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Human health risk and ecological risk assessment of metals in fishes, shrimps and sediment from a tropical river

S. Giri · A. K. Singh

Abstract Concentrations of Cd, Cu, Pb, Ni, Zn and Cr were estimated using inductively coupled plasma-mass spectrometry in sediment, water, fish and shrimp collected from the Subarnarekha River. Fish species *Mystus gulio*, *Puntius conchonius*, *Labeo calbasu*, *Labeo rohita* and *Labeo bata*, while the shrimp species *Penaeus indicus*, were used for the study. The range of Cd, Cu, Pb, Ni, Zn and Cr in all the samples was found to be 0.004–0.85, 0.75–145.2, 0.03–0.41, 1.25–21.5, 12.4–109.5 and 0.22–11.36 mg kg^{-1} fresh, respectively. The concentrations of metals in the fish and shrimp exceed the limits of Indian and international standards for food for Cu, Ni, Cd and Zn in some samples. Higher concentrations of the metals were observed in the shrimp as compared to fish samples. The calculated daily intakes of the metals through the consumption of fish and shrimps ranged from 0.30 to 27.0 % of the corresponding tolerable limits suggested by the Joint FAO/WHO Expert Committee on Food Additives. The mean target hazard quotient values for the 6 metals were below 1 for all the samples; however, the maximum was more than 1 for shrimp Cu and Cr. The results indicated that the concentration of the metals in shrimps at some locations was alarming and pose an appreciable hazard risk on human health. Potential ecological risk analysis of sediment indicated that most of the sites posed moderate ecological risk with Cd posing a considerable risk at all the sites.

Introduction

Due to their toxicity and long persistence, metal contamination is a serious threat to aquatic environment. Metals occur in the environment both as a result of natural processes and as pollutants from human activities (Garcia-Montelongo et al. 1994; Jordao et al. 2002). Sediments act as sinks and sometimes potential sources of various contaminants in aquatic systems. The accumulation and distribution of metals within the aquatic environment are governed by complex processes of material exchange affected by various anthropogenic activities and/or natural processes, including riverine or atmospheric inputs, coastal and seafloor erosion, biological activities, water drainage, and discharge of urban and industrial wastewaters (Christophoridis et al. 2009). Suspended sediments adsorb pollutants from the water, thus lowering their concentration in the water column although they may be released into the water column in response to certain disturbances (Agarwal et al. 2005), causing potential threat to ecosystems (Chow et al. 2005; Hope 2006). Bottom sediments also provide habitats and a food source for benthic fauna. Thus, pollutants may be directly or indirectly toxic to the aquatic flora and fauna.

Some metals like Zn and Cu, which are required for metabolic activity in organisms, lie in the narrow "window" between their essentiality and toxicity. Other heavy metals like Cd and Pb may exhibit extreme toxicity even at low levels under certain conditions, thus necessitating regular monitoring of sensitive aquatic environments

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(Fergusson 1990; Peerzada et al. 1990; Cohen et al. 2001). Fish and shrimps could be sampled more frequently and easily in comparison with other water creatures (Moiseenko and Kudryavtseva 2001) and are regarded as significant indicator in aquatic systems for the estimation of water pollution (Canli and Atli 2003; Brumbaugh et al. 2005; Fernandes et al. 2007). In addition, fish are most indicative factors in freshwater systems, for the estimation of trace metal pollution and risk potential of human consumption (Rashed 2001). For the normal metabolism of fish, the essential metals like copper and zinc must be taken up from water, food or sediment. However, similar to the route of essential metals, non-essential ones are also taken up by fish and accumulate in their tissues (Canli and Atli 2003; Yilmaz 2006). The shellfish (particularly the shrimp) is a major exportable item of countries like India and therefore keenly related to economy of the country (Subramanian and Sukumar 1988). Hence, it is important to investigate the levels of metals in these organisms to assess whether the concentration is within the permissible level and will not pose any hazard to the consumers (Sivaperumal et al. 2007; Uysal et al. 2008; Palaniappan and Karthikeyan 2009).

Several methods have been proposed for estimation of the potential risks to human health of heavy metals in fishes. These methods typically are based on the target hazard quotient (THQ). Although the THQ-based risk assessment method does not provide a quantitative estimate of the probability of an exposed population experiencing an adverse health effect, it does provide an indication of the risk level associated with pollutant exposure. This method of risk estimation has recently been used by many researchers (Chien et al. 2002; Wang et al. 2005) and has been shown to be valid and useful. This non-cancer risk assessment method has been applied in this study.

Consequently, an analysis of the distribution of heavy metals in sediments adjacent to populated areas could be used to investigate anthropogenic impacts on ecosystems and would assist in the assessment of risks posed by human waste discharges (Hu et al. 2002; de Mora et al. 2004; Zheng et al. 2008). Under certain conditions, these metals may accumulate to a toxic concentration level which may lead to ecological damage (Jefferies and Freestone 1984). Methods used to evaluate the ecological risk posed by heavy metals in sediments include calculation of the index of geoaccumulation (Porstner 1989), the potential ecological risk index (Håkanson 1980) and the excess after regression analysis (ERA) (Hilton et al. 1985), among which the first two indices are the most popular.

The analysis of the water, sediment and aquatic beings such as fish and shrimps could indicate the level and the tendency of the pollution. This is important not only for protection of the environment but for the quality of the fish

in the water. The study is carried out in Subarnarekha River which flows through the East Singhbhum district, which is one of India's important mineralized and industrialized areas known for ore mining, steel production, power generation, cement production and other related activities. Considering the above facts, the present study was taken up with the objectives to evaluate the metal concentrations in the surface water, sediment, fish and shrimp of the Subarnarekha River and assessment of the ecological risk of metals in the sediment and health risk of metals in the fish and shrimp of the river. To achieve the objectives, sampling of water, sediment, fish and shrimp was carried out during September 2011 from the river.

