Assessment of toxic metals in water and sediment of Pasur River in Bangladesh

Mir Mohammad Ali, Mohammad Lokman Ali, Md. Saiful Islam and Md. Zillur Rahman

ABSTRACT

This study was conducted to assess the levels of toxic metals like arsenic (As), chromium (Cr), cadmium (Cd), and lead (Pb) in water and sediments of the Pasur River in Bangladesh. The ranges of Cr, As, Cd, Pb in water were 25.76–77.39, 2.76–16.73, 0.42–2.98 and 12.69–42.67 μg/L and in sediments were 20.67–83.70, 3.15–19.97, 0.39–3.17 and 7.34–55.32 mg/kg. The level of studied metals in water samples exceeded the safe limits of drinking water, indicating that water from this river is not safe for drinking and cooking. Certain indices, including pollution load index (PLI) and contamination factor (C_f^i) were used to assess the ecological risk. The PLI indicated progressive deterioration of sediments by the studied metals. Potential ecological risks of metals in sediment indicated low to considerable risk. However, the C_f^i values of Cd ranged from 0.86 to 8.37 revealed that the examined sediments were strongly impacted by Cd. Considering the severity of potential ecological risk (PER) for single metal (E_r^i), the descending order of contaminants was Cd > Pb > As > Cr. According the results, some treatment scheme must formulate and implement by the researchers and related management organizations to save the Pasur River from metals contamination.

Key words | Bangladesh, Pasur River, sediments, toxic metals, water

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INTRODUCTION

Industrialization is a term linked with socio-economic activities (Thanoon *et al.* 2003; Jaillon & Poon 2009) that alter the infrastructure of the society through vast production (Thanoon *et al.* 2003; Abdullah *et al.* 2009). Most of the industries discharge untreated wastes that contribute toxic metals in the environment. However, industrial and agricultural as well as natural activities are the leading accountable sources of metal contamination in the aquatic environment (Sekabira *et al.* 2010; Bai *et al.* 2011; Zhang *et al.* 2011; Grigoratos *et al.* 2014; Martin *et al.* 2015). Toxic metal pollution is a great concern because of their extensive persistence, bioaccumulation and biomagnifications in the food chain (Sharma *et al.* 2007; Rahman *et al.* 2013) ultimately poses toxicity both in human and aquatic animals (Alhashemi *et al.* 2012; Ahmed *et al.* 2015; Islam *et al.* 2015a, 2015b). The disposal of urban wastes, untreated effluents from various industries and agrochemicals in the open water bodies and rivers has extended alarming levels in Bangladesh which continually increase the metals level and deteriorate water quality (Khadse *et al.* 2008; Venugopal *et al.* 2009; Islam *et al.* 2015a; 2017).

In the riverine aquatic environment, sediments have been widely used as environmental indicators for the assessment of metal pollution in the natural water (Islam *et al.* 2015c). The principal comportment of metals is a function of the suspended sediment composition and water chemistry in the natural water body (Mohiuddin *et al.* 2012). Sediment is an essential part of the river basin, with the variation of habitats and environments (Morillo *et al.* 2004). The investigation of heavy metals in water and sediments could be used to assess the anthropogenic impacts and risks posed by waste discharges to the riverine ecosystems (Yi *et al.* 2011; Saleem *et al.* 2015). Therefore, it is important to assess the concentrations of heavy metals in water and sediments of any contaminated riverine ecosystem. As a result, studies on the assessment of ecological risk from heavy metals

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contamination in sediments have gained more attention. Different methods have been widely used to assess the contamination of heavy metals in sediment such as enrichment factor (EF), contamination factor (CF), geoaccumulation index (I_{geo}) etc. (Zhang *et al.* 2013; Lin *et al.* 2013a; Liu *et al.* 2014; Islam *et al.* 2015c). To evaluate the combined risk of numerous heavy metals in sediment, the pollution load index (PLI) and potential ecological risk index (PER) have also been developed (Yang *et al.* 2009; Huang *et al.* 2013; Lin *et al.* 2013b; Islam *et al.* 2015c). The potential ecological risk index introduces a toxic–response factor for a given substance that provides a simple and quantitative value for ecological risk assessment system (Håkanson 1980).

In the world, Bangladesh is one of the largest deltas formed by the Brahmaputra, Ganges and Meghna and spreading over five countries namely, India, China, Bhutan, Nepal and Bangladesh (Islam *et al.* 2015c). In Bangladesh, everyday huge amount of untreated effluents from different industries, domestic wastes and agrochemicals are being discharged into the open water bodies and deteriorating water quality (Khadse *et al.* 2008; Venugopal *et al.* 2009). Besides, a considerable amount of toxic elements enriched suspended solids is coming down from neighboring country like India through the Teesta and the Brahmaputra Rivers (Islam *et al.* 2015c) and have been accumulated in the riverine environment. Consequently, it poses severe threats to fish and other aquatic biota. The Pasur River is one of the most important and biggest river systems in Khulna division and in the south western coast of Bangladesh. In recent years, several news in the daily newspapers specified that the river is getting polluted rapidly due to indiscriminate discharge of industrial effluents and unplanned construction of various small and large industries. The main industries located surrounding the river system are Tanneries, textile mills, oil refineries, triple super phosphate (TSP) plants, Dichlorodiphenyl trichloroethane (DDT) plants, fish processing plants, toxic metals manufacturing plants, cement factories etc. There is a possibility of coming out heavy metals from the effluents of those industries into the water of the river system and there is also likely to contaminate the aquatic organisms such as various species of fish and shellfish and other invertebrates. Several studies have been conducted in rivers and lakes giving special preference to environment during the last decade (Ozmen *et al.* 2004; Begüm *et al.* 2005; Fernandes *et al.* 2008; Pote *et al.* 2008; Praveena *et al.* 2008; Ali *et al.* 2016). But unfortunately, there is no scientific research on toxic metal pollution in the concerned area so far. Therefore, the objectives of this study are to determine the water quality parameters of the Pasur River, Bangladesh; to determine the levels of heavy metals in water and sediments in two different seasons; and to assess the ecological risk of sediments contamination by heavy metals of the Pasur River, Bangladesh.

