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ASSESSMENT OF HEAVY METALS IN RIVER WATER, SEDIMENT AND FISH MUSSEL IN RUPSHA RIVER UNDER KHULNA DISTRICT, BANGLADESH

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ABSTRACT

Sabbir W, Rahman MZ, Hasan MM, Khan MN, Ray S (2018) Assessment of heavy metals in river water, sediment and fish mussel in Rupsha river under Khulna district, Bangladesh. *Int. J. Expt. Agric.* 8(1), 1-5.

The present study was undertaken to determine heavy metal concentrations in water, sediment and muscles of certain freshwater fish and crustacean species of Rupsha River in Khulna region, the south western part of Bangladesh. Heavy metals concentrations were determined by Atomic Absorption Spectrophotometer. Heavy metals, those were measured from the river water, sediment and fish body were Arsenic (As), Mercury (Hg), Chromium (Cr), Cadmium (Cd) and Led (Pb). The concentrations of heavy metals were determined in six fish species namely *Peneaus monodon*, *Gudusia chapra*, *Channa punctatus*, *Macrognathus aculeatus*, *Glossogobius giuris* and *Mystus gulio*. Fish samples as well as heavy metal concentration of water and sediment were measured in six different sampling stations for three months during the year of 2016. The highest heavy metal concentration in water and sediment were observed near Khulna Ship Yard due to ship breaking activities and direct toxic chemical disposal in river water. The highest heavy metal concentration in fish among six species was found in giant tiger shrimp, *Peneaus monodon* (Cr: 62.81±2.55; Cd: 9.44±0.35 and Pb: 150±4.75 µg kg^{-1} respectively). Arsenic (As) was found in only sediment samples but Hg was not found at any station. The study further revealed that the concentrations of heavy metals in water, sediment and fish of the Rupsha River were within the permissible limit.

Key words: *toxicity, permissible limit, arsenic, mercury, chromium, cadmium, led*

INTRODUCTION

Heavy metal is a relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts. Fishes are widely used as bio- indicators of aquatic pollution by metals (Padmini and Kavitha, 2005). The elevation of metal levels often results in a high concentration in the bottom sediment (Cundy *et al*. 2003). These metals may accumulate to a very high toxic levels and cause acute impact on the aquatic organisms without any visible sign (Giguère *et al*. 2004). Presence of heavy metals are the indication of pollution in any aquatic environment and the toxicity of these metals stems are biologically non-degradable and have the tendency to accumulate in water, sediment and fish body (Gale *et al*. 2004). Heavy metals are accumulated and biologically magnified in fish tissues (Ayas *et al*. 2007). The investigation of heavy metals in water and sediment might be used to assess the anthropogenic and industrial impacts and risks posed by waste discharges on the riverine ecosystems. (Zheng *et al*. 2008).

Khulna city is the third largest industrial city in the south western part of Bangladesh. This city is located 50 km upstream of the Sundarban mangrove forest and adjacent with the Rupsha River (Adhikary and Hossain, 2012). A significant number of fisheries, dockyards, shipyards and factories are situated on the bank of this river. The polluting industries of Khulna such as chemical complexes, fish processing plants, steel mills, paper mills, rayon mill complexes, cement factories, paint and dye manufacturing plants, several soap and detergent factories and a number of light industrial units directly discharge untreated toxic effluent in to the Rupsha River (Chowdhury *et al.* 2010). Besides, releases of untreated toxic effluents are the major sources of heavy metals in any aquatic ecosystem. Unfortunately, no research is still conducted to assess the metal pollution of the Rupsha River including its biotic resources, sediment and water quality. Therefore, the study was conducted with an objective to assess the abundance of some heavy metals i.e. Led (Pb), Cadmium (Cd), Chromium (Cr), Mercury (Hg) and Arsenic (As) in water, sediment and fish body of the Rupsha River to estimate the status metal pollution.

MATERIALS AND METHODS

Study area

The water, sediment and fish samples were collected from six stations of Rupsha River namely Kalibari Ghat, Jailkhana Ghat, Custom Ghat, Khulna Ship yard, Rupsha Ghat and Rupsh bridge. The distance among the sampling points were approximately 1 km.

