# Chemical speciation of metals in sediment and their bioaccumulation in fish on three rivers around Dhaka City, Bangladesh

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*Abstract*—As a forward step to understand the metal bioaccumulation in fish species, a study of trace metal speciation of sediment was achieved. Trace metals were measured in sediments and two fish species, *Heteropneustes fossilis* and *Trichogaster fasciata* by using inductively coupled plasma mass spectrometer (ICP-MS). Abundance of total trace metals in sediments varied in the following decreasing order: Cr > Ni > Pb > Cu > As > Cd. Sequential extraction tests revealed that the studied metals were predominantly associated with the residual fraction, followed by the organically bound phases. The range of metal content in fishes were Cr (1.8–4.8), Ni (1.0–3.1), Cu (2.5–7.2), As (0.22–0.43), Cd (0.011–0.068) and Pb (0.85–2.7 mg/kg fw), respectively. The rank of biota-sediment accumulation factors (BSAFs) for both species were in the descending order of Cu > Pb > As > Ni > Cr > Cd. Metals accumulation in fish exceeded the international permissible standards suggests that these species are not suitable for human consumption.

*Keywords*—chemical speciation, sediment, fish, bioaccumulation, Bangladesh

## I. Introduction

Trace metal pollution in river ecosystems has become a great concern, not only due to the threat to public water supplies, but also the risk to human consumption of fishery resources [1]. Dhaka, the capital of Bangladesh with highly unplanned industries having huge amount of untreated effluents to its adjacent rivers (Turag, Buriganga and Shitalakha) which threats to the aquatic ecosystems as well as human settlement. In recent decades the accumulation and distribution of trace metals in these rivers has been paid less attention. In addition, a considerable amount of trace metals can be accumulated in the surface sediments of the rivers. In sediment, trace metals are present in a number of chemical forms, and generally exhibit different physical and chemical behaviors in terms of chemical interaction, mobility, biological availability and potential toxicity [2-3]. During sediment transportation, trace metals undergo various changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena [4], which affect their behavior and bioavailability [5].

Hence, trace metals are regarded as sensitive indicators for monitoring changes in the aquatic environment. The overall behavior of trace metals in an aquatic environment is strongly influenced by the association of metals with various geochemical phases in sediments [6]. Information on total concentration is not sufficient to assess the environmental impact of contaminated sediments. Therefore, a particular interest on geochemical speciation is needed in assessing the potential environmental impacts of trace metals.

Chemical speciation can be defined as the process of identification and quantification of different species, forms or phases of chemicals present in a material [7]. Metal speciation occurring in the sediments is in turn expected to influence metal bioavailability, and thereby metal content in biota, in particular in the soft tissues of fish and mussels [8]. Sequential extraction techniques would provide the history of metal input, digenetic transformation within the sediments and the reactivity of trace metal species of both natural and anthropogenic origin [9]. In this study, sequential extraction technique was used to evaluate the distribution of trace metals in different chemical fractions and assessment of metals bioaccumulation in two fish species.

## II. Materials and methods

### A. Study area

Dhaka having 815.8 km$^2$ metropolitan areas is surrounded by three major rivers "Turag, Buriganga and Shitalakha". These rivers are unexpectedly used as a convenient means for disposing of untreated industrial wastes. It is one of the most densely populated cities in the world with twelve million people of which less than 25% are served by sewage treatment facility [10]. The indiscriminate dumping of domestic and industrial wastes, combined with the failure of authorities to enforce existing regulations to protect the ecological health of these rivers, has aggravated the situation to the point where these rivers are dying biologically and hydrologically. Thus, these rivers have been selected for this study (Fig. 1).

### B. Sample collection and preparation

Sediments and two fish species (*H. fossilis* and *T. fasciata*) were collected from the rivers during March 2012. *H. fossils* is air-breathing demersal cat fish. It feeds on crustacea, plant matter, detritus, insects and larvae. Otherwise, *T. fasciata* is a tropical benthopelagic omnivorous, feeding on insects, larvae,

