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Environmental Contamination of Heavy Metals in Fish and Water Samples of Shitalakkhya River, Dhaka, Bangladesh

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Abstract:

Heavy metals are non-biodegradable substances which cause carcinogenic effects in animals and humans. This study was conducted to determine the concentration of lead (Pb), chromium (Cr) and cadmium (Cd) in fish and water samples from Shitalakkhya River, during pre-monsoon and post-monsoon period. In water the concentration of Pb, Cr and Cd ranged from 0.01 to 0.3159, 0.322 to 0.407 and 0.0035 to 0.0085 ppm respectively. The concentration of Pb (0.089 ppm) and Cd(0.006 ppm) was higher than the WHO guideline value. The concentrations of heavy metals were season specific and a significant (p<0.05) positive correlation exists among them in pre-monsoon period. Among the studied fish, Cr concentration was the highest in Colisafasciat us while Lepidocephalusguntea exhibited the highest accumulation of Pb. The order of heavy metal concentrations in the studied fish specieswere recorded as Cr>Pb>Cd. The analysis of fish samples revealed a significant (p<0.05) negative linear relationship between Pb and Cr while a moderate positive relationship exists between Cd and Cr. The results of this study will help us to assess the health of the river and will serve as the baseline data for the identification of hazardous sfactors in Shitalakkhya River.

Keywords: Heavy metals, correlation matrix, fish, water, Shitalakkhya River

1. Introduction

Dhaka is an overpopulated city surrounded by many rivers and inter-connected with riversand canals. River water is an important source of drinking, household, irrigation and industrial purposes. Shitalakkhya River is a tributary of the Brahmaputra and primarily flows in a southwest direction and then east of the city of Narayanganj, the second largest developed industrial area and have many industrial units including mainly dyeing and textile industries in which of about 80% industries have no Effluent Treatment Plant (ETP) (Islam et al.,2015).Due to the geographical position Shitalakkhya River receives a large amount of domestic sewage, industrial waste, agricultural pesticides and pollutants from adjacent rivers canals and direct run-off from land (Ahmed et al.,2009). Due to the over growing population as well as industries along the riverside and their pollutants are polluting this river constantly. Thus, this river serves as a sink for the industrial, commercial and municipal waste. Previous studies suggested that the characteristicsof industrial wastes are different from the other wastes (Islam et al.,2015).

Water Pollution is the major problem in urban growth centers and industrial belts. Due to lack of adequate regulatory measures and institutional setup for proper monitoring and control, pollutants from municipal, industrial and agricultural waste enter into the inland water system. Major causes of pollution that degrade water quality are industrial effluents, agrochemical, and spillage and low water flow in dry season.

The marginal people living on the bank of the Shitalakkhya River especially children consume and use this polluted water in bathing, washing and household work and are prone to different types of water borne diseases, viz. nausea, skin sore, irritation in respiratory tract (Sultana et al., 2009), typhoid, dysentery, cholera, viral hepatitis, etc. and lose their life (Islam et al., 2015).

Heavy metals have a high atomic weight and a density at least five times greater than that of water(Tchounwou et al.,2012). They are widely distributed in the environment due to their multiple applications in industrial, domestic, agricultural, technological and medical. Because of their high degree of toxicity arsenic, chromium, lead rank among the priority metals that are of public health significance. They are also sometimes considered as systemic toxicants that are even at lower level of exposure can induce organ damage. They are also classified as human carcinogens(Tchounwouet al.,2012).

The ecological balance of theheavy metalrecipient environment and the diversity of aquatic organisms are greatly affected by heavy metal concentration. The main inhabitants of waterare fishesand they cannot escape the harmful effect of these pollutants. Fish are widely used to evaluate the health of aquatic ecosystems because pollutants build up in the food chain and are responsible for adverse effects and death in the aquatic systems (Vinodhini and Narayanan, 2008).

In our study fish and water samples were collected from the Shitalakkhya River to investigate the heavy metal concentrations. 5 species of fish wereselected for the study - *Chanda nama*, *Colisafasciatus*, *Mastacembelusarmatus*, *Channa punctatus* and *Lepidocephalusguntea*. These fishes are benthopelagicand demersal in habit and they feed on benthic insect, larvae, worms and submerged plant materials mostly at night.