MATERIALS AND METHODS

Study area and sampling

This study was conducted on the Pasur River, which passes through Khulna City, close to the Sundarbans and Bay of Bengal, Bangladesh (Figure 1). Pasur River is one of the major and most important rivers in Khulna division and a distributary of the Ganges tidal floodplain area. It meets the Shibsa River within the Sundarbans, and near to the sea the river becomes the Kunga River. It is the deepest river in Bangladesh. It leaves the Madhumati River northeast of Khulna city and flows about 177 km southward past the port at Mongla and through the swampy Sundarbans region to the Bay of Bengal. Sediment and water samples were collected from 10 sampling locations of Pasur River in September, 2014 (summer) and in March, 2015 (winter). Water samples were filtered immediately after collection using 0.45 μm filters, cellulose nitrate, Millipore into polypropylene tubes using a plastic syringe (BD Plastipak, 50 mL) for dissolved metal concentrations. Samples were acidified to 0.24 M with HNO3 (65% supra pure, Merck) and kept at 4 °C in the dark until analysis. The river bed sediment samples were taken at a depth of 0 to 5 cm using a portable Ekman dredge sampler from different stations of the Pasur River at same sites of water samples. For considering the background value of preindustrial sample, sediment was taken by means of a percussion hammer corer (50–80 cm in length) for metal analysis (Schottler & Engstrom 2006). Sediment sampling was performed as prescribed in the Methods Manual for the characterization of sediments (Environment Canada & MENV 1992). Lead-210 dating by alpha spectrometry method was used to determine the age and sediment accumulation rates. The upper 2 cm of each sample was taken from the center of the catcher with an acid-washed plastic spatula to avoid any contamination from the metallic parts of the sampler. The collected samples were put into the polythene bag (sediment) and polyvinyl chloride (PVC) bottle (water). After collection samples were brought to the Fish Inspection and Quality Control (FIQC) Chemistry Laboratory, Khulna, Bangladesh. The collected sediment samples were dried at room temperature ground and sieved with 2 mm sieve and stored in airtight

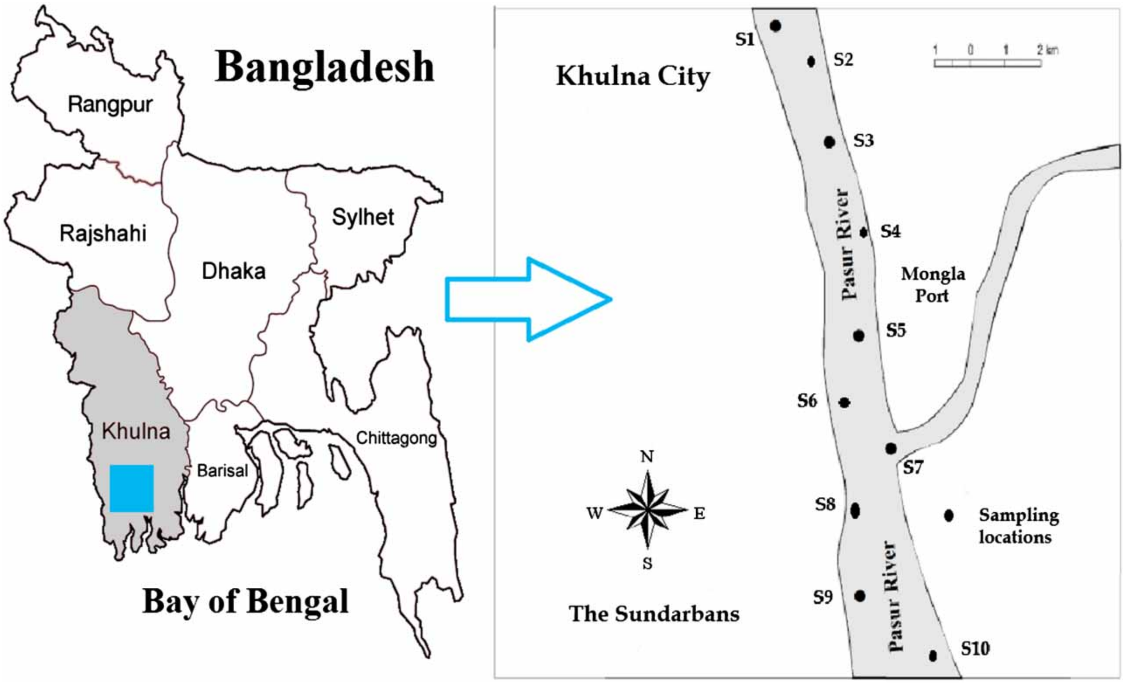

Figure 1 | Map of the study area of Pasur River, Bangladesh.

clean zip lock bag in freezer condition at 8 °C up to chemical analysis was carried out.

