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ORIGINAL PAPER

Vertical distribution and contamination assessment of heavy metals in sediment cores of ship breaking area of Bangladesh

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Abstract Vertical heavy metal profiling reflects the history of the deposition of metals and helps to understand the characteristics of accumulation in various layers of the sediment. Nevertheless, no previous studies in Bangladesh had focused on the vertical distribution of heavy metals in core sediments. In this study, vertical distribution, contamination level and potential ecological risks of six heavy metals (Zn, Cu, Pb, Cr, Ni, Mn) from the core sediment of ship breaking were assessed and compared with the non-ship breaking area of Bangladesh. The concentration (μg/g) of heavy metals in the 0–10 cm (surface), 10–20 cm (middle) and 20–30 cm (bottom) of sediment cores was as follows, respectively: Zn (35.54–100.68, 37.27–258.02, 42.78–66.45); Cu (16.38–75.25, 30.64–92.02, 34.99–52.98); Pb (4.84–132.08, BDL–204.48, BDL–23.51); Cr (14.57–42.13, 25.31–42.71, 15.26–36.34); Ni (4.02–42.23, 4.94–43.70, 4.40–43.13); Mn (198.74–764.16, 257.77–980.50, 255.62–856.44). The heavy metal content of core sediment from the shipbreaking region was substantially higher than that of non-shipbreaking area. Except for Ni, heavy metal content was highest in the middle layer, followed by the upper and lower layers of the sediment core. Contamination exponents such as enrichment factor, contamination factor and geo-accumulation index (Igeo) revealed contamination by Zn, Cu and Pb while potential ecological risk factor (E_r^i) and risk index suggested low ecological risk by studied heavy metals except for Pb. Correlation matrix, cluster analysis and principal component analysis indicated that all studied heavy metals could have similar anthropogenic origins.

Keyword Heavy metals · Vertical distributions · Contamination · Core sediments · Ship breaking area

Introduction

Heavy metal pollution is a major global concern in marine ecosystems due to its prevalence in nature, high toxicity, persistent nature, omnipresence, non-biodegradability potential and bioaccumulation through the food chain (Ahmed et al., 2019; Ahmed et al., 2015; Hossain et al., 2020; Niu et al., 2020;

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Selvam et al., 2020). These contaminants are introduced into the aquatic ecosystems from specific and dispersed sources due to both natural and anthropogenic activities (Armstrong-Altrin et al., 2015). Sedimentary habitats or rocks are the world's largest single ecosystem, maintaining the trophic state of aquatic species (Ogundele & Ayeku, 2020; Singh et al., 2005), form the base of food web and provide a room for biogeochemical cycling (Ahmadov et al., 2020). These deposits also act as an integral material by providing an indispensable cohesion between biological and chemical processes for activating ecological indivisibility (Islam et al., 2018). Since heavy metals are less soluble in water and adsorbed or deposited on bottom sediments, sediments are therefore the effective means of monitoring the health of marine ecosystems (Islam et al., 2018).

Heavy metals have a direct or indirect harmful effect on marine invertebrates, fish and humans above certain concentrations or threshold levels (Ahmed et al., 2020; Ahmed, Shaheen, et al., 2015; Chen et al., 2016). These metals alter morphologic and physiologic parameters in aquatic invertebrates, such as growth rate, swimming speed, food intake and breathing intensity, as well as efficiency, survival and life cycles (Martinez et al., 2002). Heavy metal principally causes mortality, hatching delay and spinal deformities of fish (Sfakianakis et al., 2015). Reproduction, physiological functions and growth of fish are also affected by heavy metals (Afshan et al., 2014). Heavy metals can deposit in the human body through the food chain and are very harmful agent for humans due to the lack of efficient excretion mechanism in the human body (Oluyemi et al., 2008). It causes lung cancer, proliferative lesions of prostate, bone fractures, dysfunction of liver and kidney, nerve tissue damage and hypertension in human (Rahman et al., 2019) by getting mixed up in the food chain (Liu et al., 2011; Saleem et al., 2015).