Materials and methods

Description of the study area

The Subarnarekha River is the eighth river of India by its flow (12.37 billion m^3 per year) and length. The River Subarnarekha is a rain fed river originating near Nagri village (23°18′02″N, 85°11′04″E) in the Ranchi district runs through several major cities and towns such as Jamshedpur, Chaibasa, Ranchi, Bhadrak, etc., covering a distance of about 400 km. It finally joins the Bay of Bengal at Kirtania port (21°33′18″N, 87°23′31″E) in Orissa. Before falling in the Bay of Bengal, the river flows through Ranchi, Saraikela and East Singhbhum districts of Jharkhand, West Midnapore district of West Bengal and Baleshwar district of Orissa. Of its total length, 269 km lies in Jharkhand, 64 km in West Bengal and 62 in Orissa. The Subarnarekha basin covers an area of 19,300 km^2. This area is nearly 0.6 % of the total national river basin area and yields 0.4 % of the country's total surface water resources. The six sampling stations taken up for the study are given in Fig. 1. The sample codes in the figure are given as 1, 2, 3, 4, 5 and 6 for Barabinda, Tatanagar, Mosabani, Gopiballavpur, Mahapal and Kirtania, respectively. Tatanagar is situated in highly industrialized region, while Mosabani is located in a copper mining area. Barabinda, Gopiballavpur and Mahapal are less polluted sites. Kirtania is the mouth of the river where it meets the Bay of Bengal.

Sampling collection and preparation

A total of 108 fresh fish and shrimp were collected consisting of 5 species of fish and 1 species of shrimp from 6 different locations along the Subarnarekha River. The species of fish that were used for the study were *Mystus gulio*, *Puntius conchonius*, *Labeo calbasu*, *Labeo rohita* and *Labeo bata*, while the shrimp species was *Penaeus*
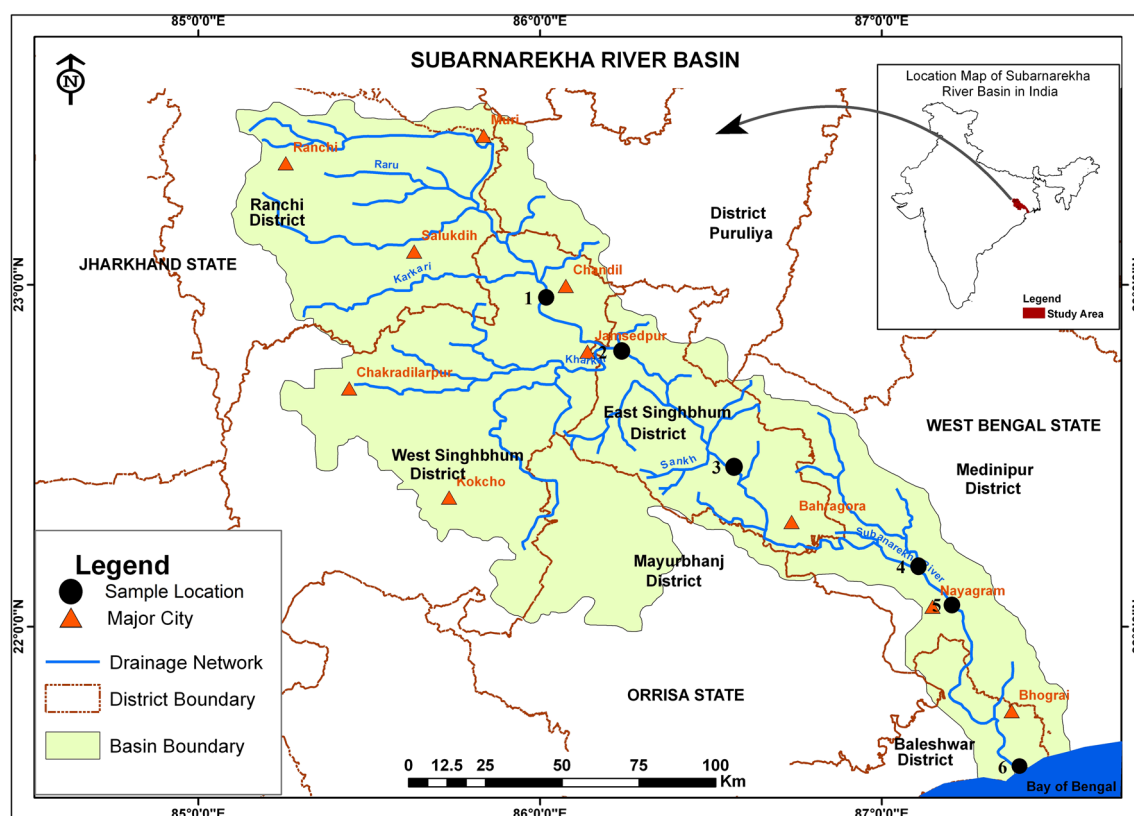
Fig. 1 Map of the study area with sampling locations

indicus. Only two commonly found species, viz. *M. gulio* and *L. rohita* were collected from the high saline region of Kirtania site. The samples were collected from fishermen catch. The species selected were found throughout the river basin and constituted the most important meal species for the local populations. Each species from each location was collected in triplicates. Fish and shrimp samples were placed in an ice box and transported to the laboratory. In the laboratory, the samples were cleaned up with tap water and deionized water and the dorsal muscle samples of each fish were removed for metal analysis. The muscle is preferred because it is a major target tissue for metal storage (Rejomon et al. 2010) and is the main edible part of the fish. Therefore, metal assessment in muscle would determine status of public health risk (Reinfelder et al. 1998). In case of shrimps, the exoskeleton was removed and the soft abdomen muscle was taken for analysis discarding the cephalothorax and tail portions. The soft tissues of fish and shrimp were thoroughly washed with Millipore water and dried to a constant weight at 105 °C in acid-cleaned Petri dishes. Pulverization and homogenization were achieved by grinding the tissue samples in mortar and pestle (UNEP/FAO/IAEA/IOC 1984). Two grams of muscle samples were digested using a mixture (7:3 v/v) of 65 % nitric acid and 70 % perchloric acid (AR grade) on a hot plate at

