in depth. Total catchment area (307 square km) is affected by tidal flows of this river throughout the year. Surface water and sediment samples were collected from 14 sites of Kirtankhola River during May-August, 2021 (summer season) and December-March, 2022 (winter season). Forty two unfiltered surface water samples (depth of 0 to 20 cm) and forty two surface sediment samples (0 to 5 cm) were collected from the center of the river at a with the help of plastic bottle and Ekman grab sampler. Water samples were then transferred into acid cleaned 100 mL polypropylene bottles and were filtered (0.45 µm filters, cellulose nitrate, Millipore). Physico-chemical analysis was done on the same day of water sampling and remaining water samples were acidified to 0.24 M with HNO₃ (65% supra pure, Merck) and kept under frozen condition until analysis of dissolved metals was carried out. After collection, sediment was then placed in a clean air tight polythene bag, sealed, labeled and transported to the laboratory of Soil Science, Patuakhali Science and Technology University for processing and analysis. Using a porcelain mortar and pestle, sediment samples were ground, homogenized, crumbled, and sieved through a 2 mm nylon sieve. The cleaned samples were maintained in polythene bags and refrigerated at 4°C for chemical analysis.

2.2. Water quality parameters

The physico-chemical properties of water such as temperature, dissolved oxygen (DO) and pH were measured. Dissolve oxygen (DO) was measured by the help of a DO meter (Digital oxygen meter, model DO-5510, Lutron electronic, PA, USA). The temperature and pH of water samples were measured by a pH meter (Model No. HI 98139, HANNA Instruments Ltd, Germany). A potable refract meter (Model No. EXTECH RF20) was used to measure the salinity. Ammonia and hardness (mg/L) were measured using the kits (HANNA Test kits, Hanna Instruments Ltd, Germany).
2.3. Sample extraction, analytical instruments and quality check

Water samples were digested using ultra-pure HNO$_3$ (Merck Germany). A 5 mL volume of concentrated HNO$_3$ was mixed with 50 mL of water sample and heated on a hot plate at 130 °C until the volume and light color reached approximately 25 mL. Until the solution is clear or light colored, HNO$_3$ addition and boiling were repeated. Volume was produced after cooling, with deionized water passing to the desired level through the Whatman no. 41 filter paper. In a microwave-safe Teflon tube, 0.5 g of dry powder of the sediment samples were weighed before 4 mL of concentrated HNO$_3$, 2 mL of concentrated HCl, and 1 mL of concentrated HF were added. The Teflon tube was heated at a temperature of 120 °C for two hours, then at 180 °C for one hour and then at 40 °C for overnight. The digested sample was allowed to cool and using 2 ppb Li and HNO$_3$ buffer solution, it was diluted to 2 mL. After digestion, samples were then filtered by filter (DISMIC® - 25HP PTF, 0.45 µm) and stored in polypropylene tubes for metals analysis. To create the calibration curve, XSTC-13 (Spex CertiPrep® USA) standard solution was utilized ($R^2 > 0.999$). Heavy metals were measured by inductively coupled plasma mass spectrometer (ICP-MS, 7800, Agilent Technologies, California, USA). To demonstrate analytical accuracy of the used procedure, triplicate measurements of the standard reference material of NMIJ CRM 7303-a lake sediment were examined in a manner identical to that described above (Table S1).

2.4. Ecotoxicological assessment

Researchers have previously used average crustal abundance or mean shale values data as baselines reference (Singh et al., 2005; Islam et al., 2015a,b,2023). In this study, certain parameters such as pollution load index (PLI), contamination factor (CF), geoaccumulation index ($I_{geo}$), degree of contamination ($C_d$), modified contamination degree ($mC_d$), enrichment
factor (EF) and potential ecological risk index (PERI) were used to assess the pollution status of heavy metals in sediment.

