



## Preliminary assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh



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### ABSTRACT

Contamination of heavy metals in sediment is regarded as a global crisis with a large share in developing countries like Bangladesh. Four heavy metals such as arsenic (As), chromium (Cr), cadmium (Cd) and lead (Pb) in sediments and water were investigated from Karnaphuli River in Bangladesh. The decreasing trend of metals were observed in water as Cr > As > Pb > Cd and in sediment Cr > Pb > As > Cd. The ranges of heavy metals in water were 13.31–53.87, 46.09–112.43, 2.54–18.34 and 5.29–27.45 µg/L and in sediments were 11.56–35.48, 37.23–160.32, 0.63–3.56 and 21.98–73.42 mg/kg for As, Cr, Cd and Pb. The level of studied metals in water samples exceeded the safe limits of drinking water, indicated that water from this river is not safe for drinking and/or cooking. Contamination factor (CF) confirmed that the sediment samples were moderate to high contamination by As, Cd and Pb. The pollution load index (PLI) values were above one (>1) indicates advanced decline of the sediment quality. This study recommended that continuous monitoring of As, Cd and Pb in water; sediment and other aquatic biota of Karnaphuli River should be directed to assess the risk of these vital metals to safe the ecology in the vicinity of this river.

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### 1. Introduction

Contamination of heavy metals in the aquatic environment has attracted global attention owing to its abundance, persistence and environmental toxicity (Islam et al., 2015a; Ahmed et al., 2015a,b). Both natural and anthropogenic activities are responsible for the abundant of heavy metals in the environment (Wilson and Pyatt, 2007; Khan et al., 2008). However, anthropogenic activities can effortlessly generate heavy metals in sediment and water that pollute the aquatic environment (Sanchez-Chardi et al., 2007). The increasing pollution by heavy metals have a significant adverse health effects for invertebrates, fish, and humans (Yi et al., 2011; Islam et al., 2014; Martin et al., 2015; Islam et al., 2015b,d; Ahmed et al., 2015c). The metal pollution of aquatic ecosystems is increasing due to the effects from urbanization and industrialization (Sekabira et al., 2010; Zhang et al., 2011; Bai et al., 2011; Grigoratos et al., 2014; Martin et al., 2015).

In the 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 compartment of metals is a function of the suspended sediment composition and water chemistry in the natural water body (Mohiuddin et al., 2012). During transportation of heavy metals in the riverine system, it may undergo frequent changes due to dissolution, precipitation and sorption phenomena (Abdel-Ghani and Elchaghaby, 2007), which affect their performance and bioavailability (Nicolau et al., 2006; Nouri et al., 2011). Sediment is an essential and dynamic 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 and industrial impacts and risks posed by waste discharges on the riverine ecosystems (Zheng et al., 2008; Yi et al., 2011; Saleem et al., 2015). Therefore, it is important to measure the concentrations of heavy metals in water and sediments of any contaminated riverine ecosystem.

Nowadays heavy metal pollution is a main problem in many developing countries like Bangladesh (Islam et al., 2015c). The unplanned urbanization and industrialization of Bangladesh have detrimental effects on the quality of water and sediment as well as

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other aquatic fauna. The disposal of urban wastes, untreated effluents from various industries and agrochemicals in the open water bodies and rivers has reached alarming situation in Bangladesh which are continually increasing the metals level and deteriorating water quality (Khadse et al., 2008; Venugopal et al., 2009; Islam et al., 2015a,c). In Bangladesh, Karnaphuli River is the largest and important river in the Chittagong City and sea port area. Because of the industrially developed area the heavy metal pollution of the Karnaphuli River is increasing day by day. The studied river receives huge amount of untreated effluents from industries such as spinning mills, dyeing, cotton, textile, steel mills, oil refineries and others. High concentration of heavy metals such as arsenic (As), chromium (Cr), cadmium (Cd) and lead (Pb) are discharged into the Karnaphuli River which pollute the water and sediments. To date, no scientific research regarding heavy metal pollution in water and sediment of the study river has been conducted so far. Therefore, the objectives of this study are to evaluate the water quality parameters of the Karnaphuli River; to determine the levels of heavy metals in water and sediment; and to assess the heavy metal pollution status in sediments.