Nowadays highly sensitive analytical procedures are available for determining and detecting metal content with high precision without any doubt. For this study we have used Atomic Absorption Spectroscopy (AAS).Islam et al., (2015) carried out an experiment on the toxicity of Shitalakkhya River. They studied the concentration of heavy metals and physico-chemical parameters in water samples. Their data suggest that the water is not safe for aquatic life as well as human health. Limited data is available on Bangladesh river water samples (Ahmad et al., 2010;Ahmad et al., 2015; Sarker et al., 2016).Therefore, the aim of this study was to determine the concentration of heavy metals in water and fish samples and to determine the existing relationship among the heavy metals in respect to different spots and seasons using spread sheet software.

2. Materials and Methods

2.1. SampleCollection

The study was conducted for a period of eight months from June 2017 to January 2018 on Shitalakkhya River. In our study we choose three spots i.e., upward stream, downward stream and effluent exit point for sample collection. The first station was near the main exit of an industrial company, second station was upward stream and third was downward stream.

2.2. FishCollection

The five species of most common fishes – *Chanda nama, Colisafasciatus, Mastacembelusarmatus, Channa punctatus, Lepidocephalusguntea* were collected from the fisher men from the said spots. Captured fish samples were kept in an ice box with ice blocks for keeping the freshness of the fish sample. After that the samples were transferred to the hatchery.

2.3. Preparationof Fish Samples

At first the scales were removed and the tissues were separated from each sample fish. Then the tissues were washed thoroughly. Each fish tissue was kept in labeled German Petridish and to dry the sample the petridishes were kept in an oven for 24 hours to constant weight at 105°C. The dried samples were grinded by using a mortar pestle. They were then kept in plastic bottle and stored in desiccators until digestion.

2.4. Digestion of Fish Samples for AAS Analysis

For digestion 1 gm portion of each grinded samples were measured by using an electric balance and were kept in labeled beaker. 4 ml of HNO_3 and 2 ml $HCLO_4$ were added at each beaker. The beaker was then kept on Hot plate at temperature 95°C. Heating continued for 1 hour 30 minutes. After completing digestion nuclease free DNAse water was added to each and make the volume 50 ml. Filtering was done by using Whatman No. 41 filter paper. Finally, the samples were ready for AAS analysis. The samples were kept in pre-cleaned polyethylene bottle until analysis of atomic absorption spectrophotometer (Eneji et al., 2011).

2.5. WaterSample Collection

Water samples were collected in 1L plastic bottle wrapped with aluminum foil. Bottles were soaked with a mixture of distilled water (975 ml), 2% HNO_3 (20 ml) and H_2SO_4 (5 ml) for about 24 hours. After a day these bottles were washed with distilled water for several times carefully and thoroughly. Finally, these bottles were dipped in double distilled water and were kept in an oven (60-70°C) for 24 hours. Then, the bottles were ready for sample collection (Ahmed et al.,2009).

2.6. Digestionof Water Samples for AAS Analysis

The water samples were digested with Nitric acid (HNO₃) described by Baker et al. (1982).Briefly, 200 ml of water was taken in a beaker by measuring cylinder and then filtered using Whatman No. 41 filter paper. After that, 2 ml HNO₃ was added and was kept in a dark place overnight to prevent the precipitation of metals. Next morning, 50ml sample was transformed into a clean beaker and 4 ml concentrated HNO₃ was added to it for digestion. The beaker was then kept on a hot plate at 95°C temperature and boiled. Heating process continued until the volume of solution dried into 20 ml. When the solution dried into 20 ml it was kept in a cool place. After that, the solution was diluted into 50 ml by adding nuclease free DNAse water and filtered using Whatman No. 41 filter paper and kept in a volumetric flask. Finally, the sample solution was ready for AAS analysis (Hseu et al.,2002).

2.7. The Working Mechanism of AAS

For the quantification of possible contamination, a blank digestion was also done for both water and fish sample. A standard solution was made for Pb, Cr and Cd. Solution was made by pipetting the required amount of solution from stock solution, manufactured by Kanto Chemical Co., INC. Before every analysis a standard solution was prepared. The samples were analyzed by using air acetylene flame with combination, as well as single element hollow cathode lamps into an atomic absorption spectrophotometer (Shimadzu, AA-7000) (Ahmed et al.,2009). Spreadsheet software was used to analyze the data and the data were tested at5% level of significance.

