The present study was conducted to figure out the heavy metals (Cd, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb and Zn) concentrations in water, sediments and fish species from the Rupsha River, Khulna, Bangladesh to spot the heavy metal contamination level. Heavy metals are dangerous because they're non-biodegradable and having an extended half-life period. The heavy metal contamination could also be an excellent concern, especially for aquatic life. The metal concentration within the water sample from the Rupsha River was significantly above the rule values of WHO and USEPA respectively. Moreover, the concentration of metal within the sediments was also greater than the respective probable effect concentrations of the sediment quality guidelines. Furthermore, consistent with the fish standards, these studied fish species weren't found to be contaminated by heavy metals. It’s concluded that each of the heavy metals from the whole sample didn't exceed the standard maximum level. This study demonstrated that water of Rupsha River isn't safe for aquatic organisms also like humans in terms of Pb, Cd and Cr contents as accumulated through consumption.
Keywords: Heavy metal; Rupsha River; sediment; fish species etc.

ABBREVIATIONS

CCC : Criterion Continuous Concentration
CMC : Criteria Maximum Concentration
DEPZ : Dhaka Export Processing Zone
EF : Enrichment Factor
ERLs : Effect Range Low
ERMs : Effect Range Median
LELs : Lowest Effect Levels
METs : Minimal Effect Thresholds
PECs : Probable Effect Concentrations
PEls : Probable Effect Level
SEls : Severe Effect Levels
SI : Supplementary Information
SQGs : Sediment Quality Guidelines
TECs : Threshold Effect Concentrations
TELs : Threshold Effect Levels
TETs : Toxic Effect Thresholds

1. INTRODUCTION

Heavy metals are environmental priority pollutants and are becoming one among the foremost serious environmental problems because of their persistence, toxicity, non-biodegradability, and skill to be incorporated into the natural phenomenon [1-3]. Industrial wastes, the geochemical structure also because the mining of metals produce a possible source of these heavy metals pollution within the aquatic environment [4,5].

Under certain environmental conditions, heavy metals may accumulate to a toxic concentration, and cause ecological damage [6,7]. Over the past hundred years, heavy metals containing industrial effluents are discharged into the world’s rivers and lakes as a result of swift and rapid industrialization [8-10] and, consequently, they aggregated in marine species and sediments. The concentration of heavy metals within the aquatic ecosystem usually is decided by the analysis of the water, sediments, and therefore the aquatic species. Generally, the chosen heavy metals exist at very less amount in water and attain considerable concentration in sediments and aggregation [11]. Surface water samples provide evidence of this condition of a river or lake, whereas the measurement of contamination in solid matrices provides evidence of pollution for extended periods [12]. Many geochemical and environmental studies of river and lake sediments are made worldwide to figure out the extent of heavy metal contamination [13-15]. Sediment could also be a serious sink of heavy metals. These metals are generally dynamically divided either as dissolved-dissociated in water or absorbable onto the fine sediments and particulate organic matter [16,17]. Despite this, it also acts as a possible source of metal contamination into the water column and aquatic biota due to desorption, remobilization, oxidation-reduction reactions, and degradation of aggregative material [18-20]. Heavy metals from runoff water are receiving by rivers water can affect the increasing toxic level within the water column, sediments and another biota. Thus pollution by heavy metals is taken under consideration a possible threat to aquatic life and eventually to human health. Khulna city is the third-largest industrial city after the position of Dhaka and Chittagong city within the south-west division of Bangladesh. Rupsha River flows at the side of Khulna city and eventually falls into Bhairab River. Plenty of industries are built up near the Rupsha River. Fish processing plants, steel mills, paper mills, rayon mill complexes, cement factories, paint and dye manufacturing plants, soap and detergent factories, also because the sort of sunshine industrial units of the Khulna, directly discharge the untreated toxic effluent into the Bhairab-Rupsha river system. These industries discharge quite 4502 m³/ha wastewater within the Rupsha River, which ultimately administered to the Sundarbans through the Bhairab-Rupsha River system [21].

So this study was carried on the brink of evaluating the anthropogenic effects in Rupsha river area on the aquatic ecosystem components including water, sediments and fish species with regard to heavy metals contamination.