80–90° until the sample becomes clear. After digestion, the samples were dissolved in 5 ml of 15 % HNO_3 (Protasowicki 1985). All the digested solutions were filtered through quantitative Whatman filter paper (No. 1) and diluted to 25 ml in the volumetric flask with ultrapure water. In parallel, blank samples and reference materials (DOLT-4) were run in triplicate in each analytical series.

Sediment and water samples were collected from the site of collection of fish samples. From each location, sediment and water were collected in five replicates. Bed surficial sediment samples were collected with a plastic spade by scooping from the upper 3–5 cm of river bed representing contemporary deposits at a water depth of about 50 cm. Then, the sediments were packed and sealed in polyethylene bags and brought to the laboratory, where they were air dried at room temperature (25–30 °C). Samples were mixed well by coning and quartering method and about 100 g of the sample was taken. The samples were transferred into a porcelain dish and dried in an oven at 110 °C for 24 h. The samples were then powdered in a dry mortar–pestle and sieved through standard sieve of 200 mesh size. The samples were then preserved for the digestion and further analysis of metals. Collected samples were taken and subjected to digestion in microwave by the method 3052 as given by USEPA (1996). 0.25 g of sample was

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Table 1 Metal concentration in certified reference material (Dogfish Liver DOLT-4 and Estuarine sediment NIST-1646a)

Element	Dogfish liver DOLT-4			Estuarine sediment NIST-1646a		
	Certified concentration (mg kg^{-1})	Observed concentration (mg kg^{-1})	Recovery (%)	Certified concentration (mg kg^{-1})	Observed concentration (mg kg^{-1})	Recovery (%)
Cd	24.33 ± 0.8	23.45 ± 0.4	96.4	0.148	0.131 ± 0.08	88.5
Cu	31.2 ± 1.1	32.54 ± 0.81	104.3	10.01	11.2 ± 0.7	112.0
Pb	0.160 ± 0.04	0.170 ± 0.05	106.2	11.7	11.07 ± 0.62	94.6
Ni	0.97 ± 0.11	0.910 ± 0.13	93.8	23.0	21.74 ± 1.1	94.5
Zn	116.0 ± 6.0	109.7 ± 2.3	94.6	48.9	42.69 ± 1.4	87.3
Cr	NA[a]			40.9	38.17 ± 1.2	93.3

[a] *NA* not available

taken and 4.5 ml HNO_3, 2 ml HF, 1 ml HCl and 0.5 ml H_2O_2 was added. The samples were digested in microwave (Anton Paar) and filtered, and the volume was made up to 50 ml by adding 2 % (v/v) nitric acid. Aliquots were preserved for the analysis of metals. Water samples for metal analysis were collected, filtered with Millipore filter paper (pore size-0.45 μm) and preserved by lowering the pH to <2 by addition of 6 N ultrapure nitric acid (Radojevic and Bashkin 1999).

Determination of metals

Concentrations of Cd, Cu, Pb, Ni, Zn and Cr were determined in water, sediment, fish and shrimp using inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer Elan DRC-e.). A calibration blank and an independent calibration verification standard was analyzed every 15 samples to confirm the calibration status of the ICP-MS. Metal concentrations were expressed as mg kg^{-1} fresh weight of fish tissue. Matrix interference (Blank) was <1 % for all elements. Recovery rates of metals spiked in fish muscles, water and sediments ranged from 88 to 110 %. Triplicates of samples analysis yielded relative percent differences of <5 %.

Validation methodology

The method of analysis was validated using DOLT-4 certified reference material (dogfish liver), supplied by the National Research Council, Canada, NRC, Division of Chemistry and NIST-1646a standard reference material (Estuarine sediment) supplied by National Institute of Standards and Technology (NIST), USA. The validation results are shown at Table 1. The accuracy and precision were checked by analyzing the certified reference material under the same conditions (Table 1). The % of recovery varied from 93.8 to 106.2 in case of fish and 87.3–112 in case of sediment.

Statistical analysis of the data

For each metal, the distribution of the combined data of the fish was verified by the curve of accumulated frequency (Miller and Miller 1989). As usually observed in environmental samples, the concentrations of the metals were better represented by the lognormal distribution and the central tendency thus is represented by the geometric average (Wayne 1990).

Calculation of estimated daily intake (EDI)

Taking the geometric mean concentration of the metals in mg kg^{-1} fresh and per day consumption of 15 g of fish (based on interview of the local consumers) the daily intake was evaluated for the metals. The estimated daily intake (EDI) of metals depends on both of the metal concentrations in fish and the consuming amounts of fish. The EDI value for an adult was calculated with the Eq. (1) according to Song et al. 2009.

$$EDI = \frac{C_{metal} \times W_{fish}}{B_w} \tag{1}$$

where EDI represents the estimated daily intake of metal through the consumption of fish for an adult (in micrograms per kilogram per day), C_{metal} is the concentration of metal in fish (in micrograms per gram, fresh weight), W_{fish} represents the daily consumption of fish (in grams per day, fresh weight), and B_w is the body weight of an adult (in kilogram). The average value of B_w used was 52 kg for Indian man (Jain et al. 1995; Dang et al. 1996). In the present study, the value of W_{fish} was 15.0 g day^{-1} was obtained through a formal survey conducted in the study area. An interview of 30 persons of 30- to 50-year age-group was conducted at each location of the six locations regarding their daily consumption rate of fish. Each person represents a household having ≥5 individuals, and thus, a total of 150 persons were effectively interviewed. An

average consumption rate of fish per person per day was calculated.

