



Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country



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ABSTRACT

The concentration and chemical fractionation of globally alarming six heavy metals (Cr, Ni, Cu, As, Cd and Pb) were measured in surface water and sediment of an urban river in Bangladesh. The decreasing trend of metals were observed in water as $Cr > Cu > As > Ni > Pb > Cd$ and in sediment as $Cr > Ni > Cu > Pb > As > Cd$. The level of studied metals exceeded the safe limits of drinking water, indicated that water from this river is not safe for drinking and/or cooking purposes. However, the investigated metals showed low mobility except for Cd and Pb which could pose a severe threat to the aquatic environment. Contamination factor (CF) and geoaccumulation index (I_{geo}) demonstrated that most of the sediment samples were moderately to heavily contaminated by Cr, As, Cd and Pb. The pollution load index (PLI) values were above one (>1) indicates progressive deterioration of the sediment quality. The extent of pollution by heavy metals in the river Korotoa implies that the condition is much frightening to the biota and inhabitants in the vicinity of the river as well.

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1. Introduction

In recent years, metal contamination in the aquatic environment has attracted global attention owing to its environmental toxicity, abundance and persistence (Sin et al., 2001; Armitage et al., 2007; Yuan et al., 2011). Large quantities of hazardous chemicals especially heavy metals have been released into rivers worldwide due to global rapid population growth and intensive domestic activities, as well as expanding industrial and agricultural production (Srebotnjak et al., 2012; Su et al., 2013; Islam et al., 2014). Rivers in urban areas have also been associated with water quality problems because of the practice of discharging of untreated domestic and industrial waste into the water bodies which leads to the increase in the level of metals in river water (Khadse et al., 2008; Venugopal et al., 2009).

The behavior of metals in the natural water is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry (Mohiuddin et al., 2012). During transport, heavy metals may undergo numerous changes in their speciation due to dissolution, precipitation, sorption, and complexation phenomena (Dassenakis et al., 1998; Akcay et al., 2003; Abdel-Ghani and Elchaghaby, 2007), which affect their behavior and bioavailability (Nicolau et al., 2006; Nouri et al., 2011). Sediment is an integral and dynamic part of the river basin, with the variety of habitats and environments. However, information on total metal concentrations is not sufficient for the assessment of environmental impact of sediment contamination which lead to the particular interest of chemical fractionation of sediment (Jain, 2004; Nwuche and Ugoji, 2010). The overall behavior of heavy metals in the aquatic environment is strongly influenced by the association of metals with various geochemical phases in sediments (Morillo et al., 2004). Geochemical speciation and distribution of metals in the defined chemical fraction also been used in predicting the potential contamination, mobility and bioavailability (Kabala and Singh, 2001; Pueyo et al., 2003; Caeiro et al., 2005). Thus, it is important to assess the concentrations and distribution of heavy metals in the riverine ecosystem.

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In Bangladesh, everyday a huge amount of untreated industrial wastes is being discharged into open water bodies and its adjacent lands. Besides, a considerable amount of heavy metal enriched suspended solids is coming down from neighboring country like India through the Teesta and the Brahmaputra Rivers. Bogra district, known as the northern capital of Bangladesh is situated on the bank of the river Korotoa which is connected to the river Teesta and Brahmaputra. The study river recently has been raised attention to public concern due to its extreme pollution. To date, no scientific research regarding heavy metal issues in the study area has been conducted so far. Therefore, the objectives of this study are – to assess the pollution status of the river Korotoa by estimating the levels of heavy metals in water and sediment, and to observe the metal enrichment in relation to chemical speciation in sediments.

2. Materials and methods

2.1. Description of the study area

This study focused on an important urban river located at the northern part in Bangladesh. The study river is originated from the Himalayas, the mother of numerous rivers. Originating from northern frontier of Bhutan, the Korotoa enters Bangladesh territory through Darjeeling and Jalpaiguri districts of West Bengal in India, and forms for some distance the boundary between Dinajpur and Rangpur districts, Bangladesh. For the present study, the river was selected that flows through the Bogra district urbanized area. The area of Bogra district about 71.56 km², total population of this district is about 350,397. The study area is located at the northern part of Bangladesh and situated between 24° 84' 91.82" N and 89° 37' 29.57" E. Thousands of villages, towns and commercial places like Shibganj, Mohasthangarh, Bogra and Sherpur have been built on both sides of the Korotoa along its 200-km path. Mohasthangarh, the capital of ancient Pundranagar, is still there beside the Korotoa as a witness of history in Bangladesh. Agriculture, aquaculture and fishing are the primary activities of the people living besides this river. This river receives domestic raw sewage, household waste, and industrial waste from surrounding habitation. During the last decades, natural and human activities have caused a complete deterioration of the river ecosystems.