The coastal region of Bangladesh is enriched by important aquatic and terrestrial habitats such as tidal flats, mangrove forests and wetlands, which are home to a wide range of ecologically and economically important species (Hossain et al., 2016). The area provides sustainable livelihood to the coastal fishing communities through a lot of goods and services (Rahman et al., 2019; Siddique et al., 2012) of approximately 30 million people inhabited in this region (Abdullah et al., 2013). However, heavy metal pollution mainly through ship breaking activities has become an increasing major concern in coastal environment due to discharge of untreated waste containing heavy metals such as As, Cr, Cu, Mn and Pb during the dismantling of large ships that creates a hostile situation (Islam et al., 2017; Saha et al., 2017). Recognizing the issue, several studies on heavy metal distribution and their level of contamination in surface sediments have recently been conducted (Aktaruzzaman et al., 2014; Hasan et al., 2013; Rahman et al., 2019; Siddiquee et al., 2012). None of these investigations have, however, focused on the core sediment's heavy metals vertical distribution that may reflect the history of metal accumulation over a prolonged period of time from adjacent regions (Nath et al., 2000; Ozaki et al., 2015), changes in the fluxes of pollutants in sediment profiles (Yang et al., 2002), leading to a better understanding of the environmental changes (Liu et al., 2011) and to comprehend the heavy metals accumulation features in diverse layers of the sediment (Li et al., 2009). Therefore, the aim of this study was to determine the qualitative and quantitative vertical distribution of heavy metals in core sediments from the Bangladesh shipbreaking area, as well as to assess contamination caused by heavy metals. The basic objectives were as follows: (1) to determine the heavy metals concentration in sediment cores, (2) to assess the vertical profile of heavy metals in core sediments, and (3) to estimate the possible ecological risk poses by heavy metals in sediment cores.

Materials and method

Study area and sampling

The coastal areas of Sitakunda, which stretch for around 10 km along the Chattagram coast from Bhatiari to Kumira, have been chosen as ship breaking areas, while the eastern part of Sandwip Island and Muradpur has been designated as non-ship breaking areas (control site). Four stations from ship breaking area, namely Salimpur (S1), Bhatiary 1 (S2), Bhatiary 2 (S3) and Madambibirhat (S4) and three stations from outside of the ship breaking area named Muradpur1 (S5), Muradpur 2 (S6), and Sandwip (S7), were selected (Fig. 1). From March to October 2017, a total of 42 sediment samples were collected in triplicate from the intertidal zone during low tide at seven