A single and simple index indicator called contamination factor (CF) is utilized to evaluate heavy metal contamination. A reference value is provided by the concentration of heavy metal in the analyzed sample and the corresponding value of heavy metal in the background value (Eq. 1).

\[
CF = \frac{C_i}{C_b}
\]  

\[ (1) \]

Where CF stands for contamination factor, Ci for the amount of a particular heavy metal in a certain area, and Cb is the corresponding value of the particular metal in the background or reference sample. According to Håkanson (1980), four grades of contamination factors are used for the monitoring of pollution of heavy metals over some time (Table S2). The degree of contamination (Cd) and modified degree of contamination (mCd) was determined as the sum of the contamination factor (CF) and was calculated using Eqs. (2 & 3).

\[
Cd = \sum_{i=1}^{n} CF
\]  

\[ (2) \]

\[
mCd = \frac{1}{n} \sum_{i=1}^{n} CF
\]  

\[ (3) \]

For the degree of contamination and modified degree of contamination four and six grades were proposed by Håkanson (1980) and Abrahim and Parker (2008), respectively (Table S2).

Sadhu et al. (2012) calculated the heavy metal pollution load index (PLI) in sediment to assess the sediment quality. The nth root of contamination factor multiplication for metal is expressed PLI and was calculated using Eq. (4).

\[
PLI = (CF^1 \times CF^2 \times CF^3 \cdots \times CF^n)^{1/n}
\]  

\[ (4) \]

Sadhu et al. (2012) grouped heavy metal contamination into three grades (Table S2).
Enrichment factor (EF) is an invaluable single-element index specifically used to monitor metal presence in an environment that are anthropogenically driven and those from natural processes or weathering actions (Asomba et al., 2023) and was calculated by using Eq. 5.

\[ EF = \frac{(C_{M}/C_{Al})_{sample}}{(C_{M}/C_{Al})_{background}} \]  

(5)

Aluminum (Al) was used as the reference element for geochemical normalization in this analysis for the following reasons: (1) Al is correlated with fine solid surfaces; (2) its geochemistry is close to that of many trace metals; and (3) it appears to be uniform in its natural concentration. As background data, local geochemical backgrounds determined from the value at down-core were used. EF values were interpreted as indicated by (Birch & Olmos, 2008), where: EF < 1 indicates no enrichment; 1 < EF < 3 indicates no enrichment; 3 < EF < 5 indicates mild enrichment; 5 < EF < 10 indicates moderately severe enrichment; 10 < EF < 25 indicates severe enrichment; 25 < FE < 50 indicates very severe enrichment; and EF > 50 indicates extremely severe enrichment.

Index of geo-accumulation \( (I_{geo}) \), which is computed using Eq. (6), is another individual element index that measures the contamination of heavy metals in sediments by contrasting present values with values before the era of industrial revolution.

\[ I_{geo} = \log_{2}(C_{n}/1.5B_{n}) \]  

(6)

Where \( B_{n} \) represents the background level of element "n" in the background sample and \( C_{n} \) is the measured concentration of trace element "n" in sediment sample. The 1.5 factor takes into account anthropogenic influences and potential changes in environmental baseline values (Hanedar et al., 2021). Müller (1981) interpreted seven classes of \( I_{geo} \) for heavy metals in sediments (Table S2).
The potential ecological risk index (PERI) was established by Håkanson (1980) for the assessment of the degree of contamination of heavy metals in sediment. The procedure of calculation is as follows:

\[ E_r^i = T_r^i \cdot CF \]  
(7)

\[ CF = \frac{C^i}{C_o^i} \]  
(8)

\[ PERI = \sum E_r^i \]  
(9)

Where \( E_r^i \) is the ecologically dangerous monomial prospective ecological risk factor and \( PERI \) is the sum of all risk factors for heavy metals in samples, \( T_r^i \) represents the toxic-response factor for a given sample (\( T_r^i \) values were 2, 10, 30 and 5 for Cr, As, Cd and Pb, respectively (Guo et al., 2010), \( CF \) is the contamination factor, \( C_o^i \) is the concentration of the metal in the examined sample and \( C_n^i \) is the heavy metal’s reference value. For the potential ecological risk of single metal (\( E_r^i \)) and for \( PERI \) of all the heavy metals in sediment samples, five toxicity levels and four classes were classified by Håkanson (1980) (Table S2).