Sample collection

Samples were collected for three months from June, 2016 to August, 2016 at ten days interval. Sediments and water sample were collected from six samplings points of the Rupsha River. The water samples were collected from 0.5 m below the water surface. The upper 10 cm of the bottom layer sediment samples were taken with Ekman grab. Each sediment core was packed separately in acid soaked clean polyethylene packets and brought to the Quality Control Laboratory of Department of Fisheries (DoF), Boyra, Khulna for analysis. In the laboratory the sediment samples were dried at 105^{o} C to constant weight, ground and the fraction passing a BS20 sieve was stored in clean acid-soaked polyethylene packets at 20^{o} C. Fish species samples were collected from fishermen at sampling sites of the Rupsha River during sampling period. Six fish species were collected from the Rupsha River namely *Peneaus monodon* (Bagda), *Channa punctatus* (Taki), *Gudusia chapra* (Chapila), *Macrognathus aculeatus* (Tara baim), *Mystus gulio* (Nona Tengra) and *Glossogobius giuris* (Bele). Consistently experiment was done with three replications.

Equipments

All the matrixes were analyzed for Pb, Cd, Cr, Hg and As by atomic absorption spectrophotometer (Model ZEEnit 700P # 150Z7P0110, Analytikjena, Germany) using Graphite Furnace for Pb, Cd and Cr, Hydride Generator system for As and Cold Vapor Hydride Generator system for Hg.

Metal analysis in water

About 250 ml of the acidified composites were taken into a 300 ml beaker where 2 ml of the concentrated HNO_3 were added. For mercury and arsenic analysis 1 ml of H_2O_2 added and heated for 30 minutes. The samples were filtered and then transferred to a 100 ml volumetric flask. Further dilution were made as per required for metal analysis by AAS (Atomic Absorption Spectrophotometer).

Sediment digestion for metal analysis

Around two gm of sample was taken in 100 ml beaker and placed on hot plate. 15 ml concentrated HNO_3 were added and the samples were heated at 120^0 C for 1 hour. 5 ml of HCl was added and heated at 120^0 C for 1 hour. Then 5 ml of $HClO_4$ was added and heated until 1-2 ml remains. For mercury and arsenic analysis 1 ml of H_2O_2 added and heated for 30 minutes and made volume with DI (De-ionized water) in 100 ml volumetric flask. Further dilution was made as per required. Finally the samples were examined with AAS for metal estimation.

Fish digestion for metal analysis

Approximately two gm of sample was taken in 100 ml beaker and placed into Muffle Furnace for overnight at 450^0C to create ash. 5ml of 6M HCl and 0.1M HNO_3 were added and the sample was heated at 120^0 C in hot plate. For mercury and arsenic analysis 1 ml of H_2O_2 added and heated for more 30 minutes and made the final volume with DI in 100 ml volumetric flask. Finally the samples were examined with AAS for metal estimation.

Analysis of As and Hg

For both Arsenic (As) and Mercury (Hg) analysis in water, sediment and fish mussel the following steps were followed.

Analysis of As

Step 1: 12.5-ml digested sample aliquots, 1.5 ml HCl were dispensed into 50 ml volumetric flask. Then 1 ml of ascorbic acid and KI mixture was added and final volume was made to 50 ml. Consequently, it took 2 hour to complete the reduction reaction of As.

Step 2: 5 ml prepared sample aliquots were dispensed into reaction vessel and readings were recorded.

Analysis for Hg

Step 1: 25-ml digested sample aliquots, 1.5 ml HNO_3 were dispensed into 50 ml volumetric flask. Then 0.5 ml of 1% $K_2Cr_2O_7$ was added and final volume was made to 50 ml.

Step 2: 5-ml prepared sample aliquots were dispensed into reaction vessel and readings were recorded.

Analytical technique and accuracy check

All the matrixes were analyzed for Pb, Cd, Cr, Hg and As by atomic absorption spectrophotometer (Model ZEEnit 700P # 150Z7P0110, Analytikjena, Germany) using GFAAS and Hydride Generator system. All the methods were in-house validated following EC657/2002. 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 (1000 ppm) supplied by Sigma Aldrich, Germany. The results were expressed as µg kg^{-1} for fish and sediment. But for water sample results were expressed in mg l^{-1}. The analytical procedure was checked using certified reference material DORM- 4 Fish protein for heavy metals. The standard deviations of the means observed for the certified materials were between 0.65–8% and the percentage recovery was between 89–99% as shown in Table 2. The results indicated a good agreement between the certified and observed values.