Water quality parameters

The physico-chemical parameters such as temperature, pH and dissolved oxygen (DO) of the river water were measured. DO were measured with a DO meter (Digital oxygen meter, model DO-5510, Lutron electronic, PA, USA). Temperature was measured by using a portable digital thermometer (Model: TKDT 10, SKF maintenance and lubrication products, Goteborg, Sweden) and pH was determined using a microprocessor pH meter (Model No. HI 98139, HANNA Instruments Ltd, Germany). Salinity was measured by potable Refractometer (Model: RF20, EXTECH instruments corporation, USA). Other parameters like hardness (mg/L), alkalinity (mg/L), ammonia (mg/L), were analyzed on using kits (HANNA Test kits, Hanna Instruments Ltd, Germany).

Chemicals and sample digestion

All standard solution for target element was supplied by Merck Germany with the highest purity level (99.98%). Ultra-pure HNO_3 was used for sample digestion. All other acids and chemicals were either supra pure or ultra-pure received form Merck Germany or Scharlau Spain. After collection, water samples were filtered through Millipore Filtration Assembly, using 0.45 mm membrane filter. The filtrate was then acidified with concentrated HNO_3 to make a pH of <2. Measured volume (50 ml) of well mixed, acidified sample was taken in a beaker. About 5 mL of concentrated HNO_3 was added and boiled at 130 °C on hot plate till the volume came to about 25 to 30 mL and light color. Addition of HNO_3 and boiling were repeated till solution becomes light colored or clear. After cooling, volume was made to desired level with deionized water (DIW) passing through the Whatman no. 41 filter paper. About 2.0 g portion of dried sediment was taken in 100 ml beaker and 15 mL of concentrated HNO_3 was added. The content was heated at 130 °C for 5 hours until 2–3 mL remaining in the beaker. After digestion, solutions were passed through Whatman no. 41 filter paper, washed with 0.1 M HNO_3 and made up to 100 mL volume with deionized water.

Analytical technique and accuracy check

All the matrixes were analyzed for Pb, Cd, Cr and As by atomic absorption spectrophotometer (Model ZEEnit700P# 150Z7P0110, Analytikjena, Germany) using a Graphite Furnace and Hydride Generator Atomic-absorption-spectrophotometer (AAS) system. All the methods are in-house validated following EC567/2002. Analytical conditions for the measurement of the heavy metals in sample using AAS were tabulated in Table 1. The instrument calibration standards were made by diluting standard (1,000 ppm) supplied by Sigma Aldrich, Switzerland. The results were expressed as mg/kg for fish and sediment and μg/L for water samples. Deionized ultrapure water was used for the experimental procedure. All glassware and containers were cleaned with 20% nitric acid, finally rinsed with deionized ultrapure water several times and oven-dried prior to use. The analytical procedure was checked using certified reference material DORM-4 Fish protein, a certified reference material for toxic metals. The fish samples were prepared and provided by the National Research Council Canada. The standard deviations of the means observed for the certified materials were between 0.65% and 8%, and the percentage recovery was between 89% and 99%, as shown in Table 2. The results indicated a good agreement between the certified and observed values.

Ecological risk calculation

Pollution load index

To assess the sediment quality, an integrated approach of PLI of the four metals was calculated according to Islam et al. (2015c). The PLI is defined as the n^th^ root of the multiplications of the contamination factor (CF) of metals.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots \times CF_n)^{1/n} \tag{1}$$

where CF_{metals} is the ratio between the content of each metal to the background values (background values of heavy metals were taken from the pre-industrial samples of the study area in Bangladesh) in sediment, $CF_{metals} = C_{metal}/C_{background}$. The background value of Cr, As, Cd and Pb in sediments were 41, 8.5, 0.92 and 23, respectively. Therefore, a PLI value of zero indicates perfection, a value of one indicates the presence of only baseline level of pollutants and values above one would indicate progressive deterioration of the site and estuarine quality (Tomilson et al. 1980; Islam et al. 2015b). The PLI gave an assessment of the overall toxicity status of the sample and is also a result of the contribution of the four metals.

Contamination factor (C_f^i) and degree of contamination (C_d)

$$C_f^i = \frac{C^i}{C_n^i}, \quad C_d = \sum_{i=1}^{n} C_f^i \tag{2}$$

where C_f^i is the single element pollution factor, C^i is the content of the element in samples and C_n^i is the reference value of the element. The reference values of Cr, As, Cd and Pb in sediments were 60, 13, 0.3 and 20 mg/kg (Yi et al. 2011; Islam et al. 2015b). The sum of C_f^i for all metals examined represents the integrated pollution degree (C_d) of the environment (Turekian & Wedepohl 1961; Loska & Danuta 2003). The ratio of the measured concentration to natural abundance of a given metal had been proposed as the index contamination factor (C_f^i) being classified into four grades for monitoring the pollution of one single metal over a period of time (Turekian & Wedepohl 1961; Håkanson 1980): low degree ($C_f^i < 1$), moderate degree ($1 \leq C_f^i < 3$), considerable degree ($3 \leq C_f^i < 6$) and very high degree ($C_f^i \geq 6$) (Table 4). Thus, the C_f^i values can monitor the enrichment of one given metal in sediments over a period of time.