Toxic units (\( \Sigma TUs \)) in sediment samples are known to be the possible acute toxicity of hazardous elements. Analysis of the toxic unit is reported as the ratio of the measured concentration of heavy metals in sediment to the probable effect levels (PELs) (Zheng et al., 2008). If the \( \Sigma TUs \) are greater than 4, the mild to acute toxicity of harmful elements persists in the sediment (Bai et al., 2011a). The TU for each metal was calculated using the formula below:

\[ TU = \frac{C_M}{PEL} \]  
(10)

\[ \Sigma TUs = TU_{metal1} + TU_{metal2} + \ldots + TU_{metaln} \]  
(11)

Where, \( \Sigma TUs \) are the sum of toxic units for heavy metals in sediment.
2.6. Statistical analysis

Microsoft Excel-2010 and SPSS 22.0 (IBM, Chicago, IL, USA) were the statistical packages used to analyze the values of heavy metals in water and sediment. Principal component analysis (PCA) was computed to identify potential origins of metals analyzed in the water and sediment of the river. The PCA analysis allowed for extraction of eigenvalues and with Kaiser Normalization, raw calculated factor loading coefficients varimax were rotated. Each variable’s mean value was used for PCA, where eigenvalue and loading value respectively >1 and >0.5 was taken for every principal component.

3. Results and discussion

3.1. Assessment of water quality parameters

The physicochemical parameters are very critical to know the status of heavy metals in riverine water system since the depleted water quality has destructive effects on the marine life. The physico-chemical parameters such as temperature, pH, dissolved oxygen (DO), salinity, hardness, alkalinity and ammonia are presented in Table 1. During the summer and winter, temperature ranged from 27.8 to 32.1 °C and 18.8 to 21.2 °C; pH ranged from 7.60 to 9.24 and 7.41 to 8.43; salinity ranged from 0.49 to 1.58 ppt and 0.73 to 2.92 ppt; hardness ranged from 114.8 to 142.2 mg/L and 132.0 to 172.6 mg/L; DO ranged from 5.34 to 10.1 ppt and 6.12 to 11.41 ppt; alkalinity ranged from 137.1 to 213.3 ppm and 167.6 to 243.7 ppm and ammonia ranged from 0.10 to 0.27 ppm and 0.15 to 0.52, respectively (Table 1). During summer season the mean value of water temperature was 30.0 °C and in winter season 18.8 °C, which was slightly higher (during summer) and lower (during winter) than the acceptable limits (25-30 °C) set by WHO (2004). In current study, the maximum hardness was observed as 142.2 mg/L (during summer) at the site S9 and 172.6 mg/L (during winter) at the site S1 which might be due to the higher salinity levels at S1 during winter and lower salinity
concentrations at S9 site during summer season (Lawson, 2011; Ali et al., 2018a). Oxygen solubility increases as the temperature decreases (Islam, 2021). As expected, low temperatures during winter season could be responsible for the highest DO value (Macan, 1980). During summer season, relatively high DO in water might be due to the high temperature cause the accelerate rate of oxygen consumption by aquatic organisms and a high rate of organic matter decomposition (Ali et al., 2016).

3.2. Metal concentration in water

The seasonal distribution of heavy metals in surface water and sediments for 14 study sites are presented in Figs. 2 and 3. The distributions of As, Cr, Cd and Pb in water and sediment have been found to be identical. In water samples, the concentration of heavy metals followed the descending order of Cr > Pb > As > Cd (Fig. 2). The concentration of four studied metals showed higher in winter compared to summer season, which might be attributed to the water dilution effect (during summer season, more rainfall cause the dilution of river water) (Haakonde et al., 2020; Proshad et al., 2020). Considering both of the season, the mean concentration of Cr, As, Cd and Pb in water sample was 33.25, 8.14, 0.48 and 21.14 µg/L, respectively which was higher than the guidelines value such as Drinking Water Standard Board (DWSB), WHO and USEPA (Table 2), suggesting that drinking and/or cooking water from this river is not safe. Interestingly, the highest levels of Cr, As, Cd and Pb were found at the sites S8 to S11, which could be due to domestic sewage and jute, pharmaceutical and other industry effluents from the Barishal district urban junction (Islam et al., 2015a; Khan et al., 2021; Kubra et al., 2023). The concentrations of heavy metals in water samples are comparable with the other studies in Bangladesh and other countries rivers in the world (Table 2).
3.3. Metal concentration in sediment