3. Results and Discussion

3.1. HeavyMetal Concentration in Water Samples

In our study we choose three spots i.e., upward stream, downward stream and effluent exit point for sample collection. The first spot (spot-1) was near the main exit of Kachpur industrial unit; second spot (spot-2) was 1 kilometer upward stream and third spot (spot-3) was 1 km downward stream. We collected water and fish samples during premonsoon and post-monsoon period. Heavy metals Lead (Pb), Chromium (Cr) and Cadmium (Cd) were determined from both water and fish samples using AAS. Table 1 describes the average concentration (ppm) of heavy metals in water samples from different sampling spots of Shitalakkhya River during pre-monsoon and post-monsoon period.

Sampling	Sampling Spots	Concentration of Heavy Metals (Ppm)					
Seasons		Pb	Average	Cr	Average	Cd	Average
Pre-monsoon (June-September)	Spot 1	0.01		0.398		0.0071	
	Spot 2	0.0139		0.401	0.40066	0.0052	
			0.0456		±0.00251		0.0062
	Spot 3	0.1129	±0.05	0.403		0.0063	±0.000
Post-monsoon (October-January)	Spot 1	0.0188		0.407	0.070	0.0035	
	Spot 2	0.3159	0 13/333	0.405	0.378	0.0061	0.006033
	Spot 3	0.0683	±0.15	0.322	10.040300	0.0085	±0.002
Mean of the average (± SD)	0.089967±0.06		0.389±0.02		0.006±0.00012		
Range	0.01-0.3159		0.322-0.407		0.0035-0.0085		

 Table 1: Average Concentration (Ppm) of Heavy Metals from Different Sampling

 Spots of Shitalakkhya River during Pre-Monsoon and Post-Monsoon Period

Among the three heavy metals, concentration of Cr was higher both in pre-monsoon and post-monsoon period. While concentration of Cd was lower than the other both in pre-monsoon and post-monsoon period. It also shows that the concentration of Pb was higher in post-monsoon period and lower in pre-monsoon period, the concentration of Cr was higher in pre-monsoon period and lower in pre-monsoon period, the concentration of Cd did not vary respectively both in pre-monsoon and post-monsoon period with mean values of 0.089967ppm, 0.389 ppm, 0.006ppm respectively. The ranges of concentration of Pb, Cr and Cd were from 0.01 to 0.3159, 0.322 to 0.407 and 0.0035 to 0.0085 ppm.

During pre-monsoon period Lead(Pb) concentration was higher 0.1129 ppm in spot 3 (Downward stream) and lower 0.01 ppm in spot 1 (near exit). The average concentration of Pb was 0.0456 ppm. During post-monsoon period Pb concentration was higher 0.315 ppm in spot 2 (Upward stream) and lower 0.018 ppm in spot 1 (Near exit). Average concentration of Pb was 0.1343 ppm. This difference may occur due to different spot and different season. Khan et al. (1998) found that the concentration of Pb ranged from 0.012 μ g/ml to 0.431 μ g/ml (Ahmed et al.,2009) which are much similar with the present study. Peran and Altipole (2010) found the concentration level of Pb was 2081 μ g/l in the sea

similar with the present study. Boran and Altinok (2010) found the concentration level of Pb was 8081 $\mu g/L$ in the sea water of the western Black Sea (Zonguldak) shore of Turkey which is much higher than the present study. Abdel-Baki et al. (2011) found that the concentration of Pb was 0.95 ppb in the water of Wadi Hanifah, Saudi Arabia which is much lower than our present study. According to WHO (1989) the recommended limit of Pb in drinking water is 0.01 mg/L which is much lower than our current study.