Potential ecological risk (PER)

Potential ecological risk index (PER) is also introduced to assess the contamination degree of toxic metals in sediments. The equations for calculating the PER were proposed by Guo et al. (2010) and are as follows.

$$E_r^i = T_r^i \times C_f^i, \quad PER = \sum_{i=1}^{m} E_r^i \tag{3}$$

where E_r^i is the potential ecological risk index of an individual element. T_r^i is the biological toxic factor of an individual element. The toxic-response factors for Cr, As, Cd and Pb

Table 1 | Analytical conditions for measurement of heavy metals in sample solution using AAS

Elements	Wavelength (nm)	Slit (nm)	Lamp current (mA)	Mode	Calibration range (mg/ L)	Detection limit (mg/ L)
As	193.7	0.8	6.0	HG-AAS	0.0–20	0.0007
Cr	357.9	0.8	4.0	GF-AAS	0.0–32	0.0009
Cd	228.8	1.2	3.0	GF-AAS	0.0–1.2	0.00003
Pb	283.3	0.8	4.0	GF-AAS	0.0–40	0.0009

Table 2 | Concentrations of metals found in certified reference materials DORM-4 from National Research Council Canada (means ± standard errors, in mg/kg as wet wt.) by AAS ($n = 3$)

Element DORM-4	Certified value	Measured value	Deviation (%)	Recovery (%)
As	6.80 ± 0.09	6.07 ± 0.13	8.07	89.19
Cr	1.87 ± 0.10	1.85 ± 0.02	0.65	99.09
Cd	0.306 ± 0.005	0.298 ± 0.01	1.66	97.06
Pb	0.416 ± 0.07	0.380 ± 0.18	6.28	91.35

were 2, 10, 30 and 5, respectively (Håkanson 1980; Xu *et al.* 2008; Guo *et al.* 2010). PER is the comprehensive potential ecological index, which is the sum of E_r^i. It represents the sensitivity of the biological community to the toxic substance and illustrates the potential ecological risk caused by the overall contamination. The Indices and grades of potential ecological risk of toxic metals pollution are given in Table 6.

Statistical analysis

The data were statistically analyzed by the statistical package SPSS 16.0 (SPSS, USA). The means and standard deviations of the toxic metal concentrations in water and sediments were calculated. Multivariate methods in terms of principal component analysis (PCA) were used to obtain the distribution of toxic metals by detecting similarities or differences in samples. The PCA was performed using Varimax-normalized rotation on the dataset using Ward's method.

RESULTS AND DISCUSSION

Water quality parameters

The physico-chemical parameters of the water column such as DO, pH, temperature etc. are presented in Table 3. Temperature is one of the most important among the external factors that influence aquatic ecology (Huet 1986). The values of temperature were ranged from 28.8 to 33.6 °C and 18.4 to 22.6 °C during summer and winter, respectively. The mean value of water temperature was found within the permissible limits set by WHO (2004), which was between 25 and 30 °C. The average pH was 6.44 and 5.95 during summer and winter, respectively (Table 3). Salinity is a measure of the salt content of the water. The salinity of freshwater is always less than 0.5%. This range of salinity is generally termed brackish, as distinct from marine or freshwaters. Mean values of salinity were observed to be 5.76 ppt in summer and 6.6 ppt in winter. In the present study, the highest hardness, 310 mg/L, was observed in site S10 during winter due to a higher level of salinity, where lower hardness of 210 mg/L during summer was observed in site S1 (Table 3) due to the lower salinity concentration (Lawson 2011). DO refers to the oxygen that is dissolved in the water and made available to aquatic life. The solubility of oxygen increases with decrease in the temperature (Singh *et al.* 1990). As was expected, the highest value of DO was recorded during winter months and may be due to the temperature in this season being low (Macan

Table 3 | Water quality parameters of Pasur River, Bangladesh

	Temperature (°C)		pH		Salinity (ppt)		Hardness (ppm)		Dissolved oxygen (DO) (ppt)		Alkalinity (ppm)		Ammonia (ppm)	
Sites	Sum	Win	Sum	Win	Sum	Win	Sum	Win	Sum	Win	Sum	Win	Sum	Win
S1	31.5	22.6	7.5	7.1	5.3	6.2	210	240	5.15	4.12	135	180	0.75	0.82
S2	31.7	21.2	7.2	6.3	5.8	6.4	220	235	7.19	5.75	110	150	0.51	0.7
S3	29.5	20.5	6.6	6.2	5.8	6.2	225	230	8.31	7.13	145	175	0.98	1.23
S4	31.7	21.8	6.2	5.8	6.1	6.7	240	250	6.15	5.12	135	165	0.75	0.86
S5	28.8	19.5	5.9	5.4	5.5	6.5	230	245	7.25	5.68	140	170	1.05	1.2
S6	33.6	22.7	6.1	5.7	5.8	7.1	235	280	9.14	8.17	155	185	0.72	0.8
S7	32.7	18.4	6.8	6.2	4.7	5.9	200	230	7.13	5.76	135	150	0.65	0.71
S8	30.8	22.5	5.9	5.3	5.8	6.7	230	260	6.11	5.74	145	190	0.54	0.7
S9	29.6	20.3	6.2	5.8	6.1	7.1	235	290	8.17	6.68	120	170	0.87	1.35
S10	29.5	21.5	6	5.7	6.7	7.2	240	310	7.23	5.77	125	185	0.75	0.86
Mean ± SD	30.94	21.1	6.44	5.95	5.76	6.6	226	257	7.18	5.99	135	172	0.76	0.92

Note: Sum = summer and Win = winter season, respectively.

1980). The DO was found to be 5.15 to 9.14 mg/L during summer and 5.12 to 8.17 mg/L in winter. The lowest value of DO was observed during summer and can be due to there being less or no rainfall and the increase in temperature that led to a decrease in DO resulting from the rate of oxygen consumption from aquatic organisms and the high rate of decomposition of organic matter. Joseph *et al.* (1993) reported that a suitable range of alkalinity is 20 to 300 mg/L for fish. In the present study, the highest alkalinity range was (110 to 155 and 150 to 190 mg/L during summer and winter, respectively), which indicates that the level of alkalinity is a suitable condition.