The concentrations of heavy metals in sediments for 14 study sites are distributed in Fig. 3. Elevated metals concentration in sediments were observed for the sites S8 to S11, which could be the fact that these sites are situated in the industrial region of the river and the substantial discharge of untreated effluent from the jute, cement, cotton and pharmaceutical industries in Barishal district urban sprawl. Owing to the reduced water flow and volume of river water during winter could help more accumulation of heavy metals in surface sediment during winter season compared to summer (Islam et al., 2015a, 2018). The mean concentration of heavy metals in sediments followed in the decreasing order of Cr > Pb > As > Cd. Like as water samples, elevated levels of heavy metals were observed in sediments at the sites S8 to S11 (Fig. 3). Both the summer and winter season, the highest Cr was observed at the site S11 (41.9 and 52.0 mg/kg, respectively) which might be due to the direct discharge of untreated waste from the petroleum, fertilizers and textile industries (Islam et al., 2015a).

The current study also compared Cr concentration in sediment with some of the studies in Bangladesh and other parts of the world and some sediment quality guidelines (Table 2). It was clear that the level of Cr concentration in sediment of the current study was lower than ASV, TEL, and PEL (Turekian and Wedepohl, 1961, MacDonald et al., 2000) (Table 2) suggesting that Cr in sediments of the present study may not pose any significant risk to the riverine ecosystem.

The mean concentration of As in sediment was 3.52 mg/kg in the summer and 5.44 mg/kg in the winter, which was lower than the mean shale value (ASV) (13 mg/kg) (Table 2). An elevated level of As was observed at sites S8-S11, which might be due to anthropogenic activities such as fertilizer and arsenic pesticide treatment (Fu et al., 2014), wood treatment by exhausting copper arsenate (Pravin et al., 2012; Baeyens et al., 2007), and tanning in relation to certain chemicals, especially arsenic sulfide (Pravin et al., 2012; Bhuiyan et al.,...
The average Cd concentration in summer was 0.18 mg/kg and in winter was 0.22 mg/kg (Fig. 3). During winter, high Cd levels were found, which may be attributable to the lower river's water volume with low water flow resulted higher precipitation/accumulation of Cd in the surface sediment (Ali et al., 2016). Average Pb concentration was observed as 17.41 and 22.55 mg/kg during the summer and winter seasons, respectively which was slightly higher than the ASV value (20 mg/kg) suggested that Pb in sediments of the current study may cause destructive impact to the riverine ecosystem. During winter season slightly higher Pb in sediments could be attributed to the impact of point and non-point sources, such as leaded gasoline, petroleum, municipal runoffs, atmospheric deposition, manufacturing of chemicals and electronics (Shikazono et al., 2012; Islam et al., 2017b). In general, most metal concentrations surpassed some well-documented norm values and were in line with some previous studies in Bangladesh and other countries (Table 2).

### 3.4. Contamination assessment of heavy metals

The contamination of sediment of the Kirtankhola River due to the enriched of heavy metals was assessed by various ecotoxicological approaches (CF, Cd, mCd, PLI, EF, $I_{geo}$, $E_r$ and PERI). All risk assessments are combined in Figs. 4, 5, 6, 7 and Table 3. The CF provides a simpler way to display heavy metals distribution in the riverine sediment and removes the need for various magnitudes to compare them. The CF values for all metals were low to moderate (1 < CF < 3) degree of contamination (Fig. 4A). Overall, the descending order of CF for heavy metals as Pb > Cr > As > Cd. Mean CF values for Cr, As, Cd and Pb were 0.60, 0.37, 0.19 and 0.64 during the summer and 0.76, 0.57, 0.23 and 0.84 during the winter season, respectively (Fig. 4A). As per the class of degree of contamination (Cd) by Håkanson, (1980), the Cd for all heavy metals showed low degree of contamination Cd < 8 (Fig. 4B).
The modified degree of contamination ($mC_d$) for heavy metals showed uncontaminated value for all sites ($mC_d < 1.5$) (Fig. 4C).