2. MATERIALS AND METHODS

2.1 Study Area

The Rupsha river skilled Khulna metropolitan city was selected for this study. Three sampling points were selected relying on the proximity to the polluted source: S1: at main industrial discharge point near glass and plastic industries, paint and dye manufacturing plants, soaps and detergent factories, paper mills also as steel mills; S2: near Rupsha fish market and Rupshaghat where the effluents of fish processing plants, wastes of brickyards and thus the wastes from agriculture runoff are discharged; S3: at low industrial discharge area
during which sewage and municipal wastes unwanted residues admixing with Fe₂O₃·2H₂O resulted from the activities of Shipbreaking yard are directly discharged.

2.2 Sample Collection

In this present investigation, a complete of 12 effluent samples, 36 water samples, 36 sediment samples, and 40 fish samples of 10 species from the three pointing zones also as nearby areas were collected within the pre-monsoon and post-monsoon, respectively with the help of the fishermen of that locality. All samples were collected in duplicate to research the heavy metals; this analysis was performed accordingly for checking repeatability.

2.3 Effluent Samples

Effluent samples were collected from the discharging point of the industries drain. Special care was taken so on follow standard sampling and preservation procedures (APHA, 1999), and to exclude large suspended materials during sample collection.

2.4 Water and Sediment Samples

Water and sediment samples were collected from three sampling points in Rupsha River. Water samples were collected in acid-washed polyethylene bottles and Whatman no. 541 paper was used. The samples were then preserved with the addition of 2 ml ultrapure HNO₃ per litre of water sample to attenuate the absorption of metals into the wall of the containers. Sediment samples were collected with a grab sampler and were placed in pre-cleaned polyethylene bags. Then, the samples were transferred to the analytical chemistry laboratory of the Institute of Nuclear Science and Technology, BAEC to analyze these. Before analysis, the sediment samples were dried, ground, sieved with a 2mm sieve, and stored in airtight plastic vials inside desiccators.

2.5 Fish Samples

Forty fish samples of 10 species (i.e., Mastacembelus armatus (common Bengali name Baim), Gudusia chapra (Chaplin), Puntius ferox (Puli), Noloterus notopterus (Foli), Corica soborna (Kachki), Setipinna phasa (Phassa), Amblypharyngodonmola (Mola), Mystus vittatus (Tangra), Heteroneustes fossilis (Singh), and Clupisoma pseudeutropius (Batashi)) were collected from the three pointing zones also the closest areas at different times of the year with the help of local fishermen from the Rupsha River. For the preparation and preservation of the fish samples, an in-depth method is described [22].

2.6 Heavy Metal Analysis

Initially, for the analysis of the heavy metals, effluent and water samples were filtered through paper Whatman no. 541 (Whatman, Germany) into 100 mL of prewashed plastic bottles and thus the analytical grade HCl (Assay: 36.5%; Fisher Scientific, USA) was used to adjust water pH to 3.5. For the heavy metal analysis in sediment samples, the dried sediment samples were digested first according to the procedure of Thompson and Benerjee (1991), during which accurately weighed sediment samples (0.25 g) were treated with 1.0 ml 70% HClO₄ and 4 ml concentrated HNO₃ during a clean Pyrex tube (12 × 2 cm). The tube was placed during a laboratory-made heating block and heated gently for 2–3 hours at 150°C in an oil bath (paraffin) until the copious fumes ceased to evolve. The temperature of the bath was raised to about 190°C and heating was continued at that temperature until the residue became dry. The dried residue sample was cooled to ambient temperature and later, it's treated with 4 ml HCl (2 M). The solution was diluted using double-distilled deionized water and filtered quantitatively (Whatman no. 541) into a 50 mL volumetric flask. Fish digestion was administered according to Hanson (1973) with some modification. An entire of 0.5 g of fish powder was taken during a digestion apparatus and a 2.5 mL of concentrated H₂SO₄ (Assay: 98%; Fisher Scientific, USA) and 4 mL of concentrated HNO₃ (Fisher Scientific, USA) was added. When the initial vigorous reaction subsided, the mixture was heated slowly in an oil bath with the addition of 3/4 drops of H₂O₂ (Assay: 30%; Sigma Aldrich, USA). This step was repeated until the mixture became clear. The mixture was heated for an extra 20 min at about 150°C and allowed to relax at temperature (25 ± 1°C). Then, the mixture was diluted properly with the double-distilled water then filtered quantitatively into a 50 mL volumetric flask.