Metal concentration in water

The results of toxic metal concentrations in surface waters are shown in Table 4. The average concentration of studied metals in water followed a decreasing order of Cr > Pb > As > Cd. The mean concentration of Cr in water was observed to be 44.3 and 53.5 μg/L during the summer and winter seasons, respectively, which was much higher than the WHO standard level for drinking water (Table 4). The average concentration of Cd was observed to be 1.20 and 1.97 μg/L during the summer and winter seasons, respectively. Interestingly, the highest value of Cd was observed at the S7 site (2.98 μg/L during winter), which might be attributed to the domestic sewage and effluents from the port area (Islam *et al.* 2015a). The average concentration of As was higher in winter (11.3 μg/L) than that in summer (8.46 μg/L), which did not exceed the WHO standard (10 μg/L) (Table 4). The average concentration of Pb in water was 20.0 and 26.7 μg/L during the summer and winter seasons, respectively, which were higher than the drinking water quality standard. Considering the toxicity reference values proposed by USEPA (1999), almost all the heavy metals, especially Cr and Cd, greatly exceeded the limit for safe water, indicating that water from this river is not safe for drinking and/or cooking. The metals in the water were seasonally variable, where the winter season exhibited higher levels than in summer (Table 4). The lower concentration of toxic metals during summer might be due to the dilution effect of water (Mohiuddin *et al.* 2012; Islam *et al.* 2015a).

Metal concentration in sediment

Toxic metal concentrations of sediments are presented in Table 5. Metals concentrations in sediments were higher in winter than summer due to the lower water flow during winter, which could assist the toxic metals to accumulate in sediment (Islam *et al.* 2015a, 2015c; Ali *et al.* 2016). Metal concentrations in samples followed the descending order of site-S9 > site-S10 > site-S4 > site-S8 > site-S3 > site-S5 > site-S7 > site-S2 > site-S6 > site-S1. Interestingly, this descending order of heavy metals among the sampling sites did not follow a downstream pattern, which might be due to the metal input in sediments from site specific characteristics such as flow of the rivers, pollution sources and waste disposal from the urban system (Ahmad *et al.* 2010; Islam *et al.* 2014). For example, S4 site is located at the upstream but the levels of metals were higher than some downstream sites, which was due to the effects of sea port activities on the river and extensive discharging of untreated effluents

Table 4 | Toxic metal concentration (μg/L) in water sample of Pasur River, Bangladesh

	Cr		**As**		**Cd**		**Pb**	
Sites	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**
S1	31.5	37.8	2.76	4.31	0.72	1.51	13.5	18.6
S2	25.7	32.5	5.48	7.76	0.62	1.10	35.8	42.4
S3	35.2	42.8	9.31	13.5	1.17	1.39	17.4	22.9
S4	55.2	65.22	7.92	10.2	1.45	2.12	14.6	17.9
S5	43.4	55.76	5.43	7.87	0.42	1.54	14.2	19.9
S6	36.7	48.2	12.4	13.5	1.28	2.67	12.6	23.8
S7	32.5	44.1	9.20	11.8	2.57	2.98	19.2	27.5
S8	69.3	77.4	13.6	16.7	1.45	2.23	12.7	15.4
S9	47.4	55.3	10.2	15.9	0.98	1.92	32.9	42.7
S10	65.9	75.5	8.32	10.9	1.37	2.31	27.5	35.8
Mean ± SD	44.3	53.5	8.46	11.3	1.20	1.97	20.0	26.7

Table 5 | Toxic metal concentrations (mg/kg dw) in sediment sample of Pasur River, Bangladesh

	Cr		**As**		**Cd**		**Pb**	
Sites	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**
S1	34.2	42.5	3.15	6.91	0.83	1.92	12.8	22.7
S2	27.9	36.3	8.57	11.8	0.54	0.99	24.3	39.2
S3	20.7	31.5	13.9	16.7	1.35	1.82	42.3	55.3
S4	59.8	70.3	6.10	7.69	1.97	2.76	25.7	38.7
S5	51.4	65.8	4.23	9.32	0.39	1.62	9.87	22.3
S6	32.7	51.3	7.89	14.7	1.84	2.97	7.34	18.4
S7	37.7	46.5	8.27	10.3	2.51	3.17	21.7	30.5
S8	60.4	83.7	12.1	15.3	0.75	1.13	11.2	16.8
S9	51.3	67.4	14.6	19.9	1.46	2.12	41.1	53.4
S10	72.8	81.3	9.91	11.7	1.74	2.53	22.5	38.9
Mean ± SD	44.9	57.7	8.87	12.4	1.33	2.10	21.9	33.6

Table 6 | Indices and grades of potential ecological risk of toxic metal pollution (Luo et al. 2007)

Contamination factor (C_f^i)	**Contamination degree of individual metal**	**Degree of contamination (C_d)**	**Contamination degree of the environment**	E_r^i	**Grade of ecological risk of individual metal**	**Potential ecological risk (PER)**	
$C_f^i < 1$	Low	$C_d < 5$	Low contamination	$E_r^i < 40$	Low risk	PER < 65	Low risk
$1 \leq C_f^i < 3$	Moderate	$5 \leq C_d < 10$	Moderate contamination	$40 \leq E_r^i < 80$	Moderate risk	65 ≤ PER < 130	Moderate risk
$3 \leq C_f^i < 6$	Considerable	$10 \leq C_d < 20$	Considerable contamination	$80 \leq E_r^i < 160$	Considerable risk	130 ≤ PER < 260	Considerable risk
$C_f^i \geq 6$	High	$C_d \geq 20$	High contamination	$160 \leq E_r^i < 320$	High risk	PER ≥ 260	Very high risk
				$E_r^i \geq 320$	Very high risk		