The estimated values of pollution load index (PLI) are summarized in Fig. S1. The PLI values were reported to be 0.26-0.58 during the summer and 0.37-0.75 during the winter season, respectively. The PLI value for heavy metals in river sediments did not indicate any contamination ($PLI < 1$) (Fig. S1). In the sampling sites (S8-S11), higher PLI values were found, which could be due to the impact of industrial activities at these sites. The PLI will provide reliable information to the communities with some understanding of the nature of the sediment in respect of metal contamination. Moreover, it helps the policy makers with important details on the pollution status to control heavy metals pollution of the study area (Suresh et al., 2012).

To show the elements of contamination and those of lithogenic origin, the enrichment factor was determined. According to the calculations made to determine the existence of any anthropogenic impact, the enrichment in Kirtankhola river was found to be minor enrichment of heavy metals ($1.5 \leq EF < 3$) (Fig. 5). Among the sites, heavy metals were enriched in sediments at the sites S8-S11of the river watershed. The EF values of the Cr, As, Cd and Pb in sediment were 1.49, 0.92, 1.49 and 1.61 during summer and 1.89, 1.43, 1.81 and 2.08 during winter. The majority of the sediment sites had heavy metal EF values greater than 1.5, indicating that severe anthropogenic activities are what caused the metals to be enriched in the watershed environment (Ustaoglu and Islam, 2020; Islam et al., 2020; Asomba et al., 2023). The work of Shirani et al. (2020) identified a higher accumulation of Cd, Pb, and Cr due to human activities in the aquatic environment of Iran which is consistent with this study.

The $I_{geo}$ findings were interpreted according to the Müller (1981). The geo-accumulation index ($I_{geo}$) values of the heavy metals in sediment are presented in Fig. 6. The $I_{geo}$ values showed the decreasing order of Cd > Cr > As > Pb. The $I_{geo}$ values of Cd showed
uncontaminated to moderately contaminated for most of the sites \((1 \leq I_{\text{geo}} < 2)\), whereas other

elements showed uncontaminated level.

The calculated value of possible ecological risk factor for all metals \(E^i_r \leq 40\) in all sites

of the study river had low levels of ecological risk (Table 3). Slight spatial variability in the

study area was illustrated by the overall potential ecological risk of heavy metals. The mean

value of ecological risk factor for As was 3.70 and 5.73 during summer and winter season,

respectively, Cr was 1.19 and 1.51 during summer and winter season, respectively, Cd was

5.67 and 6.88 during summer and winter season, respectively and Pb was 3.22 and 4.18

during summer and winter season, respectively (Table 3) which indicated low risk. The

possible ecological risk factor \(E^i_r \) values of all metals were below 40, indicating low

pollution status. Potential ecological risk index (PERI) for all metals below the value of 150

\((RI \leq 150)\), indicates a low risk. However, since the contamination of heavy metals in the

natural riverine environment is often complicated, the risk index provides only general

measure of heavy metals emission is currently available. In addition to industrial and

household waste, heavy metal concentrations in river basins depend on the geochemical

composition of sediment of the basin which needs to be explored.

Potential acute toxicity of heavy metals in sediment samples can be calculated as the sum

of the toxic units defined as the ratio of the concentration determined to the probable effect

levels (PELs) of heavy metals (Islam et al., 2017b). Toxic unit (TU) for heavy metals in

surface sediments of Kirtankhola River is shown in Fig. S2. Toxic units of heavy metals

decreased in the order of Cr > As > Cd > Pb. The number of toxic units during the winter and

summer seasons at all the sampling sites was lower than 4, suggesting low toxicity of heavy

metals to the sediment-dwelling fauna of the studied river (Wang et al., 2018, Islam et al.,