Table 1. Analytical conditions for measurement of heavy metals in aqueous solution using AAS

Elements	Wave length (nm)	Slit (nm)	Lamp Current (mA)	Mode	Calibration Range (µg / kg)	Detection limit (mg / kg)
As	193.7	0.8	6.0	HGAAS	2.5-20	0.05
Cr	357.9	0.8	4.0	GFAAS	4-32	0.019
Cd	228.8	1.2	3.0	GFAAS	0.4-1.2	0.03
Pb	283.3	0.8	4.0	GFAAS	5-40	0.025
Hg	253.7	1.2	3.0	CVHGAAS	5-20	0.02

Table 2. Concentrations of metals found in Certified Reference Materials by AAS

Parameters	Assigned Value (mg/kg)	Obtained Value (mg/kg)	Recovery %
Arsenic	6.80 ± 0.64	5.76	84.70
Cadmium	0.306 ± 0.015	0.266	86.93
Chromium	1.87 ± 0.16	1.81	96.79
Lead	0.416 ± 0.053	0.427	102.64
Mercury	0.410 ± 0.055	0.341	83.17

Statistical analysis

The data were statistically analyzed by the statistical package, SPSS 16.0 (SPSS, USA). The means and standard deviations of the heavy metal concentrations in water, fish and sediments were calculated by Microsoft Office Excel 2007.

RESULT

Heavy metal concentration in water

Heavy metals concentrations of water in six different stations of Rupsha River were measured. Arsenic (As), Mercury (Hg), Chromium (Cr), Cadmium (Cd) and Led (Pb) concentration were assessed in this study (Table 3).

Table 3. Station wise heavy metal concentration (µg l^{-1}) in water of Rupsha River

Sampling station	As	Hg	Cr	Cd	Pb
Kalibari Ghat	-	-	$4.91^{ab} \pm 0.30$	$0.92^{p} \pm 0.11$	$5.066^{xy} \pm 0.94$
Jailkhana Ghat	-	-	$4.77^{ab} \pm 0.24$	$3.824^{qr} \pm 0.29$	$6.16^{y} \pm 0.09$
Near Khulna Ship Yard	-	-	$6.27^{a} \pm 2.31$	$4.40^{r} \pm 0.66$	$9.21^{z} \pm 0.06$
Custom Ghat	-	-	$6.09^{a} \pm 0.96$	$3.66^{q} \pm 0.22$	$8.24^{z} \pm 1.39$
Rupsha Ghat	-	-	$3.17^{b} \pm 0.64$	$0.46^{p} \pm 0.05$	$3.99^{x} \pm 0.52$
Rupsha Bridge	-	-	$4.49^{ab} \pm 0.19$	$0.46^{p} \pm 0.21$	$3.76^{x} \pm 0.18$

Values in the same column with different superscripts are significantly different (p>0.05)

Among the six stations, highest concentration of Cr was observed near Khulna Ship Yard (6.27±2.31 µg l^{-1}). This may be attributed to the huge amounts of raw sewage, ship breaking activities, agricultural and industrial waste water discharged into the river (Abdel-Moati and El-Sammak, 1997). However, Cr concentration was not exceeded the maximum consumption level for human in water according to European Commission, which is 25 µg l^{-1}. Highest concentration of Cd was also found near Khulna Ship Yard 4.40±0.66 µg l^{-1}. The average concentration of Cd of all stations was below the maximum consumption level. Maximum consumption level of Cadmium (Cd) in water for human is 5µg l^{-1} according to European Commission. Pb was found 9.21± 0.06 µg l^{-1} near Khulna Ship Yard which was highest among the six stations. The lowest Pb concentration was recorded at Rupsha bridge (3.76±0.18 µg l^{-1}). The heavy metal concentration of Pb in water samples from Rupsha River was within the permissible limit. The permissible limit of Pb for human consumption according to European Commission is 50µg l^{-1}. The high level of Pb in water of Rupsha River could be attributed to the industrial and agricultural discharge as well as from spill of petrol from fishing boats and dust which holds a huge amount of led from the combustion of petrol in automobile vessels (Harvey *et al*. 2015).