The concentration of the subsequent heavy metals (Pb, Cd, Ni, Cr, Cu, Zn, Mn and As) in water, sediments and fish samples were determined by AAS (Model AA-6800, Shimadzu Corporation Japan) with digital read-out system.
3.1 The Concentration of Heavy Metals in Water and Effluent Samples

The heavy metal concentrations in Rupsha River water samples are summarized in Table 1, including mean metal concentrations with minimum and maximum values, guideline values by the varied authorities, and world average background levels. This study revealed that the concentration of heavy metals within the water samples of Rupsha River, where the effluents were directly discharged from various industries around the Rupsha River. The ranking order of mean metal contents in Rupsha River was Zn>Cu>Pb>Mn>Cr>Ni>As>Cd. The trends of heavy metals contamination in our studied samples were according to the result that was previously reported by the Hong Kong Environmental Protection Department (Cheung et al., 2013), where Zn was identified because the most abundant in river water, followed by Cu and Pb and therefore the least was Cd. During this attempt, we made a comparative study with the criterion continuous concentration (CCC) and criteria maximum concentration (CMC) values of water quality criteria (USEPA, 2009). This study revealed that concentrations of all examined metals within the water of Rupsha River were greater than CCC and CMC values, with the exception of Ni and As. However, the amount of heavy metals content in water samples collected that river was generally above reference values suggested by WHO (1993), with the exception of Cu and Mn. However, the metal concentrations altogether of water samples were mostly below or on the brink of the Bangladesh beverage standards (ECR, 1997), with elevated levels of Pb, Cd, and Cr concentrations, which might be due to an excess entry of effluent within the water bodies. The Pb, Cr, Cu and Zn contents were quite the economic effluent quality normal for Bangladesh (EQS, 1991), whereas the concentrations of Cd and As were below the quality limits. However, the concentrations of the metals in our study were significantly below the permissible limits set by the Indian Standards Institution (ISI, 1981) and also the National Environmental Quality Standards (NEQS, 1999). During this Communication, we tend to additionally conduct a one-way ANOVA test among the content of the metals in effluents, Rupsha stream water.

3.2 The Concentration of Heavy Metals in Sediment Samples

The average heavy metals concentrations in Rupsha River sediments weren't above respective level with exception of Cr. To assess the impacts of heavy metals in sediments, the metal concentrations obtained from Rupsha River sediment samples were compared with sediment quality guidelines (SQGs) (Table 2).
Table 1. The heavy metals concentration in water and comparison with water quality guidelines (in ppm)

|                  | Pb   | Cd   | Ni   | Cr   | Cu   | Zn   | Mn   | As   | Reference                                      |
|------------------|------|------|------|------|------|------|------|------|------------------------------------------------|
| Rupsha River     | 0.136| 0.008| 0.048| 0.058| 1.32 | 3.68 | 0.088| 0.027| In the study of water samples of the Rupsha river |
| CCC (Criterion   | 0.0025| 0.00025| 0.052| 0.011| 0.009| 0.120| NG   | 0.150| USEPA (2009)                                   |
| Continuous       |      |      |      |      |      |      |      |      |                                                |
| concentration)   |      |      |      |      |      |      |      |      |                                                |
| CMC (Criteria    | 0.065| 0.002| 0.470| 0.016| 0.013| 0.120| NG   | 0.340|                                                |
| Maximum          |      |      |      |      |      |      |      |      |                                                |
| Concentration)   |      |      |      |      |      |      |      |      |                                                |
| WHO              | 0.01 | 0.003| 0.02  | 0.05 | 2.0  | 3.0  | 0.5  | 0.01 | WHO                                            |
| Organization     |      |      |      |      |      |      |      |      |                                                |
| Bangladesh       | 0.05 | 0.005| 0.1   | 0.005| 1.0  | 5.0  | 0.1  | 0.05 | ECR (197)                                      |
| drinking water   |      |      |      |      |      |      |      |      |                                                |
| standards        |      |      |      |      |      |      |      |      |                                                |
| Background       | 0.0002| 0.00002| 0.0003| NG   | 0.001| 0.010| 0.006| NG   | Kelvin’s et al., (2000)                        |
| concentrations,  |      |      |      |      |      |      |      |      |                                                |
| the world average|      |      |      |      |      |      |      |      |                                                |