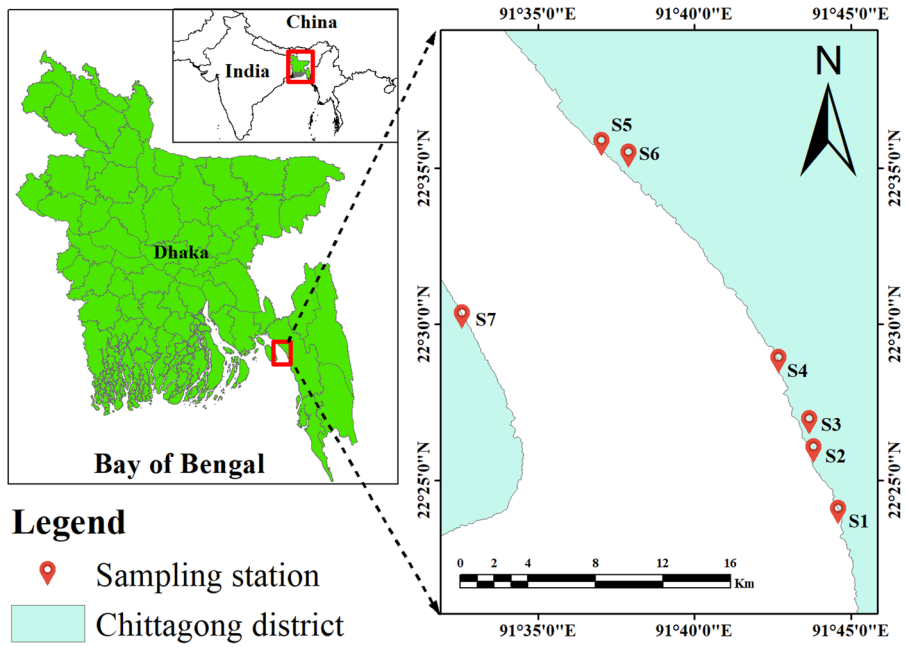

Fig. 1 Study area showing the sampling sites

separate stations. A plastic pipe of 4.5 cm inner diameter and 30 cm long was employed to gather the core sediments. The sediment cores were carefully cut into every 10 cm, 0–10 cm (surface), 10–20 cm (middle), 20–30 cm (bottom) and were subsequently placed in polythene bags and stored in ice box.

Determination of heavy metals

Samples of the sediment were exsiccated at room temperature and transformed into powder in order to sieve with 0.5-mm strainer (Dalman et al., 2006). 1.0 g of each dry sample was taken into separate beaker and mixed with 10 ml of concentrate nitric acid (HNO_3) take advantage of Microwave Digestion System (WX-6000) (Hossain et al., 2019). The samples were put on hotplate into a digestion chamber and digested at 50–60 °C for 2 h and then gradually increased the temperature until it becomes concentrated paste type. Each solution was diluted with distilled water and makes the volume to 25 ml and was filtered and collected into clean and sterilized plastic bottles (tezaron tube). For the heavy metals analysis, observation was optimized through setting up atomic absorption spectrophotometer (AAS) with flame status (Dalman et al., 2006). Then the blanks (deionized water), standards, and prepared (collected sediment) samples were aspirated into the flam of AAS (AA-7000 SHIMADZU) following standard procedure (Ranjan et al., 2008). The calibration curves were obtained for concentration vs absorbance. Statistical data analysis was carried through the least square method using the fitting of a straight line. The results were in line with the reference data (within ± 10%), and the relative standard deviation (RSD) was higher than 5% for all tests. Precision of diagnostic strategy was ensured by referenced sediment material CRM320 ($N = 3$) (Hossain et al., 2019). All preparations were performed utilizing distilled water, and all equipments were drowned in HNO_3 (10%) for < 24 h and washed repeatedly.

Assessment of sediment pollution

The contamination extent of sediment cores through heavy metals was measured using enrichment factor (EF), contamination factor (CF), geo-accumulation index (Igeo) and ecological risks and was assessesed through potential ecological risk (E_r^i), risk index (RI) values.

Enrichment factor (EF)

The enrichment factor reflects the extent of heavy metals enrichment in the environment, and generalized EF is applied to distinguish sources of metals—anthropogenic or natural means (Sayadi et al., 2010)—which was computed through Eq. (1). Manganese was employed as the subject element to measure anthropogenic metal enrichments (Islam et al., 2018) as Mn concentration was maximum (Bhuiyan et al., 2020) in the core sediments. World average shale values of heavy metals were applied as background standard from Turekian and Wedepohl (1961).

$$\mathrm{EF} = \frac{\left(\frac{C_{\mathrm{metal}}}{C_{\mathrm{Mn}}}\right)\mathrm{sample}}{\left(\frac{C_{\mathrm{metal}}}{C_{\mathrm{Mn}}}\right)\mathrm{shale}} \quad (1)$$

where C_{metal} is the metal concentration in relation to Mn levels in sediment cores. An EF value of higher or lower than 1 suggests heavy metal sources in sediment, e.g., either human activities or natural (Chen et al., 2007, 2016). The enrichment factor classified into five contamination category (Birch & Olmos, 2008) as follows: deficiency to moderate enrichment ($2 \leq \mathrm{EF} < 5$), moderately severe enrichment ($5 \leq \mathrm{EF} < 10$), severe enrichment ($10 \leq \mathrm{EF} < 25$), very severe enrichment ($25 \leq \mathrm{EF} < 50$) and extremely high enrichment ($\mathrm{EF} \geq 50$).