2.2. Sample collection and preparation

A total of 80 samples (water and sediment) were collected during February–September, 2013 (winter and summer season). Samples were collected from ten different stations (S1–S10) from upstream to downstream of the river (Fig. 1). Unfiltered water samples were collected from the center of the river for total metal analyses. The samples were then transferred into acid cleaned 100 mL polypropylene bottles. One mL of ultrapure nitric acid was added in each polypropylene bottle to achieve a pH of ~1 (Cenci and Martin, 2004). At each point, composite sediment samples were collected using standard protocol (US EPA, 2001). The river bed sediment samples were taken at a depth of 0 to 5 cm using a portable Ekman grab sampler. Three composite samples of mass approximately 200 g were collected at each station. The upper 2 cm of each sample was taken from the center of the catcher with an acid-washed plastic spatula to avoid any contamination from the metallic parts of the sampler. For considering the preindustrial sample, sediment was taken by means of a percussion hammer corer (50–80 cm in length) for metal analysis (Schottler and Engstrom, 2006). Sediment sampling was performed as prescribed in the Methods Manual for the characterization of sediments (Environment Canada and MENV, 1992). Lead-210 dating by alpha spectrometry method was used to

determine the age and sediment accumulation rates. Composite sediment samples were collected into polyethylene air tight bags in the field and transported to the central laboratory of Patuakhali Science and Technology University, Bangladesh, for pre-treatment. The samples were dried in oven at 45 °C for 48 h to gain constant weight. The dried samples were then ground using mortar and pestle and sieved through 106 µm aperture. The lower particle size fraction was homogenized by grinding in an agate mortar and stored in labeled glass bottles until chemical analyses were carried out.

2.3. Sample digestion and metal extraction

All chemicals were analytical grade reagents and Milli-Q (Elix UV5 and MilliQ, Millipore, USA) water was used for solution preparation. The Teflon vessel and polypropylene containers were cleaned, soaked in 5% HNO₃ for more than 24 h, then rinsed with Milli-Q water and dried. For metal analysis, 20 mL water sample and 0.5 g of sediment sample was treated with 5 mL 69% HNO₃ acid and 2 mL 30% H₂O₂ in a closed Teflon vessel and was digested in a Microwave Digestion System. The digested solution was then filtered by using syringe filter (DISMIC® – 25HP PTFE, pore size = 0.45 µm) Toyo Roshi Kaisha, Ltd., Japan and stored in 50 mL polypropylene tubes (Nalgene, New York). Afterwards, the vessels were cleaned by Milli-Q water and dried with air.

For chemical partitioning of metals, sediment samples were analyzed using Tessier sequential chemical extraction procedure (Tessier et al., 1979). The sequential extraction procedure was divided into five operationally defined chemical fractions: (F1) the exchangeable fraction: readily soluble and exchangeable; (F2) the carbonate bound and specifically adsorbed fraction: carbonate-bound, specifically adsorbed and weak organic and inorganic complexes; (F3) the Fe-Mn oxides fraction: bound to iron and manganese oxides (Fe-Mn oxides); (F4) the organic/sulphide fraction: bound to stable organic and/or sulphide (organic) complexes; and (F5) the residual fraction: held in primary and secondary minerals within their crystal structure. The detailed geochemical fractionation procedure of sediment is presented in Table 1.

2.4. Instrumental analysis and quality assurance

For heavy metals, samples were analyzed by using inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS operating conditions and parameters for metal analysis in samples are presented in Table S1. Multi-element Standard XSTC-13 (Spex CertiPrep®, USA) solutions was used to prepare calibration curve. The calibration curves with $R^2 > 0.999$ were accepted for concentration calculation. Multielement solution (Agilent Technologies, USA) 1.0 µg/L was used as tuning solution covering a wide range of masses of elements. All test batches were evaluated using an internal quality approach and validated if they satisfied the defined internal quality controls (IQCs). For each experiment, a run included blank, certified reference materials (CRM) and samples were analyzed in duplicate to eliminate any batch-specific error. Before starting the analysis sequence, relative standard deviation (RSD, <5%) was checked by using tuning solution purchased from the Agilent Technologies. Quality control of laboratory methods involved the analysis of the following reference materials: NMIJ CRM 7303 – Lake Sediment. The measured mean and standard deviation of elemental values for reference materials reported in Table S2. Comparison is made with the certified values, which in both cases confirmed that the sample preparation and instrumentation conditions provided good levels of accuracy and precision.

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