Heavy metal concentration in sediment

The heavy metal concentration in sediment was significantly different among the stations (Table 4). Among the sampling stations highest average concentration of Arsenic (As) was found 1.86±0.27 µg kg^{-1} near Khulna Ship Yard and lowest was found 1.30±0.07 µg kg^{-1} at Rupsha Ghat. Concentration level of Mercury (Hg) in sediment samples were below the detection limit.

Table 4. Station wise heavy metal concentration (µg kg^{-1}) in sediment of Rupsha River

Sampling station	As	Hg	Cr	Cd	Pb
Kalibari Ghat	$1.39^{a} \pm 0.19$	-	$3196.0^{c} \pm 12.96$	$2105.8^{f} \pm 14.34$	$1810.4^{p} \pm 12.52$
Jailkhana Ghat	$1.68^{ab} \pm 0.25$	-	$3932.4^{d} \pm 152.33$	$2705.6^{g} \pm 12.16$	$6416.6^{q} \pm 23.67$
Near Khulna Ship Yard	$1.86^{b} \pm 0.27$	-	$4208.4^{e} \pm 19.70$	$2879.8^{h} \pm 10.47$	$12446.6^{r} \pm 452.90$
Custom Ghat	$1.84^{b} \pm 0.29$	-	$4206.0^{e} \pm 6.04$	$2712.6^{g} \pm 14.86$	$8523.8^{s} \pm 6.42$
Rupsha Ghat	$1.30^{a} \pm 0.07$	-	$3196.4^{c} \pm 17.00$	$1301.2^{i} \pm 7.46$	$1438.0^{t} \pm 35.97$
Rupsha Bridge	$1.31^{a} \pm 0.20$	-	$3168.2^{c} \pm 30.05$	$1894.8^{j} \pm 8.20$	$2088.8^{p} \pm 19.25$

Values in the same column with different superscripts are significantly different (p>0.05)

The metals concentrations in bottom sediment varied widely and exhibited fluctuations between different sampling stations. All the metals attained their maximum values near Khulna Ship Yard may be due to ship breaking activities and direct toxic chemical discharged into the river. Hg was not found in sediment samples.

Arsenic (As) concentrations in sediment among the six stations showed significant difference. Among the sampling stations, highest average concentration of Arsenic (As) was 1.86±0.27 µg kg^{-1} near Khulna Ship Yard and lowest concentration was 1.30±0.07 µg kg^{-1} observed in Rupsha Ghat. As concentration in sediments might be attributed to the anthropogenic activities such as ship breaking activities and direct release of toxic chemicals in the river water, treatment from the fertilizers and arsenical pesticides industries (Fu *et al*. 2014; Ahmed *et al*. 2016), treating of wood by exhausting copper arsenate (Pravin *et al*. 2012; Baeyens *et al*. 2007) and tanning in relation to some chemicals especially arsenic sulfide (Bhuiyan *et al*. 2011). Highest average concentration of Chromium (Cr) was recorded 4208.4± 19.70 µg kg^{-1} near Khulna Ship Yard. High level of Cr indicates its higher input, which might be originated from the urban and industrial wastes (Mohiuddin *et al*. 2012). Higher Chromium (Cr) concentration in sediment attributed as a consequence of direct discharging untreated wastes from petroleum, fertilizers and textile industries (Facetti *et al*. 1998; Islam *et al*. 2015). Cadmium (Cd) is widely distributed in the earth's crust at an average concentration of about 0.1 mg kg^{-1} and is commonly found in association with zinc (Zn). Furthermore, highest Cd concentration was found near Khulna ship Yard station (2879.8 ± 10.47 µg kg^{-1}). The high level of Cd in sediments at Khulna Ship Yard could be attributed to the ship breaking activities, industrial and agricultural discharge as well as from spill of petrol from fishing boats which were distributed in the River (Giguere *et al*. 2004). Average Pb concentration in Rupsha River was significantly different among the six stations. Highest Pb concentration was found near Khulna Ship Yard (12446.6 ± 452.90 µg/kg) and lowest in Rupsha Ghat (1438.0 ±35.97 µg kg^{-1}). Higher Led (Pb) concentration in sediment was found due to the effect from point and non-point sources; such as gasoline, petroleum, municipal runoffs and atmospheric deposition (Mohiuddin *et al*. 2012).