Contamination factor (CF)

The contamination factor of sediment cores was determined using Eq. (2). Hakanson, (1980) interpreted CF as follows: low contamination ($\mathrm{CF} < 1$), moderate contamination ($1 \leq \mathrm{CF} < 3$), considerable contamination ($3 \leq \mathrm{CF} < 6$) and very high contamination ($\mathrm{CF} \geq 6$).

$$\mathrm{CF} = \frac{\mathrm{Cn\ sample}}{\mathrm{Bn\ shale}} \quad (2)$$

where Cn sample is the heavy metal contents in sediment; Bn shale is the background shale value of a conferred metal (Turekian & Wedepohl, 1961).

Geo-accumulation index (Igeo)

Geo-accumulation index has extensively been used in sediments and soils heavy metal experiments (Amin et al., 2009) that is applied to quantify the magnitude of pollution through heavy metals which is developed by Müller, (1979) and calculated as Eq. (3):

$$\mathrm{Igeo} = \log 2\,(\mathrm{Cn}/1.5\mathrm{Bn}) \quad (3)$$

where Cn is the measured metal contents in sample and Bn is the reference metal value in the earth's crust (Turekian and Wedapohl, 1961). The geo-accumulation index was categorized into seven classes that states different contamination level (Müller, 1979) as follows: Class 0, practically uncontaminated ($\mathrm{Igeo} < 0$); Class 1, uncontaminated to moderately contaminated ($0 < \mathrm{Igeo} \leq 1$); Class 2, fairly contaminated ($1 < \mathrm{Igeo} \leq 2$); Class 3, fairly to great extent ($2 < \mathrm{Igeo} \leq 3$); Class 4, great extent ($3 < \mathrm{Igeo} \leq 4$); Class 5, great extent to extremely contaminated ($4 < \mathrm{Igeo} \leq 5$); Class 6, extremely contaminated ($\mathrm{Igeo} > 5$).

Potential ecological risk factor (E_r^i) and risk index (RI)

The ecological risk was estimated by risk index through potential ecological risk factor of a definite heavy metal in sediment cores. Hakanson, (1980) developed a methodology to estimate the extensive potential ecological risk of heavy metals which is defined as Eq. (4).

$$E_r^i = T_r^i \times \frac{\mathrm{Ci}}{\mathrm{Co}} \quad (4)$$

where Ci is the metal contents in the ith sediment; Co is the same metal contents in reference sediment; $\mathrm{T}^{\mathrm{i}}{}_{\mathrm{r}}$ is the biological toxicity factor of a particular metal that was pointed out as Cu = Pb = Ni = 5, Cr = 2 and Zn = 1 (Suresh et al., 2011).

The enormity of sediment pollution through heavy metals is appraised by the potential ecological risk index in conformity with the heavy metal toxicity accompanying environmental response. It was calculated as Eq. (5):

$$\mathrm{RI} = \sum E_r^i \quad (5)$$

where RI is the aggregation of all risk factors; E is the exiguous potential ecological risk factor; r is the toxic repercussion factor of a given metal, which explains the toxic and sensitivity requirement. The values for Cr, Mn, Cu, Zn and Pb are 2, 1, 5, 1 and 5, respectively (Hakanson, 1980). The E_r^i and RI consist of five classes: low ecological risk ($E_r^i < 40$ and RI < 150), moderate ecological risk ($40 \leq E_r^i < 80$ and $150 \leq$ RI < 300), considerable ecological risk ($80 \leq E_r^i <$ 160 and $300 \leq$ RI < 600), very high ecological risk ($160 \leq E_r^i < 320$ and $600 \leq$ RI < 1200), extreme ecological risk ($320 \leq E_r^i$ and $1200 \leq$ RI) (Hakanson, 1980).