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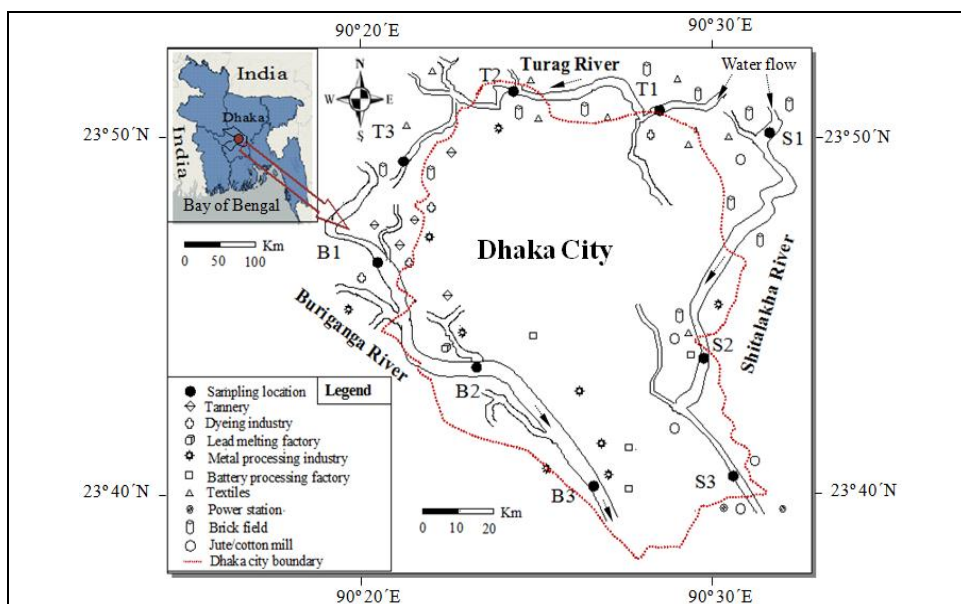
Figure 1. Map of the study area in Bangladesh

plankton, algae and detritus from sediment. At each sampling point, composite sediment samples were collected using standard protocol [11]. The river bed sediment samples were taken at a depth of 0 to 5 cm using a portable Ekman grab sampler. Fish samples were collected by the help of fishermen. After collection, samples were transported to the laboratory of Dhaka University, Bangladesh, for pre-treatment. The samples were freeze dried to obtain constant weight. The samples were homogenized by grinding in an agate mortar, sieved through 106 μm aperture and stored in labeled glass bottles until chemical analyses. The pre-processed samples were brought to Yokohama National University, Japan, for chemical analysis.

## C. *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% $HNO_3$ for more than 24 h, then rinsed with Milli-Q water and dried. For chemical partitioning of metals, sediment samples were analyzed by chemical extraction procedure proposed by Tessier et al. [12] and sequential extraction procedure is shown in Table 1. Samples were digested in a microwave digestion system (Berghof-MWS2, Berghof speedwave®). The microwave digestion system has been designed to performed chemical digestion procedures under extreme pressure and temperature conditions. Digestion reagents used were 5 mL 69% $HNO_3$ acid (Kanto Chemical Co, Japan) and 2 mL 30% $H_2O_2$ (Wako Chemical Co, Japan). After digestion, the solution was then filtered using DISMIC® - 25HP PTTF syringe filter (pore size = 0.45 μm) (Toyo Roshi Kaisha, Ltd., Japan) and stored in 50 mL polypropylene centrifuge tubes (Nalgene, New York).

TABLE 1. Geochemical extraction procedure of metals in sediments

| Fraction | Procedure |
|---|---|
| F1 (Exchangeable) | Sample extracted at room temperature for 1 h with 7.5 ml of 0.05 M ammonium acetate with continuous agitation. |
| F2 (Bound to carbonates) | Residue from fraction 1 extracted with 10.0 ml of 0.17 M acetic acid (pH 7.0) for 5 h with continuous agitation. |
| F3 (Fe-Mn oxides bound) | Residue from fraction 2 extracted with 20.0 ml of hydroxyl ammonium chloride (pH 5.0) in 25% (v/v) acetic acid, at $96 \pm 3$ ℃ with occasional agitation for 5 h. |
| F4 (Organic matter bound) | Residue from fraction 3 extracted with 5.0 ml of 0.02 M $HNO_3$ and 5.0 ml of 30% $H_2O_2$ at $85 \pm 2$ ℃ for 2 h with occasional agitation. Followed by the addition of 6.0 ml of $H_2O_2$ as above for 3 h. After cooling, 5.0 ml of 3.2 M ammonium acetate in 20% (v/v) $HNO_3$ with continuous agitation for 30 min. |
| F5 (Residual) | Residue from 4 extracted with a hydrochloric/nitric acid (1:1, v/v) mixture and digested under controlled pressure and temperature in closed vessel. |

