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Assessment of heavy metals in sediments of Shitalakhya River, Bangladesh

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Abstract Concentrations of Cu, Zn, Fe, Mn, Ni and Cr have been estimated in sediments of the Shitalakhya River at Polash-Ghorashal area, Narsingdi, Bangladesh. 36 samples of sediments from nine sampling point at different locations of Shitalakhya River were collected to determine the concentration of Cu, Zn, Fe, Mn, Ni, Cr and the samples were analyzed by atomic absorption spectrophotometer (AAS). The obtained results were compared with national and international guidelines. The levels of heavy metal concentrations in sediments were found to decrease in the order of Fe > Mn > Zn > Ni > Cu > Cr, respectively. The heavy metal concentration in sediment of Shitalakhya was below the recommended safe limits of heavy metals by WHO, FAO and other international standards. Contamination factor (CF) of Zn and Cu at sampling point Fsd2 show higher (> 1) values due to the influence of external discrete sources like wastage catalysts of ZnO and CuO. Geo-accumulation index values of the study indicate as non-contaminated to moderately contaminate.

Key words: sediment, heavy metals, CRM, trace elements, point source

1. Introduction

Heavy metal contamination in sediment is one of the largest threats to environmental quality and human health. It is often stated that sediment is the most important reservoir or sink of metals and other pollutants.[1] The river systems in Bangladesh carry 2.4 billion tons of sediments, a part of which deposited in the floodplains each year.[2] Strategically Shitalakhya is the most important river for Dhaka dwellers in terms of its use in domestic life. The Shitalakhya River is distributing of the Brahmaputra River. It flows through the red heard soil of Gazipur, Kaliganj, Narayanganj and meets with Meghna river at Kolagachia of Munsiganj. The river Receives effluents from five jute mills, two fertilizer factories, one sugar mill, one cement industry, one textile industry, one dairy plant, two food processing industry, one hardboard mill, one paper mill and one of joint thermal power plant within 13 km range of its flow

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in Ghorashal region. Shitalakhya River is the source of industrial water. Surface water is used in industry for cooling, process, steam generation, safety and miscellaneous purpose.

This paper investigates the level of Fe, Mn, Cu, Zn, Ni, Cr in sediments in Shitalakhya River near Ghorashal region where many red category industries are situated. The aim this study is to assess the pollution status and to explore the industrial impacts of heavy metals on the study area.

2. Experimental

2.1. Sampling locations, collection of water and sediment samples

Sediment sampling stations were selected on the basis of three industries such as fertilizer factories, Seven Ring Cement Industry and paper mill. Sampling was carried out from December, 2011 to October, 2012 for four seasons namely December (Dry season), March (Pre-monsoon), July (Monsoon) and October (Post Monsoon). 36 sediments samples were collected. About 800 g of wet sediment were collected. The samples were air dried, crushed, sieved and transferred to the zip-lock plastic bags. The samples were finely powered and dried at 105 °C for 2 hours. Then the dried samples were digested.

The sampling points are shown in *Fig.* 1. Nine sampling station are selected on the basis of two fertilizer factories, Seven Ring Cement Industry and paper mill. FSd1 is located 100 m upstream from the point source of Urea Fertilizer Factory (UFF). The other sampling points such as FSd2, FSd3, FSd4, CSd1, CSd2, PSd1, PSd2, PSd3 are located 5 m, 400 m, 800 m, 10 km, 11 km, 12 km, 12.5 km and 13 km are situated downstream from the point source of UFF respectively.