from the port. The average concentrations of toxic metals in sediments were in the decreasing order of Cr > Pb > As > Cd. Chromium concentration in sediment was higher than other metals as a consequence of direct discharging of untreated wastes from petroleum, fertilizers and textile industries (Facetti et al. 1998; Islam et al. 2015a). However, the high level of Cr for site S10 (72.8 and 81.3 mg/kg in summer and winter, respectively) indicates its higher input, which might be originating from urban and industrial wastes (Mohiuddin et al. 2012). In the present study, total Cr was estimated. There are differences in toxicity between trivalent and hexavalent Cr, with hexavalent Cr being far more toxic. This difference makes an impact on the total Cr measurements. Therefore, this study suggested that hexavalent Cr should be measured to assess the risk posed by hexavalent Cr in the study area. The mean concentration of As in sediment was observed to be 8.87 mg/kg in summer and 12.4 mg/kg in winter, which was near the average shale value (ASV) (13 mg/kg). A high As concentration might be attributed to anthropogenic activities such as treatment from the fertilizers and arsenical pesticides industries (Fu et al. 2014), treating of wood by exhausting copper arsenate (Pravin et al. 2012) and tanning in relation to some chemicals, especially arsenic sulfide (Bhuiyan et al. 2011).

The average concentration of Cd was 1.33 mg/kg in summer and 2.10 mg/kg in winter (Table 5). A high level of Cd was found during winter, which might be due to the differences in water capacity of the river, where low water flow in winter resulted in the precipitation of Cd in sediment; thereby raising its concentration (Islam et al. 2015c). The average concentration of Cd in the sediment of Pasur River was slightly higher than in other studies such as Bangshi River, Bangladesh, mean: 0.61 mg/kg (Rahman et al. 2014); Korotoa River, Bangladesh, mean: 1.2 mg/kg (Islam et al. 2015c); River Ganges in India, range: 0.12–1.2 mg/kg

(Gupta *et al.* 2009) and the Toxicity reference value 0.6 mg/kg (USEPA 1999) indicated that Cd might pose a risk to the surrounding ecosystems. The elevated level of Cd in the sediment of Pasur River might be due to the effects of industrial activity, atmospheric emissions, leachates from defused Ni-Cd batteries and Cd plated items (Islam *et al.* 2014, 2015c). The average concentration of Pb was observed to be 21.9 and 33.6 mg/kg during the summer and winter seasons, which were higher than the ASV value (20 mg/kg), which could be due to the effect of point and non-point sources; such as leaded gasoline, petroleum, municipal runoff and atmospheric deposition (Mohiuddin *et al.* 2012; Shikazono *et al.* 2012), chemicals and electronics manufacturing, cables, oils, tire and cement factories, and steel works near the study river in the Khulna district. As shown in Figure 2, there was a strong correlation between water and sediment for the studied metals, indicating their similar distribution to the riverine system of the studied river.

Assessment of ecological risk

Håkanson (1980) developed a methodology to assess ecological risks for aquatic pollution control. The methodology is based on the assumption that the sensitivity of the aquatic system mainly depends on its productivity. The calculated PLI values of metals in sediments are summarized in Figure 3. The PLI values ranged from 5.38 to 14.5 during summer and 10.6 to 19.7 during winter, confirming that the sediment of the studied river was contaminated (PLI > 1). Higher PLI values were observed in sampling site S9, which might be due to the effects of sea port activities. The PLI can provide some understanding to the populations about the quality of the sediment. In addition, it also delivers essential information to the decision makers on the pollution status of the study area (Suresh *et al.* 2012). For both seasons, higher PLI values were observed in sampling sites S4, S9 and S10, which might be due to the effects of the port, various industries and urban activities at these sites.

The contamination factor (C_f^i), degree of contamination (C_d), ecological risk (E_r^i) and risk index (PER) classes are shown in Table 6. In the present study, values of contamination factor (C_f^i) showed in the descending order of Cd > Pb > As > Cr in sediments (Table 7). The assessment of integrated metal pollution in sediment was based on the degree of contamination (C_d). The degree of contamination of most sites showed a considerable to low degree of contamination, and followed the descending order of Cd > Pb > As > Cr. The element specific degree of contamination (C_d) in the studied sediment was moderate class, where the range of degree of contamination was 2.98–15.1 (Table 7). Among the studied metals, Cd showed moderate contamination for some sites, whereas Pb posed a very low contamination factor in all sites (Table 7).

The ecological risk factor for individual element (E_r^i) and the potential ecological risk index (PER) are