## 2. Materials and methods

### 2.1. Study area and sampling

This study was conducted on the Karnaphuli River, which passes through Chittagong City, close to the Bay of Bengal, Bangladesh (Fig. 1). The name of the sampling sites with their GIS coordinates is presented in Table S1. Karnaphuli River is one of the major and most important rivers in Chittagong and the Chittagong hill tracts, originating in the Lushai hills in Mizoram State of India. It travels through 180 km of mountainous wilderness formation of a slight circle at Rangamati and then follows a zigzag course before it forms two other prominent loops, the Dhuliachhari and the Kaptai. It runs over the district in a zigzag path and after a course of about 170 km falls into the Bay of Bengal and about 16 km southwest of Chittagong town. About 40 composite sediment and water samples were collected from 10 sampling locations of Karnaphuli River in September, 2014 (summer) and in March, 2015 (winter). During winter, there is no rainfall, and river water levels decrease; during summer, river water levels increase due to heavy rainfall. Considering the water flow in the studied river, summer season exhibited higher than winter season which can cause the variation of metals concentration in water and sediment. Water samples were filtered (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 HNO<sub>3</sub> (65% supra pure, Merck) and kept at 4 °C in the dark until analysis. Sediment samples were collected by Ekman dredge from different stations of the Karnaphuli River at same sites of water samples. The collected samples were put into the polythene bag (sediment) and 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.

### 2.2. Water quality parameters

Physico-chemical parameters like temperature, pH and dissolved oxygen (DO) of the river water were measured. Water samples were collected on spot using water sampler for the detection of physicochemical parameters. Temperature and pH were determined using a microprocessor pH meter (Model No. HI 98139, HANNA Instruments Ltd., Germany). Salinity was measured by potable Refractometer (Model: EXTECH RF20). Other parameters

like hardness (mg/L), dissolved oxygen (mg/L), alkalinity (mg/L), ammonia (mg/L), were analyzed on using kits (HANNA Test kits, Hanna Instruments Ltd., Germany).

### 2.3. Chemicals and sample digestion

All standard solution for target element was supplied by Merck Germany with highest purity level (99.98%). Ultra-pure HNO<sub>3</sub> was used for sample digestion. All other acids and chemicals were either supra pure or ultra-pure received from 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<sub>3</sub> 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<sub>3</sub> was added and boiled at 130 °C on hot plate till the volume came to about 25–30 mL and light color. Addition of HNO<sub>3</sub> and boiling were repeated till solution becomes light colored or clear. After cooling, volume was made to desired level with 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<sub>3</sub> was added. The content was heated at 130 °C for 5 h until 2–3 mL remaining in the beaker. After digestion materials were passed through Whatman no. 41 filter paper, washed with 0.1 M HNO<sub>3</sub> solution and made up to 100 mL volume with deionized water.

### 2.4. Analytical technique and accuracy check

All the matrixes were analyzed for Pb, Cd, Cr and As by atomic absorption spectrophotometer (Model ZEEnit 700P# 150Z7P0110, AnalytikJena, Germany) using GF-AAS and Hydride Generator 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 S2. The instrument calibration standards were made by diluting standard (1000 ppm) supplied by Sigma–Aldrich, Switzerland. The results were expressed as mg/kg for fish and sediment while µg/L for water sample. De-ionized ultrapure water was used for the experimental procedure. All glassware and containers were cleaned by 20% nitric acid, finally rinsed with De-ionized ultrapure water for several times and oven-dried prior to use. The analytical procedure was checked using certified reference material DORM-4 Fish protein for heavy metals. This 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 0.65–8% and the percentage recovery was between 89 and 99% as shown in Table S3. The results indicated a good agreement between the certified and observed values.

### 2.5. Assessment of heavy metals in sediment

In the interpretation of geochemical data, choice of background values plays a significant contribution. Several researchers have used the average shale values or the average crustal abundance data as reference baselines (Loska and Danuta, 2003; Singh et al., 2005; Islam et al., 2015a). The degree of contamination from heavy metals could be evaluated by determining the contamination factor (CF), pollution load index (PLI) and geoaccumulation index (*I*<sub>geo</sub>).

#### 2.5.1. Pollution load index (PLI) and contamination factor (CF)

To evaluate the sediment quality, combined approaches of pollution load index of the four metals were calculated according to Islam et al. (2015c). The PLI is defined as the *n*th root of the multiplications of the contamination factor of metals (CF).

$$(1) \text{PLI} = (\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \dots \times \text{CF}_n)^{1/n}$$

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