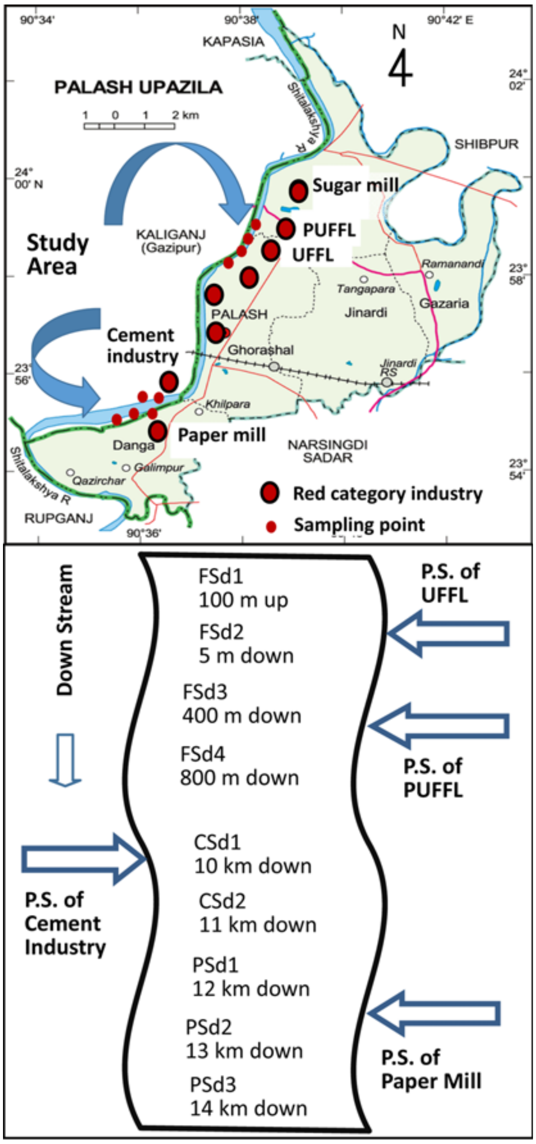

Fig. 1. Study area and locations of the sampling stations of sediments along the Shitalakhya River basin in Polash-Ghorashal region (P.S.: Point Source; UFF: Urea Fertilizer Factory; PUFF: Polash Urea Fertilizer Factory; Red category is worst class of four category industries[4]).

2.2. Digestion of sediment samples

Sediment samples were digested according to the HNO_3/HF/$HClO_4$ digestion method (ASTM, 2003).[3] All reagents used were MERCK and BDH analytical grade.

2.3. Chemical Analysis

The concentration of trace elements in sediment samples were estimated by atomic absorption spectrophotometer (Model no. 240 AA, Agilent, Australia) using air-acetylene flame technique. The calibration curves were prepared by Certified Reference

Materials (CRM) that were verified by NIST.

3. Results and Discussion

3.1. Seasonal variation of heavy metals in sediments

Fig. 2 highlights the present study of sediments in Shitalakhya River of four seasons. The obtained concentration of Fe, Mn, Zn, Ni, Cu and Cr of the analyst samples were found ranged 14039.57-42943.63, 126.00-869.13, 36.86-455.86, 15.73-66.55, 29.96-76.25 and 10.68-58.45 mg/kg respectively. The highest concentration of Cu (76.25 mg/kg), Zn (455.86 mg/kg), Ni (66.51 mg/kg) in sediments were recorded at the point source (FSd2) of Urea Fertilizer Factory while the highest concentration of Fe (42943.63 mg/kg) was found at the point source (CSd1) of Seven Ring Cement Industry where as the lowest concentration (14039.57 mg/kg) found at the point source of paper mill (PSd2) in pre-monsoon. Fe in cement industry showed highest concentration because the cement industry generally use slag as additives which containing mainly calcium oxide, silicon oxide, iron oxide, and other metal oxides. The industrial works of various types of repairs, ship repairs and mechanic workshops also the source of Fe to the point source of cement industry. The metal Fe is to consider the main factor that determines adsorption