*NG: Not Given
Source: [35]

Table 2. Concentration of trace metals in sediment and comparison with sediment quality guidelines (in ppm)

|                  | Pb   | Cd   | Ni   | Cr   | Cu   | Zn   | Mn   | As   | Reference                                      |
|------------------|------|------|------|------|------|------|------|------|------------------------------------------------|
| Rupsha River     | 62.40| 5.56 | 31.34| 67.72| 31.95| 121.35| 508.38| 2.22 | In the study of sediment samples of the Rupsha river |
| TECs             |      |      |      |      |      |      |      |      |                                                |
| LEL              | 31.0 | 6.0  | 16.0 | 26.0 | 16.0 | 120.0 | 460.0 | 6.0  | NYSDEC (1999)                                  |
| LEL              | 31.0 | 6.0  | 16.0 | 26.0 | 16.0 | 120.0 | 460.0 | 6.0  | Persaud et al. (1992)                          |
| ERL              | 46.7 | 1.2  | 20.9 | 81.0 | 34.0 | 150.0 | NG   | 8.2  | Long et al. (1995)                             |
| TEL              | 35.0 | 0.596| 18.0 | 37.3 | 35.7 | 123  | NG   | 5.9  | Smith et al. (1996)                            |
| MET              | 42.0 | 0.9  | 35.0 | 55.0 | 28.0 | 150.0 | NG   | 7.0  | EC & MENVIQ (1992)                             |
| PECs             | 110.0| 9.0  | 50.0 | 110.0| 110.0| 270.0 | 1100.0| 33.0 | NYSDEC (1999)                                  |
| SEL              | 250.0| 10.0 | 75.0 | 110.0| 110.0| 820.0 | 1100.0| 33.0 | Persaud et al. (1992)                          |
| ERM              | 218.0| 9.6  | 51.6 | 370.0| 270.0| 410.0 | NG   | 70.0 | Long et al. (1995)                             |
| PEL              | 91.3 | 3.53 | 36   | 90.0 | 197.0| 315.0 | NG   | 17.0 | Smith et al. (1996)                            |
| TET              | 170.0| 3.0  | 61.0 | 100.0| 86.0 | 540.0 | NG   | 17.0 | EC & MENVIQ (1992)                             |

*NG: Not Given
Source: [35]
Table 3. Concentration of heavy metals on wet weight basis in fish and comparison with fish standards (in ppm)

|                | Pb   | Cd  | Ni   | Cr   | Cu   | Zn   | Mn  | As  | Reference                                      |
|----------------|------|-----|------|------|------|------|-----|-----|-----------------------------------------------|
| This Study     | 0.92 | 0.05| 0.58 | 0.26 | 4.62 | 35.20| 4.97| 0.78| In the study of fish samples of the Rupsha river |
| Australian National Health & Medical Research Council (ANHMRC) | 2.0  | 2.0 | NG   | NG   | 30.0 | 1000.0| NG  | 1.14| Bebbington et al. (1977)                       |
| Western Australian Food & Drug Regulations | NG   | 5.5 | 5.5  | 5.5  | NG   | 40.0 | NG  | NG  | Plaskett and Potter (1979)                     |
| Australia New Zealand Food Authority (ANZFA) | 1.0  | NG  | NG   | NG   | 10.0 | 150.0| NG  | 1.0 | Alam et al. (2002)                             |
| Turkish Legislation | 1.0  | 0.1 | NG   | NG   | 20.0 | NG   | NG  | NG  | Dural et al. (2007)                            |
| Spanish Legislation | 2.0  | 1.0 | NG   | NG   | 20.0 | 50.0 | NG  | NG  | Usero et al. (2003)                            |
| UK Food Standard Committee Report | 2.0  | <0.2| NG   | NG   | 20.0 | NG   | NG  | NG  | Cronin et al. (1998)                           |
| Hong Kong Food Regulation | 6.0  | 2.0 | NG   | NG   | NG   | NG   | NG  | NG  | (1999)                                        |

*NG: Not Give

Source: [35]
The SQGs were grouped into two categories. One was threshold effect concentrations (TECs), including lowest effect levels (LELs) (NYSDEC, 1999), effect range low (ERLs) [26,27], threshold effect levels (TELs) [28], and minimal effect thresholds (METs) [28]. The opposite was probable effect concentrations (PECs), including severe effect levels (SELS) (NYSDEC, 1999), effect range median (ERMs) [29], probable effect level (PELs), and toxic effect thresholds (TETS) [30,29]. The TECs indicated contamination concentrations below that harmful effect on sediment-dwelling organisms weren’t expected and also the PECs indicated contamination concentrations above that harmful effect were expected to occur frequently [31].