Chromium (Cr) concentration was higher 0.403 ppm in spot 3 (Downward stream) and lower 0.398 ppm in spot 1 (Near exit) during pre-monsoon period. Average concentration of Cr was 0.4 ppm. Cr concentration was higher 0.407 ppm during post-monsoon period in spot 1 (near exit) and lower 0.322 ppm during post-monsoon period in spot 3

(downstream). Average concentration of Cr was 0.378 ppm. The concentration levels of Cr also indicate that the concentration level is consistently higher in each 3 spot of pre-monsoon period compared to post-monsoon period. Khan et al.(1998) found that the concentration of Cr ranged from 0.015 to 0.491 μ g/ml (Ahmed et al., 2009) in the water of the GBM estuary, values that are quite similar to the present study. Boran and Altinok (2010) found that the concentration of Cr was 5824 μ g/L in the sea water of the western Black Sea (Zonguldak) shore of Turkey which is much higher than the present study. Abdel-Baki et al. (2011) found that the concentration of Cr was 6.4 ppb in the water of Wadi Hanifah, Saudi Arabia which is much lower than our present study. A recent data on heavy metal analysis of Shitalakkhya River (Islam etal.,2015) showed that the concentration level of Cr in the water ranged from 0.0371-0.1023 mg/L which is much lower than our present study.

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Cadmium (Cd) concentration was higher 0.0085 ppm during post-monsoon period in spot 3 (downward stream) and lower during post-monsoon period in spot 1 (near exit). While the concentration is higher 0.0071 ppm in spot 1 (near exit) and lower 0.0052 ppm in spot 2 (upward stream) during pre-monsoon period. However, the average value of Cd did not vary significantly both in pre-monsoon and post-monsoon period. Ahmed (1998) reported that the concentration level of Cd ranges between 0.018 ppm to 0.007 ppm in water of the Sundarban Forest Reserve (Ahmed et al.,2009). According to WHO (1989) the recommended limit of Cd in drinking water is 0.003 mg/L which is much lower than the present study. According to Environmental Quality Standard (EQS) the standard value of Cd for coastal water of Bangladesh is 0.3 μ g/g (EQS 1991). Boran and Altinok (2010) found that the concentration of Cd was 1686 μ g/L in the sea water of the western Black Sea (Zonguldak) shore of Turkey which is much higher than the present study. Abdel-Baki et al. (2011) found that the concentration of Cd was 0.87 ppb in the water of Wadi Hanifah, Saudi Arabia which is much lower than our present study. A recent data on heavy metal analysis of Shitalakkhya River (Islam et al.,2015) showed that the concentration level of Cd in the water ranged from 0.0065-0.0152 mg/L which was higher than our present study.

Heavy metals	Pb(ppm)	Cr(ppm)	Cd(ppm)
Pb	1.0000000	0.8224367*	0.0574330
Cr	0.8224367*	1.0000000	-0.5206827*
Cd	0.0574330	-0.5206827*	1.0000000

Table 2: Correlation Matrix of Heavy Metals during Pre-Monsoon Period for Water Samples *Values >0.5 or < -0.5 are significantly Correlated

From the correlation matrix of the pre-monsoon data, the correlation between Pb and Cr is 0.8224367, which indicates that there is a high positive (p<00.5) linear correlation between Pb and Cr. The correlation between Cd and Cr is -0.5206827 which indicates a moderate negative relationship (p<0.05) between Cd and Cr (Table-2).

Heavy metals	Pb (ppm)	Cr (ppm)	Cd (ppm)
Pb	1.0000000	0.3399480	0.1782526
Cr	0.3399480	1.0000000	-0.8647862*
Cd	0.1782526	-0.8647862*	1.0000000

Table 3: Correlation Matrix of Heavy Metals during Post-Monsoon Period for Water Samples *Values >0.5 or < -0.5 are significantly Correlated

From the correlation matrix of the post-monsoon data we found that the correlation between Pb and Cr is 0.3399480 which indicates a weak positive linear correlation between Pb and Cr. Moreover, the correlation between Cd and Cr is -0.8647862 which suggests a strong negative relationship (p<0.05) between Cd and Cr. From the correlation matrix of the pre-monsoon data, the correlation between Pb and Cr was higher (), however from the correlation matrix of the post-monsoon data, we find that the correlation between Pb and Cr is 0.3399480 which indicates a weak positive linear correlation between Pb and Cr is 0.3399480 which indicates a weak positive linear correlation between Pb and Cr is 0.3399480 which indicates a weak positive linear correlation between Pb and Cr is 0.3399480 which indicates a weak positive linear correlation between Pb and Cr. These data demonstrate that the correlation between the heavy metals might vary because of seasonal differences.