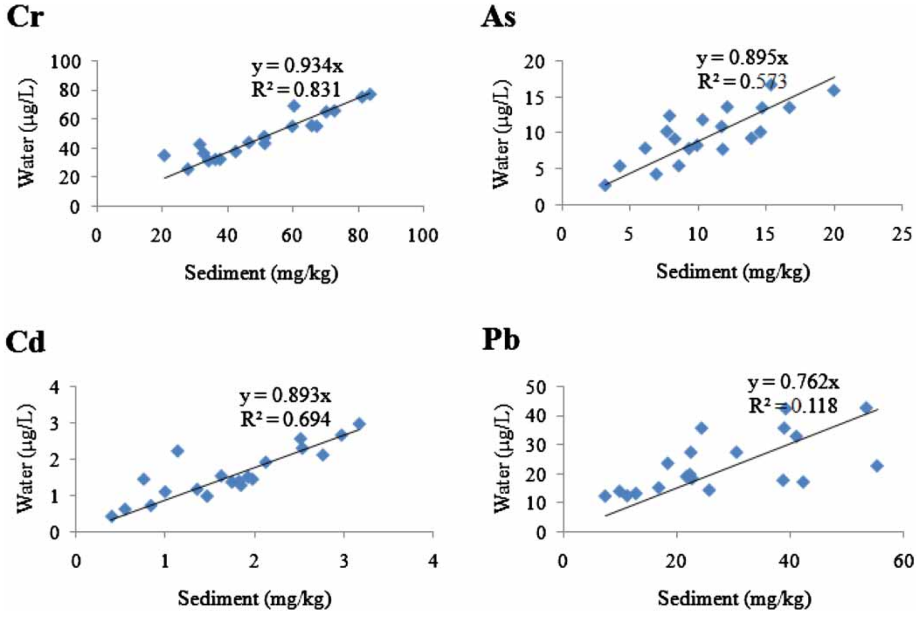

Figure 2 | Correlation of toxic metals between water and sediment of Pasur River, Bangladesh.

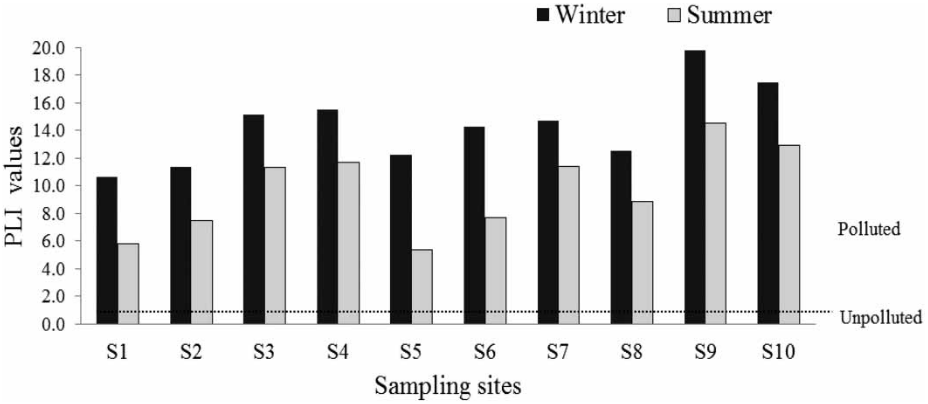

Figure 3 | PLI value of sediment collected from Pasur River, Bangladesh.

summarized in Table 8. The potential ecological risk factor of toxic metals in sediment were in the descending order of Cd > Pb > As > Cr. Considering the potential ecological risk factor (E_r^i) for the individual elements, Cd showed very high potential ecological risk with an E_r^i factor ranging from 25.7 to 251 (Table 8). The sites S4, S6 and S7 showed a considerable ecological risk for Cd, which might be due to the application of dumping of oily materials from the Mongla port area and waste disposal from the town and port (ATSDR 2008). The potential ecological risk indexes (PERs) in the sampling sites ranged from 41.0 to 223, indicating considerable risk (Table 8). Ecological risk assessment showed that Cd posed potential ecological risk for all sites, whereas other sites showed a very low level of contamination by the other elements.

Table 7 | Contamination factor, degree of contamination and contamination level of toxic metals in sediment collected from Pasur River, Bangladesh

		Contamination factor (C_f^i)					
Sites	**Season**	**Cr**	**As**	**Cd**	**Pb**	**Degree of contamination**	**Contamination level**
S1	Summer	0.57	0.24	2.77	0.64	4.22	Low
	Winter	1.12	0.20	0.86	2.23	4.40	Low
S2	Summer	0.46	0.66	1.80	1.22	4.14	Low
	Winter	0.91	1.14	0.96	1.82	4.83	Low
S3	Summer	0.34	1.07	4.50	2.12	8.03	Moderate
	Winter	0.92	0.37	2.40	1.79	5.48	Moderate
S4	Summer	1.00	0.47	**6.57**	1.29	9.32	Moderate
	Winter	1.22	0.62	1.63	2.84	6.31	Moderate
S5	Summer	0.86	0.33	1.30	0.49	2.98	Low
	Winter	1.38	1.03	2.75	2.21	7.37	Moderate
S6	Summer	0.55	0.61	**6.13**	0.37	7.65	Moderate
	Winter	2.61	3.46	5.51	3.48	15.1	Considerable
S7	Summer	0.63	0.64	**8.37**	1.09	10.7	High
	Winter	2.45	3.62	4.53	2.23	12.8	Considerable
S8	Summer	1.01	0.93	2.50	0.56	5.00	Moderate
	Winter	1.92	2.42	4.49	3.04	11.9	Considerable
S9	Summer	0.86	1.12	4.87	2.06	8.90	Moderate
	Winter	1.75	1.53	3.43	3.51	10.2	Considerable
S10	Summer	1.21	0.76	5.80	1.12	8.90	Moderate
	Winter	2.22	2.66	5.47	3.79	14.1	Considerable

Note: Bold indicates very high contamination ($C_f^i > 6.0$).