In this present study, the chosen heavy metal concentrations in Rupsha River sediment didn’t exceed the respective probable effect concentrations (PECs), with the exception of Cr, indicating low to moderate level of pollution. Sedimentary metals concentrations within this study were but the previously reported values by Ahmad et al. (2010) and Karbassi et al., (2008). However, in contrast, our values from this study were above the reported values by Raphael [32].

### 3.3 The Concentration of Heavy Metals in Fish Samples

The mean heavy metal concentrations, also as concentration ranges within the muscles of 10 fish species taken from the Rupsha River, are summarized in Table 3. The mean metal concentrations in fish samples studied were decreased within the sequence of Zn>Mn>Cu>Pb>As>Ni>Cr>Cd, respectively. The variability of these heavy metals level in several species depends on feeding habits, ecological demands, metabolism, age, size and length of fish, and their habitats [33]. One-way ANOVA test revealed that the heavy metals concentration in 10 various fish species differed significantly. Our studied values were compared with the suggested limits of metals in fishes, suggested by different authorities (Table 3). It needs to be noted that every of the metal concentrations during this study was assessed on a dry weight basis. A factor of 4.8 (considering 79% moisture content of fish) was followed to see our values with the rule values that were presented on a wet weight basis [34]. Table 3 displays that the mean metal concentrations in fish samples are below the prescribed limits. However, the extent of Pb in C. Soborna among the ten species was above the proposed acceptable limit for human consumption. From the literature survey, it had been apparent that the fish samples of C. Soborna were bottom-living and thus sediments could be the most sources of Pb contamination therein fish because the mentioned fish was nearly always in-tuned with sediment. Additionally, the quantity of lead may be a ubiquitous pollutant that finds its way into the Rupsha River due to the discharge of commercial effluents from fish process plants, steel mills, paper mills, rayon mill complexes, cement factories, paint and also dye producing plants, soap and detergent factories and variety of sunshine industrial units etc. Our values were but the reported values by Fowler et al. (1975) and De et al. (2010), and quite the reported values by T¨urkmen et al. (2008), Lakshmanan et al. (2009), Raphael et al. (2011), and Pintaeva et al. (2011). However, there was an appropriate agreement between our values and therefore the values previously reported by Sharif et al. (1993) for the seafood species from an excellent number of rivers in Bangladesh.

### 4. CONCLUSION

The heavy metal contaminations became a severe problem in Bangladesh. This study visualizes that nearly all observed values exceed the quality levels for the water of the Rupsha River and fish samples. The Pb concentration was obtained above all acceptable limits altogether water samples and in Coricasoborna (Kachki) fish among 10 fish species. Therefore, aquatic organisms are at extreme risk. The Pb, Cr, Cu, and Zn metals concentrations were found to be above effluent quality standard for Bangladesh (EQS.1991) among effluent samples. It indicates that Rupsha River water is contaminated through disposals of commercial effluents, chemical complexes, and fish processing plants, steel mills, municipal waste runoff, sewage etc. within the sediment sample, all metals concentrations were below the prescribed limits with exception of Cr. This study demonstrated that water of Rupsha River isn’t safe for aquatic organisms also like humans in terms of Pb, Cd and Cr contents as accumulated through consumption. As Pb extent was observed in highest level the both in River water and fish species, citizenry, also as fishes, maybe repeatedly vulnerable to constipation, anaemia, brain diseases, heart diseases, vital sign with chronic exposure. Hence, necessary steps must be taken to get rid of heavy metals from the effluent samples and sewage before discharging into water bodies so as to sustain a far better
aquatic environment and ecological balance. Therefore, continuous monitoring of the extent of heavy metals concentration within the Rupsha River is crucially needed since this water source is a crucially required source of beverage, irrigation, and fish for the inhabitants within the studied area.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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