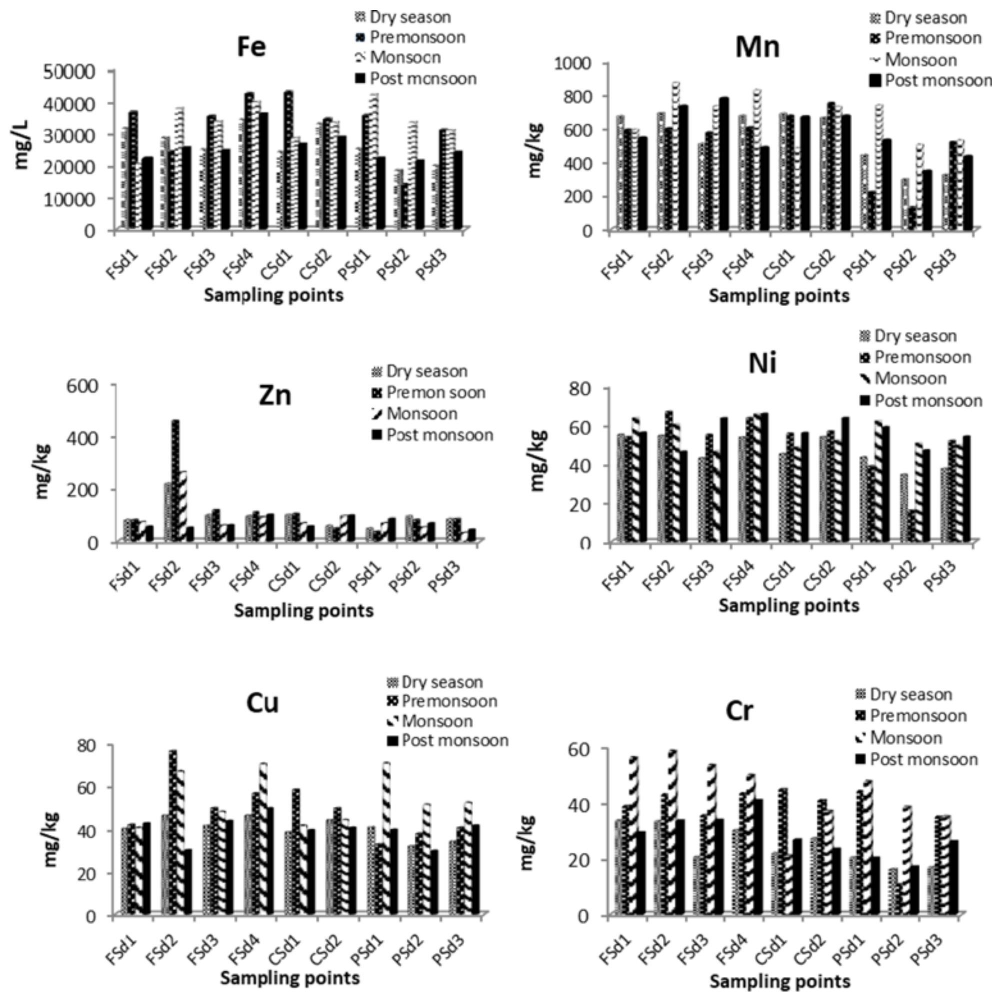

Fig. 2. Seasonal variation of heavy metals in sediments at different points of Shitalakhya River.

capacity, because of high specific surface of Fe^{3+}. Moderately high level of iron is also noted in the sediments that is consistent with high levels of iron in local surface soils[5]. The paper mill generally uses different types of organic chemicals for sizing, pulping, deinking, stickies control and cleaning and abundantly use wastages paper. As a result, suspended solids of wastage paper were observed near the point source of paper mill. Among the sampling stations the average Fe in sediment varies approximately in the order: Monsoon > Premonsoon > Dry season > Postmonsoon.

The concentration of Mn is higher than Ni, Cu, Cr and Zn. Concentration of Cu in sediments are comparatively higher than Cr & Ni. The concentration of Cr & Ni slightly higher at the point source of Urea Fertilizer Factory (FSd2) than other sampling points because inside the Urea Fertilizer Factory (UFF) different types of wastage catalyst. Among the sampling stations the average Cu in sediment varies approximately in the order: Monsoon> Premonsoon > Dry season > Postmonsoon. This indicates greater turnover of the element upstream during rainy season. Among the four seasons for the point source of UFFL (FSd2) Zn and Cu concentrations were lowest in post monsoon. Because in April to October the fertilizer factories were shut down and on the other hand in monsoon this point was overlapped by natural source like siltation.