3.2. HeavyMetal Concentration in Fish Samples

In this study, five species of fishes were collected from Shitalakkhya River and analyzed for determining heavy metals concentration to characterize and evaluate present scenario of the fish body contamination (Figure 1).

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Figure 1: Concentration of Heavy Metals in Fish Samples of Shitalakkhya River

In our study we found the order of heavy metal concentration in fishes Cr>Pb>Cd.Maximum concentration of Cr (0.403 ppm)was found Colisafasciatus. observed in The order of concentration was Cr as Colisafasciatus>Channapunctatus>Chandanama>Mastacembelusarmatus>Lepidocephalusguntea. Maximum concentration Pb (0.1525)ppm) was found in Lepidocephalusguntea. The order of Pb concentration of wasLepidocephalusquntea>Channapunctatus>Chandanama>Mastacembelusarmatus>Colisafasciatus (Figure.1). According to WHO (2005), the allowable concentration of Pb and Cd were 200 and 500 ppb respectively (Abdel-Baki et al., 2011). According to Turkish Food Codex (2002), the maximum levels of the metals for human consumption may not exceed for Cd 0.05 and/or 0.1 mg/kg fish, for Pb 0.2-0.4 mg/kg fish (Boran and Altinok, 2010). In our study concentration of Pb and Cd in each of the fish sample is within the allowable limit. Concentrations of metals in muscle tissues were all below the recommended Food and Agriculture Organization (FAO) maximum limits for Pb (0.5 mg Kg-1), Cd (0.5 mg Kg-1) in fish (Ikem et al., 2003). The range of Cr was $1.543 \pm 0.021 - 2.143 \pm 0.015$, Cd was $1.110 \pm 0.017 - 1.653 \pm 0.021$ and Pb was $2.056 \pm 0.025 - 2.730 \pm 0.010 \mu g/g$ dry wt, respectively (Vinodhini and Narayanan, 2008) which was higher than our present study.

Heavy metals	Pb (ppm)	Cr(ppm)	Cd(ppm)
Pb	1.0000000	-0.7722186*	-0.3723819
Cr	-0.7722186*	1.0000000	0.6407372*
Cd	-0.3723819	0.6407372*	1.0000000

Table 4: Correlation Matrix among Heavy Metals in Fish Sample *Values >0.5 or < -0.5 are significantly Correlated

From the correlation matrix data, the correlation between Pb and Cr was-0.7722186, which indicates that there is a strong negative (p<0.05) linear correlation between Pb and Cr. The correlation between Cd and Cr is 0.6407372 which indicates a moderate positive (p<0.05) relationship between Cd and Cr (Table 4).

4. Conclusions

In water samples the concentration of Pb, Cr and Cd varied seasonally and spatially from 0.01 to 0.3159, 0.322 to 0.407 and 0.0035 to 0.0085 ppm respectively. The mean concentration of Pb and Cd was higher than WHO guideline values. In *Chanda nama* the concentrations of Pb, Cr and Cd were 0.098, 0.365 and 0.002 ppm respectively. In *Lepidocephalusguntea* the concentrations of Pb, Cr and Cd were 0.1525, 0.358 and 0.0021 ppm respectively. In *Colisafasciatus* the concentrations of Pb, Cr and Cd were 0.0287, 0.403 and 0.0049 ppm respectively. In *Colisafasciatus* the concentrations of Pb, Cr and Cd were 0.0287, 0.403 and 0.0049 ppm respectively. In *Colisafasciatus* the concentrations of Pb, Cr and Cd were 0.1278, 0.378 and 0.0057 ppm respectively. In *Mastacembelusarmatus* the concentrations of Pb, Cr and Cd were 0.0881, 0.362 and 0.0042 ppm respectively. Comparatively higher concentration of heavy metals was accumulated in *Colisafasciatus*. The order of heavy metals in fish samples were below the FAO permissible limit. However, it is quite evident that there was bioaccumulation of heavy metals in fish tissues and condition may get worse if fish is exposed to such polluted environment for prolonged period of time. With the gradual development of industry, intensive use of pesticides and untreated domestic sewage as well as polluted discharge from neighboring may further deteriorate the situation in future. Therefore, a regular monitoring of heavy metals in aquatic environment as well as fish is necessary.

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