Risk from the intake of metals through ingestion: target hazard quotient

Several methods have been proposed to estimate the potential risks of toxic metals on human health, in which the THQ and hazard index (HI), proposed by the USA Environmental Protection Agency (USEPA 1989), have been recognized as one of the reasonable indexes for the evaluation associated with the intake of metals by consuming the contaminated foods (Hough et al. 2004; Chary et al. 2008). This is the ratio of the EDI (milligrams per kilogram body weight per day) of a chemical to a reference dose ($R_f D$, milligrams per kilogram per day) defined as the maximum tolerable daily intake of a specific metal that does not result in any deleterious health effects (Eq. 2) (USEPA 1989):

$$THQ = EDI/R_f D \qquad (2)$$

If the value of THQ is above 1 (i.e., THQ > 1), this means that the exposed population via the consumption of contaminated foods is likely to experience obvious deleterious effects. The higher the THQ value is the higher will be the probability of the hazard risk on human body.

For the risk assessment of multiple metals containing in fish, a total HI was employed by summing all the calculated THQ_i values of metals as described in Eq. (3) (USEPA 1989).

$$HI = \sum_{i=1}^{n} THQ_i \qquad (3)$$

where THQ_i is the target hazard quotient of an individual element of metals, HI is the total hazard index for all the six metals studied in the present study, and n is 6.

Assessment of potential ecological risk

Håkanson (1980) developed a methodology to assess ecological risks for aquatic pollution control. The methodology is based on the assumption that the sensitivity of the aquatic system depends on its productivity. The potential ecological risk index (R_I) was introduced to assess the degree of heavy metal pollution in sediments, according to the toxicity of heavy metals and the response of the environment:

$$R_I = \Sigma E_r^i \qquad (4)$$

$$E_r^i = T_r^i C_f^i \qquad (5)$$

$$C_f^i = C_n^i / C_0^i \qquad (6)$$

where R_I is calculated as the sum of all risk factors for heavy metals in sediments, E_r^i is the monomial potential ecological risk factor, T_r^i is the toxic response factor for a given substance, which accounts for the toxic and sensitivity requirement, and the values for Cd, Cu, Pb, Ni, Zn and Cr are 30, 5, 5, 5, 1 and 2, respectively (Hilton et al. 1985; Wang et al. 2011). C_f^i is the contamination factor, C_n^i is the concentration of metals in the sediment, and C_0^i is a reference value for metals. Due to lack of relevant background data of unpolluted sediment in the study area, the average sediment background values in India which are 0.3, 28, 11.2, 37, 16 and 87 mg kg^{-1} for Cd, Cu, Pb, Ni, Zn and Cr, respectively, (Subramanian et al. 1985) were adopted in the study.

According to Gan et al. (2000), the potential ecological risk of coastal sediments posed by heavy metals can be classified into the following categories:

Low risk: $E_r^i < 30$; $R_I < 100$

Moderate risk: $30 \le E_r^i < 50$; $100 \le R_I < 150$:

Considerable risk: $50 \le E_r^i < 100$; $150 \le R_I < 200$:

Very high risk: $100 \le E_r^i < 150$; $200 \le R_I < 300$:

Disastrous risk: $E_r^i \ge 150$; $R_I \ge 300$.

Results and discussion

Distribution of metals in fish and shrimp

The results of the metal analysis are provided in Table 2. The average concentration of triplicate samples of each species is given alongside each species in the Table. The range of Cd, Cu, Pb, Ni, Zn and Cr of all the samples was found to be 0.004–0.85, 0.75–145, 0.03–0.41, 1.25–21.5, 12.4–110 and 0.22–11.4 mg kg^{-1} fresh, respectively. Highest concentration of Zn and Cr was found in *P. indicus* from Tatanagar, while for Cd, Cu, Ni and Pb, it was *P. indicus* collected from Mosabani. The concentrations of metals in the fish and shrimp exceeded the limits of Indian standards for food (Awasthi 2000) for Ni and Zn (1.5 and 50 mg kg^{-1}, respectively) in more than 50 % of the samples. In 10 % of the samples, the concentration of Cu also exceeded the Indian limit of 30 mg kg^{-1}. While comparing with international standards, levels of Pb were well below thresholds of concern, whereas Cd, Cu and Zn were above the acceptable limits for human consumption (i.e., 40.0, 30.0, 0.5 and 0.5 mg kg^{-1}, fresh weight for Zn, Cu, Cd and Pb, respectively) set by the FAO (1983) food standards for

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Table 2 Metal concentration of fish and shrimp (mg kg^{-1}) collected from Subarnarekha River of India (each value is average of three samples)