## D. Instrumental analysis and quality assurance

For trace metals, samples were analyzed by using inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700 series). Multi-element Standard XSTC-13 (Spex CertiPrep® USA) solutions was used to prepare calibration curve. Internal calibration standard solutions containing 1.0 mg/L of Indium (In), Yttrium (Y), Beryllium (Be), Tellurium (Te), Cobalt (Co) and Thallium (TI) were purchased from Spex Certi Prep® USA. 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.

# III.   Results and discussions

## A.  Speciation of metals in sediment

The mobility and toxicity of metals are mainly dependent on metal speciation in the aquatic environment. The relative distribution of trace metals in different geochemical fractions are presented in Table 2 and Fig. 2. Chemical fractionation differentiates metals of natural origin those derived from anthropogenic sources. In general, results of the sequential extraction indicated that the residual fraction dominated the Cr (48–66%), Ni (29–75%), and As (41–66%) distribution in sediments. This result suggested that Cr, Ni and As had the strongest associations to the crystalline sedimentary components and likely reflected the geological characteristics [13]. In contrast to other metals, Cr, Ni and As were the least mobilisable since a considerable proportion of these metals were in the non mobile fraction, which means they are less available to the aquatic fauna and have less chances of entering into the human food chain [14].

The metals like Cd and Pb represent an appreciable portion in carbonate phase, as these metals have special affinity towards carbonate and may co-precipitate with its minerals.

According to the partitioning pattern, a considerable proportion of Cd and Pb were associated with mobilisable fraction (exchangeable and carbonate bound) and can be more available to aquatic life. The lower degree of association of Cr (1.3–19%) in carbonate fraction in the river sediments may arise due to the inability of $Cr^{3+}$ to form a precipitate or complex with carbonates [9]. The reducible fraction contains metals associated with Fe–Mn oxides, which can be mobilized by changes in the redox potential of the sediments and become bioavailable. Among the non–lithogenic fractions the Fe–Mn oxy-hydroxide is the scavenger for Ni, As and Pb. This attributes to the adsorption, flocculation and co-precipitation of trace metals with the colloids of Fe and Mn oxy-hydroxide [15]. Further, organic bound Cr, Cu and Pb seem to be the second dominant fraction among the non lithogeneous. Copper was identified as the highest proportion (49–69%) in the organic fractions. This phenomenon can be explained by the affinity of metals to organic matter, especially humic substances, which are the component of natural organic matter and chemically active in complexing metals [16]. Additionally, organic substances are known to exhibit a high degree of preferential selection for divalent ions [17]. Copper can be retained by sediment through exchange and specific adsorption but precipitation may also be an important mechanism of retention in polluted sediments. A considerable portion of Cu associated organically bound fraction shows a strong association of Cu with organic matter at most of the sampling sites. This behavior can be explained by the well known high affinity of Cu to humic substances, which are a fraction of natural organic matter and chemically active in complexing such metals [18]. Copper is generally adsorbed to a greater extent than other metals; the high affinity of $Cu^{2+}$ ions for soluble organic ligands may greatly increase their mobility in sediments [19].

TABLE 2. Total and fraction concentration of metals in sediments (mg/kg dw, min-max), (n=9)

| Metals | Exchangeable | Bound to carbonates | Fe-Mn oxides bound | Organic matter bound | Residual | Total |
|--------|--------------|---------------------|--------------------|----------------------|----------|-------|
| Cr | 10-50 | 5-99 | 20-122 | 45-997 | 256-1195 | 395-2471 |
| Ni | 1.4-4.1 | 2.8-99 | 64-121 | 42-117 | 110-335 | 242-606 |
| Cu | 2.6-12 | 7.5-25 | 3.4-12 | 80-280 | 42-135 | 127-405 |
| As | 0.58-1.1 | 0.49-5.5 | 6.1-13 | 0.65-10 | 20-34 | 33-58 |
| Cd | 3.1-9.3 | 1.9-5.1 | 0.74-2.3 | 1.5-5.2 | 4.9-9.9 | 14-29 |
| Pb | 5.1-49 | 20-400 | 13-120 | 17-462 | 22-815 | 70-1846 |