Heavy metal concentration in Fish body

Heavy metals concentrations of six different fish species of Rupsha rive were measured. Arsenic (As), Mercury (Hg), Chromium (Cr), Cadmium (Cd) and Lead (Pb) concentration were assessed in this study. No Arsenic (As) and Mercury (Hg) was found. The mean concentrations of heavy metal recorded in fish samples were shown in the Table 5.

Table 5. Species wise heavy metal concentration (µg/kg) in Fish of Rupsha River

Species	**As**	**Hg**	**Cr**	**Cd**	**Pb**
Peneaus monodon (Bagda)	-	-	62.81^{a} ± 2.55	9.44^{w} ± 0.35	150.00^{p} ± 4.75
Gudusia chapra (Chapila)	-	-	24.45^{b} ± 1.40	4.44^{x} ± 0.43	28.32^{q} ± 3.14
Channa punctatus (Taki)	-	-	53.52^{c} ±2.22	6.95^{y} ± 0.13	81.48^{r} ± 2.21
Macrognathus aculeatus (Tara baim)	-	-	62.59^{a} ± 3.06	9.39^{w} ± 0.40	126.34^{s} ± 5.56
Glossogobius giuris (Bele)	-	-	43.15^{d} ±1.15	5.35^{z} ± 0.33	41.83^{t} ± 9.28
Mystus gulio (Nona Tengra)	-	-	50.36^{c} ± 16.43	5.80^{z} ± 0.39	71.37^{r} ± 3.14

Values in the same column with different superscripts are significantly different (p>0.05)

Fish are sensitive to various types of pollutants. Fish and other organisms can absorb metals through their respiratory surfaces. Another mode of uptake is by the adsorption of metals on the body surfaces. Many fishes show respiratory distress with heavy metal toxicity. Chromium (Cr) is required for organisms in small quantities as an essential trace metal nutrient and is widely used in refractory materials like bricks. Cr concentration was significantly different among the stations. But, all species contain less Cr concentration than maximum consumption level, which is 1 mg kg^{-1}. Highest concentration level of Cd was found 9.44 ± 0.35 µg kg^{-1} in Bagda which is benthic feeder and lowest in Chapila (4.44±0.43 µg kg^{-1}) which is surface feeder. In aquatic system, Led (Pb) was found to be quite toxic to many organisms even in small concentration. In the present study, Pb concentration was found within the acceptable level where the highest mean concentration found to be 150 ±4.75 µg kg^{-1} in Bagda and the lowest was 28.32±3.14 µg kg^{-1} in Chapila. Pb concentration was significantly different in different species of fish may be due to feeding habit. Arsenic (As) and Mercury (Hg) were not found in the fish samples from Rupsha River. However, Rahman *et al*. (2012) measured the concentrations of eight heavy metals (Pb, Cd, Ni, Cr, Cu, Zn, Mn, and As) in the muscles of ten species of fish collected from Bangshi River at Savar in Bangladesh in two different seasons. The concentrations of the studied heavy metals, except Pb in *Corica soborna*, were found to be below the hazard limits. The study also showed that, Zn was the most and Cd was the least accumulated metal in the studied fish muscles which is very similar to our study.

CONCLUSION

In the present study concentrations of As, Hg, Cr, Cd and Pb were found lower than the safe values in water, sediment and fish body of the Rupsha River. But the direct discharges of Industrial effluents, sewage and municipal wastes without treatment as well as agricultural and urban runoff polluted the Rupsha River by heavy metals and might create an adverse effect on this riverine ecosystem in coming decades. Water and sediments from Khulna Ship Yard had greater concentrations of all studied metals than others stations due to ship breaking activities and release of toxic chemicals directly to the river. Actually Ship Yard is the only station that breaks the ship in the south western part of Bangladesh. Giant Tiger Shrimp (Bagda) had higher heavy metal content than other species available in the Rupsha River. The values for heavy metals indicate increasing trend of bioaccumulation and fish consumption may cause many health problems and diseases to human if the current trend of bioaccumulation continues without taking stern measures against heavy pollution. However, further research is necessary to make a pathway to reduce the metal pollution level of the Rupsha River.

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