Locations	Species	Cd	Cu	Pb	Ni	Zn	Cr
Barabinda (sample code 1)	*P. indicus*	0.051	21.2	0.159	14.5	30.8	1.44
	M. gulio	0.005	0.75	0.327	3.36	67.3	0.695
	P. conchonius	0.004	1.41	0.234	1.72	63.7	0.592
	L. calbasu	0.006	2.51	0.266	2.41	81.9	0.496
	L. rohita	0.004	5.62	0.145	1.52	52.1	0.325
	L. bata	0.004	1.60	0.28	1.7	40.3	0.726
Tatanagar (sample code 2)	*P. indicus*	0.621	29.5	0.325	21.3	109.5	11.36
	M. gulio	0.026	1.17	0.256	5.53	77.5	0.961
	P. conchonius	0.029	5.16	0.146	3.40	89.4	1.279
	L. calbasu	0.005	1.48	0.085	1.73	99.1	0.68
	L. rohita	0.005	7.68	0.325	3.42	79.3	1.051
	L. bata	0.23	2.96	0.359	3.45	65.2	1.52
Mosabani (sample code 3)	*P. indicus*	0.852	145.2	0.412	21.5	96.4	4.23
	M. gulio	0.101	14.0	0.341	7.51	47.4	0.503
	P. conchonius	0.063	10.6	0.237	13.9	81.3	1.397
	L. calbasu	0.008	13.5	0.096	15.2	75.3	0.512
	L. rohita	0.098	20.8	0.136	4.57	49.3	0.826
	L. bata	0.51	46.4	0.214	4.36	54.4	0.745
Gopiballavpur (sample code 4)	*P. indicus*	0.045	14.3	0.063	5.36	12.4	1.05
	M. gulio	0.039	1.26	0.091	3.01	52.1	0.577
	P. conchonius	0.021	1.25	0.045	5.26	63.3	0.985
	L. calbasu	0.006	1.26	0.054	10.2	52.4	0.412
	L. rohita	0.054	5.32	0.112	1.32	35.6	0.254
	L. bata	0.14	19.6	0.025	2.59	52.1	1.04
Mahapal (sample code 5)	*P. indicus*	0.052	10.3	0.052	5.89	14.3	0.69
	M. gulio	0.027	1.11	0.081	2.15	42.6	0.215
	P. conchonius	0.017	3.33	0.031	7.97	42.1	1.123
	L.calbasu	0.007	0.97	0.058	11.5	48.6	0.547
	L. rohita	0.061	4.25	0.096	1.25	42.7	0.314
	L. bata	0.21	16.3	0.031	2.31	45.2	0.89
Kirtania (sample code 6)	*P. indicus*	0.049	21.7	0.078	6.89	25.2	0.358
	M. gulio	0.007	1.91	0.087	8.06	42.6	0.964
	L. rohita	0.02	1.21	0.062	8.23	71.3	0.582
Geometric mean		0.031	5.16	0.121	4.68	52.2	0.784
Geometric standard deviation		4.75	3.85	2.23	2.26	1.64	2.14

fish. A comparison with the European food standards (EC 2001), for fish (Pb: 0.2–0.4 mg kg^{-1}and Cd: 0.05–0.10 mg kg^{-1}, fresh weight), also showed that Pb was lower than the guidelines for the edible part of the examined fish, whereas Cd was above the acceptable limits for human consumption.

Table 3 provides the metal concentration in fish of this study and other rivers by various researchers. All the listed rivers are under vigorous anthropogenic influence including industries and mining, the condition similar to the Subarnarekha River. However, the metal concentrations in the tissue of fish vary among different studies. This may be attributed to differences in metal concentrations, chemical characteristics of water from which fish were sampled, ecological needs, metabolism, feeding patterns of fish, age and the season in which studies were carried out. It can be depicted from the table that the concentrations of most of the metals were higher in the Asian rivers which demonstrate that the metal contamination in the Asian rivers is of serious

Table 3 Comparison of metals (mg kg^{-1}) in fish samples with other river water studies

Location	Cd	Cu	Pb	Ni	Zn	Cr	Reference
Buriganga River, Bangladesh		3.36–6.34	8.03–13.52	8.25–11.21			Ahmad et al. 2010
Ipo stream, Nigeria		17.85	24.14	2.79			Friday et al. 2009
Magani confluence, Nigeria		0.46	1.24		0.09		Atolaye and Aremu 2007
Yangtze River	ND-2.0	0.36–18.8	0.009–10.1		0.79–50.8	ND-0.81	Yi et al. 2011
Ogba River, Benin City, Nigeria		3.81	0.25	0.04	4.27		Obasohan and Eguavoen 2008
Ganga, West Bengal, India		1.1–5.4	0.006–0.02		4.9–12.2		Bhattacharya et al. 2008
Ganga, Kolkata	0.046	0.96	3.50		12.59	0.077	Aktar et al. 2011
Tingjiang river, China	–	1.60	0.128	0.015	4.87	0.052	Liu et al. 2012
Pearl river, China	0.10–0.17	0.06–0.35	0.11–0.52	0.04–0.36	2.67–19.1	0.09–0.36	Cheung et al. 2008
Danube river, Croatia	0.013–0.018		0.015–0.039				Zrnčić et al. 2012
Subarnarekha River, India	0.031	5.16	0.121	4.68	52.2	0.784	Present study

concern. However, the metal concentration in fish of the Subarnarekha River was in the range of other studies.

On analyzing the data, it can be inferred that the concentration of metals in the fish and shrimp species was related to the locations and species. The concentrations of the metals were visibly more in two locations, i.e., Tatanagar and Mosabani. Tatanagar is under the influence of intense industrialization and urbanization, while Mosabani is associated with active copper mining. Thus, almost all the metals have a pronounced effect on the fish and shrimp samples collected from these locations as compared to other locations. Mining and metallurgical industries are characterized with anthropogenic alteration of the biogeochemical cycles of elements and source of serious environmental pollution related to the emission of metals (Nriagu et al. 1998; Allen-Gil et al. 2003; Pyle et al. 2005). Several ways such as natural leaching of mine tailings, acid mine drainage and erosion from the mining areas are related to the discharge of pollutants containing metals into the surrounding environments (Moiseenko and Kudryavtseva 2001; Higueras et al. 2004; Riba et al. 2005; Mayes et al. 2010). Thus, aquatic environments are always the straight collector of metal elements from the mining sites and metallurgical industries (Tarras-Wahlberg et al. 2001; Sapkota et al. 2008). The mining effluents increase metal levels in the aquatic systems, which may impact aquatic life. Moreover, water contaminated by metal mining is the major source for metal accumulation in fish (Rashed 2001; Bervoets et al. 2005; Borgmann et al. 2007).