## B. Metals bioaccumulation in fish species

The concentrations of Cr, Ni, Cu, As, Cd and Pb in the edible portion of two benthic fish species from three rivers were listed in Table 3. The concentration of metals varied considerably among the fish species. However, as a whole the concentration of studied metals in the *T. fasciata* was higher than *H. fossilis* species. The concentrations of trace metals in fish samples were higher than the permissible levels in fish as per FAO & WHO guidelines (The guideline values are decided based on contaminants, toxins and many substances regarding their occurrence in fish and their significance for human and animal health). The highest mean concentration of Cu was observed in *H. fossilis* (6.0 mg/kg fw) in Buriganga River; whereas, the lowest mean concentration of Cd was observed in *T. fasciata* (0.014 mg/kg fw) in Shitalakha River (Table 3). The measured high concentrations of trace metals in the fish samples of Buriganga River might be due to the untreated wastewater discharged from various industries such as dyeing, batteries, metal processing and tanneries [10]. The biota-sediment accumulation factor (BSAF) is an index of the ability of the fish species to accumulate a particular metal with respect to its concentration in sediment. It was calculated as the ratio between the metals concentration in fish species and that in the sediment [20].

In this study, BSAF was calculated by using metals concentration in fish species (mg/kg dw) and total metal content in sediment (mg/kg dw) and values for BSAFs are given in Table 4. The mean concentration of Cr, Ni, Cu, As, Cd and Pb in sediments collected from different stations have been calculated as 844, 411, 251, 42, 19 and 385 mg/kg dw, respectively. On the basis of calculated BSAF, Cu had the highest for both fish species, while Cd showed the lowest. The trends of average BSAFs for metals in both fish species were in the descending order of Cu > Pb > As > Ni > Cr > Cd. The BSAF values for Cu varied from 0.041 to 0.105 for *H. fossilis* and 0.034 to 0.090 for *T. fasciata* which was the highest among the selected six metals, suggesting higher rate of accumulation in fish species.

The BSAFs for trace metals in *T. fasciata* were notably higher than the values obtained for *H. fossilis*. This can be explained by the sediment ingesting as well as omnivore feeding behavior of *T. fasciata* which may lead to the much greater BSAFs in this study. Therefore, between the two species analyzed in this study, *T. fasciata* can be used as a potential bio-indicator for the contamination of trace metals in those riverine environments.

TABLE 3. Metal concentration in fish species (mg/kg fw, Mean±SD) of three rivers in Bangladesh (vertically, different letter indicates significant difference at $p<0.05$ level among fish species of each river), (n=3)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Turag | *H. fossilis* | 2.4±0.25[a] | 1.1±0.16[a] | 5.1±0.67[a] | 0.28±0.02[a] | 0.026±0.004[a] | 1.3±0.08[a] |
| | *T. fasciata* | 2.9±0.67[a] | 2.5±0.20[b] | 3.7±0.38[b] | 0.29±0.11[a] | 0.015±0.002[b] | 1.5±0.05[b] |
| Buriganga | *H. fossilis* | 2.8±0.93[a] | 3.0±0.018[a] | 6.0±1.1[a] | 0.34±0.04[a] | 0.034±0.010[a] | 1.4±0.10[a] |
| | *T. fasciata* | 4.5±0.24[b] | 3.0±0.04[a] | 4.1±0.56[b] | 0.28±0.01[b] | 0.049±0.018[a] | 2.5±0.26[b] |
| Shitalakha | *H. fossilis* | 2.9±0.64[a] | 1.5±0.12[a] | 5.8±0.20[a] | 0.37±0.07[a] | 0.024±0.010[a] | 1.2±0.29[a] |
| | *T. fasciata* | 3.6±0.42[a] | 1.8±0.67[a] | 3.0±0.48[b] | 0.37±0.04[a] | 0.014±0.002[a] | 1.3±0.36[a] |
| Permissible limits [21] | | 1 | 0.9 | 4.5 | NA | 0.1 | 0.5 |