In the present investigation of Ni in sediments was rather insignificant for seasonal variation. It was observed that most of the sampling stations were mild variation of four seasons except the Psd2 and lowest concentration was recorded at the same point PSd2 in premonsoon. This point is located near to the point source of paper mills and in premonsoon anthropogenic sources such as industrial effluents especially organic wastage is predominated and other seasons influenced by natural sources. The Cr concentration of all the sediment samples were significant in monsoon that is due to the same reason as Ni. Fe_2O_3-Cr_2O_3 catalyst is used in high temperature shift converter in the ammonia plant of Urea Fertilizer Factory.

As the catalyst is not regenerated it is replaced by new catalyst when it is deactivated. Therefore above 50 years old Urea Fertilizer Factory stored enormous amounts of the catalyst in open yard of the factory. During the rainy season used catalyst washed away to the river through point source. As a result of Cr concentration was high at Fsd2 and decreases with increasing distances and sampling point Psd1 slightly high due to local geological effect. The weathering of minerals is one of the major natural sources, while industrial sources include different types of catalyst used in ammonia and urea plant, use of fertilizers, washing away of wastage of fertilizer factories catalyst, and leakage from service, pipes, irrigation and herbicides.

3.2. Statistical analysis

Pearson's correlation coefficient of heavy metal elements in sediments of Shitalakhya River are summarized in *Table* 1. Mn is significantly positive correlated with Fe, which may suggest a common origin. Fe is a major constituent of sediments as a structural element of clay and organic matter,[6] Fe occurs in clays as oxides and hydroxide minerals goethite, hematite, maghemite and lepidocrocite. Mn also occurs as oxides, but more complex, lithiophorite and birnessite. Fe has a strong positive correlation with many minor elements (such as Mn) in sediments, in which it is considered a natural element content in sediments, Cu is also significantly positively correlate with Zn, Ni, Fe, Mn, and Cr. Generally, trace metals come from geological and industrial sources.

Table 1. Correlation matrix among the parameters. N= 36

	Fe	Mn	Zn	Ni	Cu	Cr
Fe	1					
Mn	0.527**	1				
Zn	0.010	0.208	1			
Ni	0.497**	0.696**	0.300	1		
Cu	0.593**	0.520**	0.563**	0.582**	1	
Cr	0.679**	0.578**	0.245	0.587**	0.643**	1

**Correlation is significant at the 0.01 level (2-tailed). N = No. of samples

3.3. Geo-accumulation index of sediments

The geo-accumulation index is a quantitative measure of the degree of pollution in aquatic sediments. Geochemical background values are used to calculate the geo-accumulation index (I_{geo}) which categories seven classes of contamination of environmental samples[7].

$$I_{geo} = \log_2[C_n/1.5 \times B_n]$$

Where C_n is the measured content of element "n" and B_n is the element's content in "average shale" value that is obtained from Turekian and Wedepohl (1961)[8] in this study. The factor 1.5 is introduced to include possible variations of the background values due to lithogenic effects. I_{geo} value < 0, 0-1, 1-2, 2-3, 3-4, 4-5, >5 indicates uncontaminated, uncontaminated to moderately contaminated, moderately contaminated, moderately to strongly contaminated, strongly contaminated, strongly to extremely strongly contaminated and extremely contaminated respectively. According to geo-accumulation index value, the result of current study of heavy metals in sediment is classified to be in class1 (0-1) which is designated as uncontaminated to moderately contaminate.

3.4. Pollution load index and contamination factor of sediments

The extent of pollution by trace metals has been assessed by employing the method on pollution load index (PLI). PLI for particular cite has been evaluated following method proposed by Tomilson *et al*. (1980)[9].

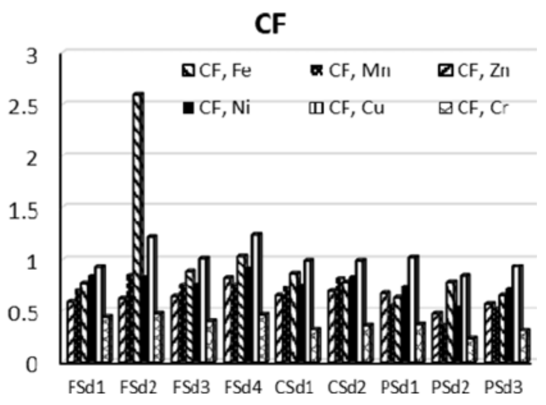

Fig. 3. Average contamination factor of the Present study.