The sensitivity of crustaceans to metals is well documented, and the importance of shrimp for environmental monitoring studies as bioindicators of metal pollution has been emphasized by several investigators (Larsson et al. 1985; Yusof et al. 2004; Yilmaz and Yllmaz 2007). In the present study also, on comparing the metals concentration in the fish and shrimp species it can be easily conjectured that irrespective of the locations, the shrimps accumulated more metals than the fish species. Shrimps are benthic organisms that feed by stirring the sediment up and collecting very small particles of organic matter, and so they would be exposed to the metals bound to this food (FSA 2005; Pourang et al. 2005).

In the present investigation, the concentration of metals in the muscle tissues followed a trend of Zn>Cu>Ni>Cr>Pb>Cd. The concentration of Zn in fish was highest among all the metals. This observation was similar to the observation of other workers for many species of fish in different aquatic systems (Tekin-Ozan 2008; Yilmaz and Dogan 2008). This can be attributed to the fact that Zn is present in many enzymes (Karadede and Unlu 2000; Alhas et al. 2009). In shrimps, the trend was little different being Zn>Cu>Ni>Cr>Cd>Pb.

Distribution of metals in water and sediment

The average concentrations of metals in surface water and bed sediment of Subarnarekha River are given in Table 4. The results depict that the range of Cu, Ni, Zn and Cr in the surface water in µg l^{-1} is 0.48–16.5, 0.82–4.57, 5.22–13.2 and

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Table 4 Average concentration of metals in surface water and bed sediment of Subarnarekha River ($n = 5$)

Locations	Cd	Cu	Pb	Ni	Zn	Cr
(a) Surface water ($\mu g\ l^{-1}$)						
Barabinda	N.D[a]	1.76	N.D	0.98	12.9	0.86
Tatanagar	N.D	0.55	N.D	0.82	13.2	1.25
Mosabani	N.D	16.5	N.D	4.57	12.4	1.16
Gopiballavpur	N.D	4.6	N.D	2.25	6.42	0.22
Mahapal	N.D	0.48	N.D	1.43	5.22	0.03
Kirtania	N.D	7.8	N.D	3.68	5.64	1
IS 10500 limit[b]	10	50	50	20	5,000	50
WHO limits[c]	3	2,000	10	70	3,000	50
(b) Sediment ($mg\ kg^{-1}$)						
Barabinda	0.64	63.9	83.0	45.5	126.4	123.2
Tatanagar	0.744	44.4	65.0	27.7	182.1	70.6
Mosabani	0.778	168.5	48.1	36.9	53.6	53.7
Gopiballavpur	0.784	57.7	48.3	30.1	49.8	50.3
Mahapal	0.789	43.2	37.6	39.2	59.5	94.0
Kirtania	0.709	25.7	26.1	25.3	52.2	75.0
Indian average[d]	0.3	28	11.2	37	16	87
Shale average	0.3	45	20	68	95	90

[a] *ND* not detected

[b] IS:10500 IS 2012

[c] WHO 2004

[d] Subramanian et al. 1985

[e] Turekian and Wedepohl 1961

Table 5 Correlation coefficients of metals between fish and different matrices

	Cd	Cu	Pb	Ni	Zn	Cr
Sediment	−0.36	**0.95**	**0.74**	−0.23	**0.77**	−0.28
Water	–	**0.62**	–	**0.68**	**0.84**	**0.61**

Bold values indicate significant correlation at the 0.05 level

0.03–1.25, respectively. Cd and Pb were not detected in any of the samples. Comparing with WHO standards (WHO, 2004) and Indian Standards (IS:10500 2012), it can be inferred that none of the metals in any locations crossed the either limits. However, the highest concentration of Cu and Ni was found in Mosabani, while Tatanagar recorded the highest concentration of Zn and Cr. Considering all the sampling locations, the range of Cd, Cu, Pb, Ni, Zn and Cr in mg kg^{-1} in the bed sediments was found to be 0.709–2.64, 25.7–168.5, 26.1–83.0, 25.3–45.5, 49.8–182.1 and 50.3–123.2, respectively. A comparison with average Indian values of metals for sediments (Subramanian et al. 1985) and average concentration of metals in Shale (Turekian and Wedepohl 1961)

depicted that almost all the locations for all the metals exceeded the values. As the study area is characterized by the presence of metal bearing formations and mining and industrial operations, it is expected to have elevated levels of metals in sediment (Forstner and Wiltman 1983; Preston and Chester 1996). The sediment accumulated more metals than the water in this study as have been observed by Besada et al. (2001), Chindah et al. (2003) and Eja et al. (2003). Sediment is the major depository of metals holding more than 99 % of total amount of a metal present in the aquatic system (Odiete 1999).

Relationships between heavy metal levels in fish and in the environment

To assess the association between the different matrices, i.e., fish, water and sediment, correlations of the metals were determined between the different matrices and the coefficients are depicted in the Table 5. The results suggested a strong association of the Zn, Cu, Ni and Cr between the water and the fish samples and Zn, Pb and Cu between sediment and fish samples. The positive correlation of metals between water and fish tissues has been reported by other studies also (Zyadah 2005; Fatma 2008). Cu, Zn and Pb in the fish samples are found to be associated with the sediments. This is in accordance with other researchers (Chandra Sekhar et al. 2004; Fernandes et al. 2008; Obasohan and Eguavoen 2008; Vicente-Martorell et al. 2009). Cd was not detected in water samples, and the correlation between sediment and fish samples was not significant. This may be attributed to the fact that Cd is a highly mobile and potentially bioavailable metal and was primarily scavenged by non-detrital carbonate minerals, organic matter, and iron–manganese oxide minerals (Prusty et al. 1994).