Table 8 | Potential ecological risk factors (E_r^i) and potential ecological risk indexes (PER) of toxic metals in sediments of Pasur River, Bangladesh

		Potential ecological risk factor (E_r^i)					
Sites	**Season**	**Cr**	**As**	**Cd**	**Pb**	**Risk index (PER)**	**Pollution level**
S1	Summer	1.14	2.42	83.0	3.19	89.7	Moderate
	Winter	2.23	1.96	25.7	11.1	41.0	Low
S2	Summer	0.93	6.59	54.0	6.09	67.6	Moderate
	Winter	1.82	11.4	28.7	9.12	51.0	Low
S3	Summer	0.69	10.7	135.0	10.6	157	Considerable
	Winter	1.84	3.71	72.1	8.95	86.6	Moderate
S4	Summer	2.00	4.69	**197**	6.43	210	Considerable
	Winter	2.44	6.23	48.8	14.2	71.7	Moderate
S5	Summer	1.71	3.25	39.0	2.47	46.4	Low
	Winter	2.75	10.3	82.6	11.0	107	Moderate
S6	Summer	1.09	6.07	**184**	1.84	193	Considerable
	Winter	5.22	34.6	**165**	17.4	223	Considerable
S7	Summer	1.26	6.36	**251**	5.43	264	Very high
	Winter	4.89	36.2	135	11.2	188	Considerable
S8	Summer	2.01	9.33	75.0	2.81	89.1	Moderate
	Winter	3.84	24.2	134	15.2	178	Considerable
S9	Summer	1.71	11.2	146	10.3	169	Considerable
	Winter	3.50	15.3	103	17.5	139	Considerable
S10	Summer	2.43	7.62	**174**	5.62	189	Considerable
	Winter	4.44	26.6	**164**	18.9	214	Considerable

Note: Bold indicates high ecological risk ($E_r^i > 160$).

To identify the source of heavy metals in sediment of different sites of Pasur River, a PCA was performed, which has been considered to be an effective tool for source identification (Bai *et al.* 2011; Anju & Banerjee 2012; Cai *et al.* 2012). The PCA was performed on the dimensionless standardized form of the dataset and is presented in Figure 4. In the current study, three principal components were extracted from the values of toxic metal concentrations in water and sediments (Figure 4). In the PCA, the first two PCs were computed and the variance explained by them was 50.0 and 25.8% in water and 41.1 and 30.6% in sediment (Figure 4). Among the two groups, one group revealed similar loadings of Cd, As and Cr in water and Cr, Cd, As and Pb in sediments, indicating that these were mostly contributed by anthropogenic activities (Renner 2004; Manzoor *et al.* 2006; Shah & Shaheen 2007). The depositions of atmospheric particulates released by automobiles were believed to contribute these metals in the urban areas, from where the water and sediment samples were composed (Manzoor *et al.* 2006; Pandey *et al.* 2012). PCA exposed that the apportionment of the same kind of heavy metals in water and sediments were not alike (Figure 4), which might be due to the emission of toxic metals to the environment and addition by the water.

CONCLUSIONS

Contamination of four toxic metals was investigated in the surface water and sediments of Pasur River, located at the southern part of Bangladesh. Slightly higher levels of metals were observed during winter compared to summer season. As some of the selected metals exceeded the safe levels, the water from contaminated sites should not be used without treatment. The contamination factor (CF) and PLI exposed that sediments in this study were unpolluted to extremely polluted by the studied metals. The PCA indicates that Cd, As and Cr in water and Cr, Cd, As and Pb in sediments were predominantly contributed by anthropogenic activities. For individual metals, Cd had high ecological risk for some sites, whereas the potential ecological risk indexes of this metal showed considerable potential ecological risk of the study area. Therefore, the present research recommends that the point sources of toxic metals in the vicinity of the Pasur River should be strictly

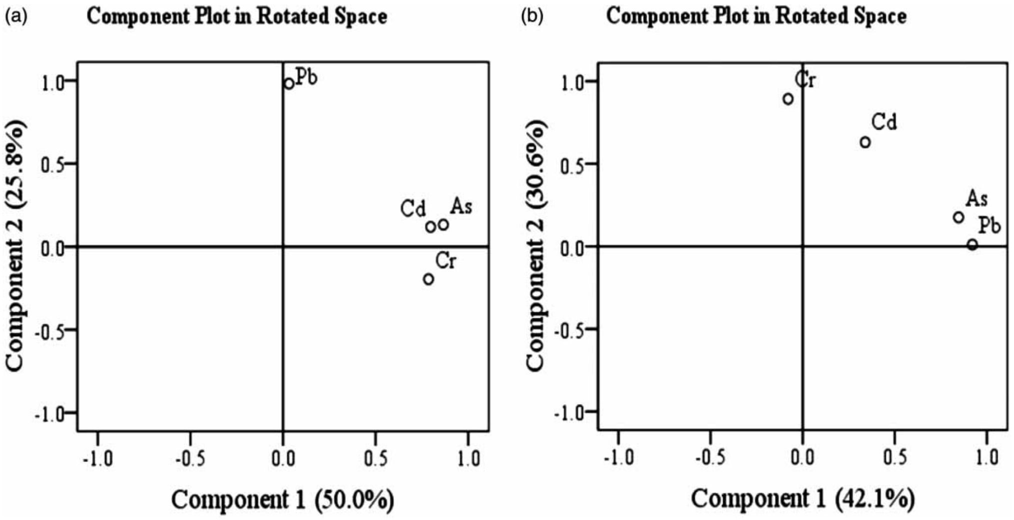

Figure 4 | PCA of toxic metals in water (a) and sediment (b) collected from Pasur River, Bangladesh.

monitored for a comprehensive risk assessment and protecting the health of the riverine ecosystem.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest. This study mainly focuses on the toxic metals concentration in surface water and sediments including the ecological risk assessment in a coastal river of Bangladesh. We extensively monitored the present pollution status of trace metals in the riverine samples. Our research mainly focused on the identification of environmental problems related to metals pollution, and we did not receive any financial support or have any other relationship with other people or organizations.

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