2018).
3.5. Sources apportionment of heavy metals

For the identification of the main factors which affect the sources of heavy metals in water and sediment, PCA analysis was used (Table 4 & Fig. S3). In this study, three primary sources (industry, agricultural activities and domestic wastes) were identified for metal pollutants in water and sediment of the river basin (Ahmed et al., 2016; Xu et al., 2020; Zhang et al., 2018). The concentration and distribution profile depicted that the analyzed heavy metals in water and sediments of the watershed might be the result of anthropogenic activities (Rani et al. 2021; Kumar et al. 2021) which involves complicated environmental and human-derived processes (Kumar et al. 2022). Both water and sediment samples, Cr and Cd may originate from the similar sources as they showed strong loading in the first component, whereas As and Pb originated from different source (Table 4). The top three significant components in water (Eigenvalue > 1) explained 95.90% of the overall variability across samples, according to PCA data (42.33% for PC1, 28.46% for PC2 and 25.11% for PC3). PC1 included Cr, and Cd; PC2 included As, third group (PC3) included Pb (Table 4 and Fig. S3). In sediment, the first principal component (PC1), second principal component (PC2) and third principal component (PC3) contributed 39.70%, 28.06% and 27.75% of the total variance respectively and PC1 showed loading with Cr and Cd (Fig. S3), PC2 showed positive loading for As and the PC3 showed positive loading for Pb ($P<0.01$) (Table 4 and Fig. S3). As a result, the first three principal groups in the water and sediment samples of the research area can account for Cr and Cd variation in the analyzed set of data. The burning of waste materials, industrial and vehicular emissions, unauthorized dumping of crude wastes from industries and excessive use of chemical fertilizers in crop fields at the Kirtankhola River watershed are the likely sources of these components in both water and sediments (Rahman et al. 2019; Zhuang et al., 2021).
4. Conclusions

In recent decades, evaluation of heavy metals in water and sediment of the riverine ecosystem is very important for efficient management of the watershed. The study aim was to assess the water quality parameters, ecological risk with the possible sources of heavy metals in water and sediments of the Kirtankhola River, Bangladesh. The mean concentration of heavy metals in water and sediments followed in the decreasing order of Cr > Pb > As > Cd. In general, water and sediments of the study river have been unpolluted to moderately polluted. The PCA analysis revealed that heavy metal pollution originates from three different sources such as industrial activities, agricultural activities, and natural sources which threaten the entire river ecosystem. In the current research, the mean concentration of Cr, As, Cd and Pb in water sample was higher than the Drinking Water Standard Board (DWSB), WHO and USEPA guidelines, suggesting that drinking and/or cooking water from Kirtankhola River is not safe. The average pollution load was surprisingly higher in winter than in summer. The contamination factor (CF), pollution load index (PLI) and geoaccumulation index ($I_{geo}$) showed that sediments were low polluted due to heavy metals contamination. Further study is recommended for preservation of river ecosystem health with holistic ecological and human health risk assessments and reducing the discharge of industrial effluent and domestic wastewater to conserve this important fishing resource in Bangladesh.

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Authorship contribution statement
Md Saiful Islam - Conceptualization, sample collection, data analysis and writing the manuscript and lead the project.

Md Towhidul Islam - Conceptualization, visualization, writing and editing the manuscript.

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Shamsuddin Shahid - Conceptualization, writing and editing the manuscript.

Abu Reza Md Towfiqul Islam - Conceptualization, writing and editing the manuscript.

Mir Mohammad Ali - Conceptualization, data analysis and writing the manuscript.

Abubakr M Idris - Conceptualization, fund acquisition, data analysis and writing the manuscript.

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Figures

Figure 1

Map showing the study area of Kirtankhola River located at the southern part of Bangladesh
Figure 2

Heavy metals distribution in water collected from an urban river (Kirtankhola), Bangladesh during summer and winter season.
Figure 3

Heavy metals distribution in sediment collected from an urban river (Kirtankhola), Bangladesh during summer and winter season.
Figure 4

Contamination factor (A), degree of contamination (B) and modified degree of contamination (C) of heavy metals in sediments of an urban river (Kirtankhola) in Bangladesh during summer and winter season.

Figure 5
Enrichment factor of heavy metals in sediments of an urban river (Kirtankhola) in Bangladesh during summer and winter season.

Figure 6

Geoaccumulation index ($I_{geo}$) of heavy metals in sediments of an urban river (Kirtankhola) in Bangladesh during summer and winter season.

Supplementary Files

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- Tables1to4.docx
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