Health risk and ecological risk assessment

Estimation of daily intake of metals by consuming fish

The survey method adopted for the study area showed that the average consumption of fish including shrimps per person per day is 15 g. If the levels of metal concentrations (Table 2) recorded in this study are representative of metal concentrations in the fish and shrimps tested and consumed by the interview sample, then the EDI values of metals for an adult via the consumption of fish are shown in Table 6. The data of provisional tolerable daily intake (PTDI) suggested by the Joint FAO/WHO Expert Committee on Food Additives (JECFA 1999, 2003) are also listed. In the present study, it may be noted that the $R_f D$ of

Table 6 Estimated dietary intakes (EDI) of metals by consuming fish and shrimp collected from Subarnarekha River in India

Species	Heavy metals					
	Cd	Cu	Pb	Ni	Zn	Cr
P. indicus						
Concentration[a]	0.28	40.36	0.18	12.58	48.09	3.19
EDI[b]	0.08	11.64	0.05	3.63	13.87	0.92
M. gulio						
Concentration[a]	0.03	3.37	0.20	4.94	54.92	0.65
EDI[b]	0.01	0.97	0.06	1.42	15.84	0.19
P. conchonius						
Concentration[a]	0.03	4.36	0.14	6.45	67.95	1.08
EDI[b]	0.01	1.26	0.04	1.86	19.60	0.31
L. calbasu						
Concentration[a]	0.01	3.95	0.11	8.20	71.46	0.53
EDI[b]	0.00	1.14	0.03	2.36	20.61	0.15
L. rohita						
Concentration[a]	0.04	8.74	0.16	2.42	51.8	0.55
EDI[b]	0.013	2.52	0.047	0.697	14.94	0.16
L. bata						
Concentration[a]	0.22	17.37	0.18	2.88	51.43	0.98
EDI[b]	0.06	5.01	0.05	0.83	14.83	0.28
PTDI[c]	1	500	3.57	5	1,000	3

[a] The mean values of heavy metal concentrations in fish and shrimp, in mg kg^{-1} fresh

[b] EDI values, in µg/kg body wt/day

[c] PTDI values (in µg/kg body wt/day) of all the metals were based on the data suggested by The Joint FAO/WHO Expert Committee on Food Additives (JECFA) (1999, 2003). The PTDI value of Cr was based on the reference dose (R_fD) of Cr(VI) established by US Environmental Protection Agency (2011)

3 µg kg^{-1} day^{-1} for Cr(VI) established by USEPA (2011) is taken as the PTDI value of total Cr because of its unavailable PTDI data. From the EDI of the studied metals through the consumption of fish, it can be suggested that the consumption of average amounts of these fish does not pose a health risk for the consumers as the values obtained were below the FAO/WHO (1999) limits for metals intake. The present study showed that the contributions of these fish and shrimp to daily intake of Cd, Cu, Pb, Ni, Zn and Cr were 0.89, 0.30, 0.98, 27.0, 1.51 and 7.54 %, respectively, of PTDI as suggested by JECFA.

Low dietary intake of Pb, Zn and Cu was also observed for the fish and shrimp species, and the maximum EDI observed in *M. gulio*, *L. calbasu* and *P. indicus* only accounts for 1.68, 2.06, and 2.32 %, respectively, of the PTDI value. However, relative high EDI levels of Cd, Ni and Cr are found for *P. indicus*, in which the EDI values account for 8.0, 72.6 and 30.7 % of the PTDI values,

respectively. The EDI value of Ni is quite high in all the species studied, highest being in *P. indicus*, which accounts for 72.6 % of the PTDI value.

Risk assessment of metals by consuming fish

The THQ values of metals by consuming fish for an individual adult are shown in Table 7. The results showed that the total THQ values (HI) of metals range at the following sequence: *P. indicus* > *L. bata* > *P. conchonius* > *L. calbasu* > *M. gulio* ≥ *L. rohita*. Because of the unavailable R_fD data of total Cr, 3 µg kg^{-1} day^{-1} of R_fD value for Cr(VI) is considered as that of total Cr by assuming that all Cr in samples is Cr(VI). Under the strict criterion, the mean THQ values of Cd, Pb and Zn were <0.1 for all the studied species; however, the maximum THQ values were calculated for the species of *P. indicus*, i.e., 0.25, 0.03, 0.31 and 0.11, respectively, for Cd, Pb, Ni and Zn. It can also be

Table 7 Target hazard quotients (THQ) of metals by consuming fish and shrimp collected from Subarnarekha River in India