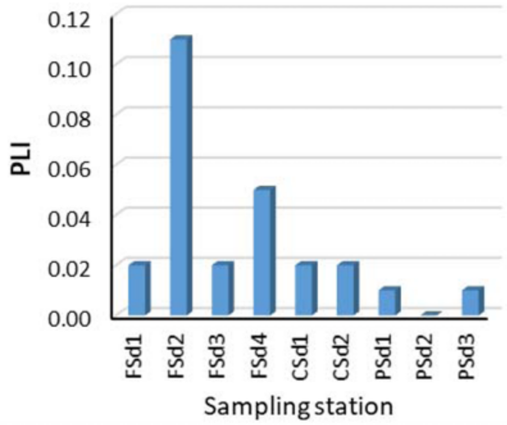

Fig. 4. Pollution load index of sediments.

This parameter is expressed as PLI = ($CF_1 \times CF_2 \times \ldots\ldots CF_n$), where n is the number of metals and CF is the contamination factor {(Metal concentration in the sediment)/(Background value of the metal)}. Authors adopted the average shale value for background value that was used for calculation of geo-accumulation index.

The assessment of sediment contamination was carried out using the contamination factor and the degree of contamination, based on four classification categories recognized by Håkanson (1980)[10] are given; contamination factor (CF) CF < 1, 1 ≤ CF <3, 3 ≤ CF < 6, CF > 6 indicates low contamination, moderate contamination, considerable contamination and very high contamination respectively.

Results of the current study represent that the contamination factor values of most of the metals such as Fe, Mn, Ni, Cr in the study area are low (< 1). But only CF values of Zn and Cu at sampling point F_{sd2} show higher (> 1) values due to the influence of external discrete sources like wastage catalysts of ZnO and CuO that are deposited in the inside the Urea Fertilizer area. According to Håkanson contamination factor this point shows moderately contamination. The values of pollution load index were found to be generally low (<1) in all the sampling stations. The PLI value >1 expressed the sediment is polluted whereas PLI value <1 indicates no pollution[11] (Abrahim *et al*., Chakravarty and Patgiri, 2009)[12]. The PLI value ranged from 0 to 0.11

indicates that the sediments of Shitalakhya River are in non-polluted condition. Lower values of PLI imply no industrial effects for metal pollution.

4. Conclusions

The heavy metal concentration in sediment of Shitalakhya was below the recommended safe limits of heavy metals by WHO, FAO and other international standards. For sediments among the four point sources (FSd2, FSd4, CSd1 & PSd2), point sources of Urea Fertilizer Factory (FSd2) is the most vulnerable though that is not exceeded the severe effect level. The concentration of Mn is higher than Ni, Cu, Cr and Zn. Concentration of Cu in sediments are comparatively higher than Cr & Ni. The concentration of Cr & Ni slightly higher at the point source of Urea Fertilizer Factory (FSd2) than other sampling points because inside the Urea Fertilizer Factory (UFF) different types of wastage catalyst such as ZnO, CuO, Cr_2O_3, Fe_3O_4, NiO are deposited that are not maintained solid waste management's regulation. On the other hand, UFF use different types of bearing in the rotating equipment. This bearing consists of different alloy like brass metal containing Zn and Cu. Brass is susceptible to stress corrosion cracking, especially from ammonia.

Assessment of pollution in sediments by heavy metals was evaluated using contamination factor, modified degree of contamination, geo-accumulation index and pollution load index. According to geo-accumulation index all of the sampling stations are uncontaminated to moderately contaminate and pollution load index indicates no pollution in the studied area. According to contamination factor Zn and Cu in sediments shows moderate contamination at the point source of Urea Factory (FSd2). Modified degree of contamination suggested that Zn in sediment shows moderate degree of contamination and Cu in soil also shows low degree of contamination respectively at the same point. With the gradual development of industry, intensive use of pesticides and discharge of untreated industrial and domestic sewage may further exacerbate the situation in coming years.

Acknowledgements

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