TABLE 4. Biota-sediment accumulation factors (BSAFs) of metals in fish species

| | T1 | T2 | T3 | B1 | B2 | B3 | S1 | S2 | S3 |
|---|---|---|---|---|---|---|---|---|---|
| *H. fossilis* (n=9) | | | | | | | | | |
| Cr | 0.019 | 0.011 | 0.009 | 0.005 | 0.011 | 0.009 | 0.016 | 0.019 | 0.021 |
| Ni | 0.014 | 0.012 | 0.007 | 0.026 | 0.027 | 0.017 | 0.011 | 0.014 | 0.010 |
| Cu | 0.078 | 0.043 | 0.058 | 0.059 | 0.051 | 0.041 | 0.080 | 0.080 | 0.105 |
| As | 0.024 | 0.023 | 0.026 | 0.022 | 0.027 | 0.018 | 0.040 | 0.021 | 0.025 |
| Cd | 0.006 | 0.006 | 0.005 | 0.005 | 0.005 | 0.002 | 0.006 | 0.001 | 0.003 |
| Pb | 0.057 | 0.030 | 0.034 | 0.031 | 0.002 | 0.008 | 0.026 | 0.026 | 0.015 |
| *T. fasciata* (n=9) | | | | | | | | | |
| Cr | 0.024 | 0.012 | 0.013 | 0.006 | 0.016 | 0.023 | 0.019 | 0.031 | 0.021 |
| Ni | 0.032 | 0.025 | 0.017 | 0.027 | 0.028 | 0.017 | 0.009 | 0.021 | 0.014 |
| Cu | 0.058 | 0.050 | 0.044 | 0.037 | 0.034 | 0.048 | 0.050 | 0.090 | 0.057 |
| As | 0.018 | 0.019 | 0.040 | 0.018 | 0.020 | 0.016 | 0.035 | 0.035 | 0.030 |
| Cd | 0.004 | 0.003 | 0.003 | 0.006 | 0.008 | 0.008 | 0.003 | 0.002 | 0.002 |
| Pb | 0.072 | 0.034 | 0.039 | 0.054 | 0.005 | 0.013 | 0.023 | 0.034 | 0.018 |
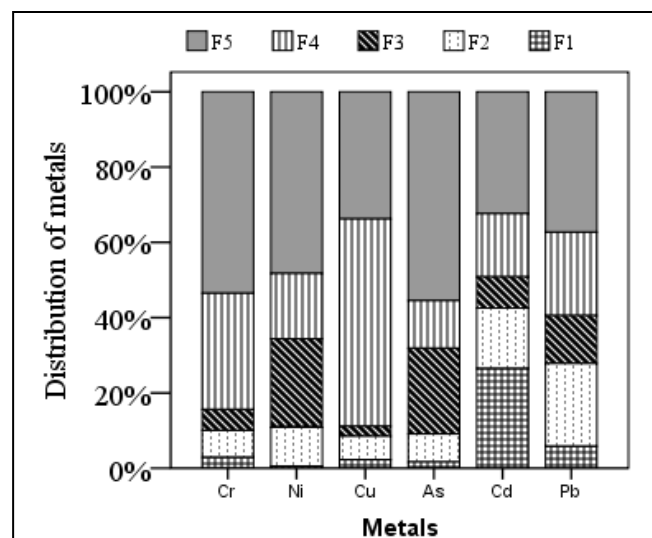
Figure 2. Relative distribution of metals in sediment of different chemical fractions (Table 1 for F1-F5)

The BSAFs of metals in fish species followed the following decreasing order of site T1 > S2 > S3 > S1 > T3 > B1 > T2 > B2 > B3. As a whole, the highest BSAF value of Cu was obtained at S3 site, whereas the lowest of Cd at S2 site (Table 4). The bioaccumulation of individual metal among the sampling sites were not similar pattern due to the environment specific phenomenon.

# IV.  Conclusion

Sequential extraction technique was applied for portioning of selected trace metals in sediments of the studied rivers showing its association with various geochemical forms. The abundance of metals in chemical fractions was the following decreasing order: residual > organic > Fe-Mn-oxides > carbonate > exchangeable. The concentration of trace metals in *T. fasciata* was slightly higher than *H. fossilis*, which is due to their mode of feeding behavior. Similarly, the calculated values of BSAFs in *T. fasciata* were higher than *H. fossilis*, suggested that *T. fasciata* can be used as potential bio-indicator for metal pollution. This study has shown that metal are accumulated in fish species and exceeded the safe recommended levels established by FAO & WHO, indicating that these species are not safe for consumption to the local residents.

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