Species	THQ						
	Cd	Cu	Pb	Ni	Zn	Cr	HI
P. indicus							
Range	0.013–0.25	0.074–1.05	0.004–0.03	0.077–0.31	0.012–0.11	0.034–1.09	0.26–2.14
Mean	0.08	0.29	0.01	0.18	0.05	0.31	0.92
M. gulio							
Range	0.001–0.03	0.005–0.10	0.007–0.03	0.031–0.12	0.041–0.07	0.021–0.09	0.12–0.36
Mean	0.010	0.024	0.016	0.071	0.053	0.063	0.24
P. conchonius							
Range	0.001–0.02	0.009–0.08	0.003–0.02	0.025–0.20	0.040–0.09	0.057–0.13	0.17–0.53
Mean	0.008	0.031	0.011	0.093	0.065	0.103	0.31
L. calbasu							
Range	0.001–0.02	0.007–0.1	0.004–0.02	0.025–0.22	0.047–0.09	0.040–0.07	0.20–0.45
Mean	0.002	0.028	0.009	0.118	0.069	0.051	0.28
L. rohita							
Range	0.001–0.03	0.009–0.15	0.005–0.03	0.018–0.12	0.034–0.08	0.024–0.10	0.14–0.38
Mean	0.013	0.063	0.013	0.035	0.050	0.053	0.23
L. bata							
Range	0.001–0.15	0.012–0.33	0.002–0.03	0.025–0.06	0.039–0.06	0.07–0.15	0.17–0.69
Mean	0.063	0.125	0.015	0.042	0.049	0.095	0.39

Table 8 Heavy metal potential ecological risk indexes of the sediment of the Subarnarekha River

Locations	E_r^i						R_I
	Cd	Cu	Pb	Ni	Zn	Cr	
Barabinda	**64**	11.41	**37.05**	6.14	7.90	2.83	**129.3**
Tatanagar	**74.4**	7.93	29.02	3.74	11.38	1.62	**128.1**
Mosabani	**77.8**	**30.09**	21.46	4.98	3.35	1.23	**138.9**
Gopiballavpur	**78.4**	10.30	21.57	4.06	3.11	1.16	**118.6**
Mahapal	**78.9**	7.71	16.77	5.30	3.72	2.16	**114.6**
Kirtania	**70.1**	4.59	11.66	3.42	3.26	1.72	94.7

E_r^i is the individual heavy metal potential ecological risk index, R_I is the total heavy metal potential ecological risk index; bold types indicates the sample sites with moderate or considerable ecological risk

noted that the maximum THQ levels of Cu and Cr were more than 1, i.e., in *P. indicus*, but their mean values were totally far below 1.

THQ value proposed by USA EPA is an integrated risk index by comparing the ingestion amount of a pollutant with a standard reference dose and has been widely used in the risk assessment of metals in contaminated foods (Storelli 2008). The THQ value has been recognized as one

of the reasonable parameters for the risk assessment of metals associated with the consumption of contaminated fish and shellfish (Chien et al. 2002; Zheng et al. 2007; Storelli 2008). In the present study, the average HI values for all the species were below 1, which indicated that the intakes of metals by consuming these do not result in an appreciable hazard risk on human body. However, the HI value for *P. indicus* was 0.92 which is near to 1 thus indicating probable risk in consumption. Furthermore, the highest values of HI in case of *P. indicus* also exceeded the limit of 1 indicating potential risk to the human. The highest values of HI were in the samples collected from the locations of Tatanagar and Mosabani. This indicated potential contamination of shrimp samples with metals which may be attributed to the contribution of the high levels of these metals in aquatic environments from copper mines and urban effluents. Metals have a toxic impact, but detrimental impacts become apparent only when long-term consumption of contaminated fish and shrimp occurs. It is therefore suggested that regular monitoring of metals in fish and other aquatic organisms should be performed in order to prevent excessive buildup of these metals in the human food chain. Further investigation is recommended seasonal variability of essential and toxic metals in other consumed fish species for safeguarding human health.

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Potential ecological risk assessment of sediment

Using Eq. (4–6), the potential ecological risk indices E_r^i and R_I for each site were obtained and are listed in Table 8. According to these data, Cd posed a considerable ecological risk at all the sites. Additionally, Cu and Pb also posed moderate ecological risks in one site each. The high ecological risks of these three heavy metals in freshwater ecosystems were consequences of their high toxic response factors.

R_I represents the sensitivity of various biological communities to toxic substances and illustrates the potential ecological risk caused by heavy metals. Five sites out of six exhibited moderate ecological risk, the highest being at Mosabani which is under the influence of industrial and mining activities. The R_I values were clearly related to the degree of anthropogenic disturbance. The sources of heavy metal pollution in the river are influenced by many factors, both natural and manmade.

Conclusion

Accumulation of metals by different fish and shrimp species from Subarnarekha River assumes importance due to its flowing from large-scale industrial and mining-related areas. The concentrations of metals in the fish and shrimp exceeded the limits of Indian standards for food for Cu, Ni and Zn in many samples. The study also suggested that irrespective of the locations the shrimps accumulated more metals than the fish species. The results furthermore suggested a strong association of the Zn, Cu, Ni and Cr between the water and the fish samples and Zn, Pb and Cu between sediment and fish samples. The mean THQ values of for the 6 metals were below 1 for all the samples; however, the maximum THQ was more than 1 for *P. indicus* in case of Cu and Cr. Also, the total THQ value (HI) calculated was also nearing 1 for the same species which signified the potential health risk to highly exposed consumers. The shrimps, being a favorite food of people in this region, the high consumption of it can lead to chronic disorders, e.g., renal failure, bone disorders, etc., as this has high concentration of metals. As fish and shrimp are staple food for human being, the accumulation of metals exceeding the permissible limits is a serious health concern. Analysis of the potential ecological risk of sediment heavy metal concentrations showed that most sample sites in the Subarnarekha River presented a moderate ecological risk. According to the potential ecological risk index for a single regulator (E_r^i), Cd represented a considerable risk at all sites and a moderate risk for Cu and Pb at one site. The ecological risk for all factors (R_I) showed that five out of six sample sites belonged in the category of moderate risk. The study thus highlighted the metal accumulation in fish and sediment of the Subarnarekha River. As the high metal availability in the river is attributed to anthropogenic origin, adequate strategies are to be adopted in order to control their presence so that the possible health hazards to different life forms including man can be prevented.

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