Analysis of data

The statistical analyses were accomplished for the analysis of data through paleontological statistics (PAST) software (Hammer et al., 2001). Multivariate and univariate statistical analyses like Pearson's correlation matrix (CM), principal component analysis (PCA) and cluster analysis (CA) were carried out to examine momentous relationships among the heavy metals of core sediments (Varol & Şen, 2012). CM, CA and PCA were applied to identify contamination sources (natural and/or anthropogenic).

Results and discussion

Vertical profiles of heavy metal in sediment cores

The concentrations of heavy metals varied significantly ($p < 0.05$) among depths of 0–10 cm, 10–20 cm, 20–30 cm. The overall vertical profiles of heavy metals (Zn, Cu, Pb, Cr, Mn) were as follows: Heavy metal contents were relatively higher in the middle layer (10–20 cm) followed by upper layer (0–10 cm) and bottom layer (20–30 cm) of sediment core except Ni, which was higher in upper layer; Zn, Pb and Mn concentration and variation were relatively higher in the middle layer; Cu and Cr concentration was high in middle layer while high concentration variation was in upper layer (Fig. 2). The similar trends of the vertical profiles of heavy metals (middle > surface > bottom) point out common sources of each heavy metal (Chen et al., 2016). The alteration in vertical concentration of heavy metals in ship breaking area may be due to their different discharge and accumulation characteristics of sediment cores at different depth (Chen et al., 2016). High concentration of heavy metals was observed to be correlated with the sediments of fine-grained (Kumar et al., 2016).

The mean concentration (μg/g) of heavy metals in surface layer (0–10 cm) was for Zn: 76.6 ± 39.4), Cu: 45.9 ± 22.6, Pb: 61.9 ± 54.9, Cr: 30.8 ± 11.6, Ni: 32.3 ± 14.1, Mn: 586 ± 187; in middle layer (10–20 cm) was for Zn:100 ± 77.1, Cu: 51.4 ± 20.5, Pb: 68.3 ± 78.7, Cr: 31.6 ± 9.44, Ni: 32.1 ± 12.5, Mn: 638 ± 254; in bottom layer (20–30 cm) was for Zn: 53.9 ± 8.68, Cu: 42.5 ± 5.73, Pb: 14.2 ± 7.81, Cr: 29.4 ± 7.36, Ni: 30.8 ± 12.4, Mn: 622 ± 234, respectively. The higher heavy metal concentrations reflect the effects of the ship breaking activities that discharged concerned heavy metals include Pb, Zn, Cu, Cr and Mn (Hossain et al., 2016). The high levels of Zn, Pb, and Mn in the sediment cores may be due to persistent discharge of these metals. (Chen et al., 2016). Heavy metal concentrations higher in the middle layer also reported by Wang et al. (2015) may be due to settle down of metals in sediments cores as commercial ship breaking activities have been started in 1969 (Hossain et al., 2016). Higher content of heavy metals in the middle layer denotes historical deposition of these studied heavy metals in the sediment cores (Nawrot et al., 2019).

Spatial distribution of heavy metals in sediment cores

Significant differences ($p < 0.05$) were noticed in concentration of heavy metals among stations (S1–S7). The mean contents of heavy metals (Zn, Cu, Pb, Cr) in the sediment cores from the ship breaking area (S1–S4) were considerably higher than those from the non-ship breaking area (S5–S7) (Fig. 3). Ni and Mn are relatively high in stations S1 to S6, which may be due to release from natural sources accumulated in past by ship breaking and low only in S7, a site far away opposite from ship breaking area. The overall heterogeneous spatial distribution of heavy metals in the sediment cores can be attributed to the presence of point sources (Islam et al., 2017). Higher content of heavy metals in the ship breaking areas compared to the non-ship breaking areas was also reported by others (Hasan et al., 2013; Siddiquee et al., 2012). The

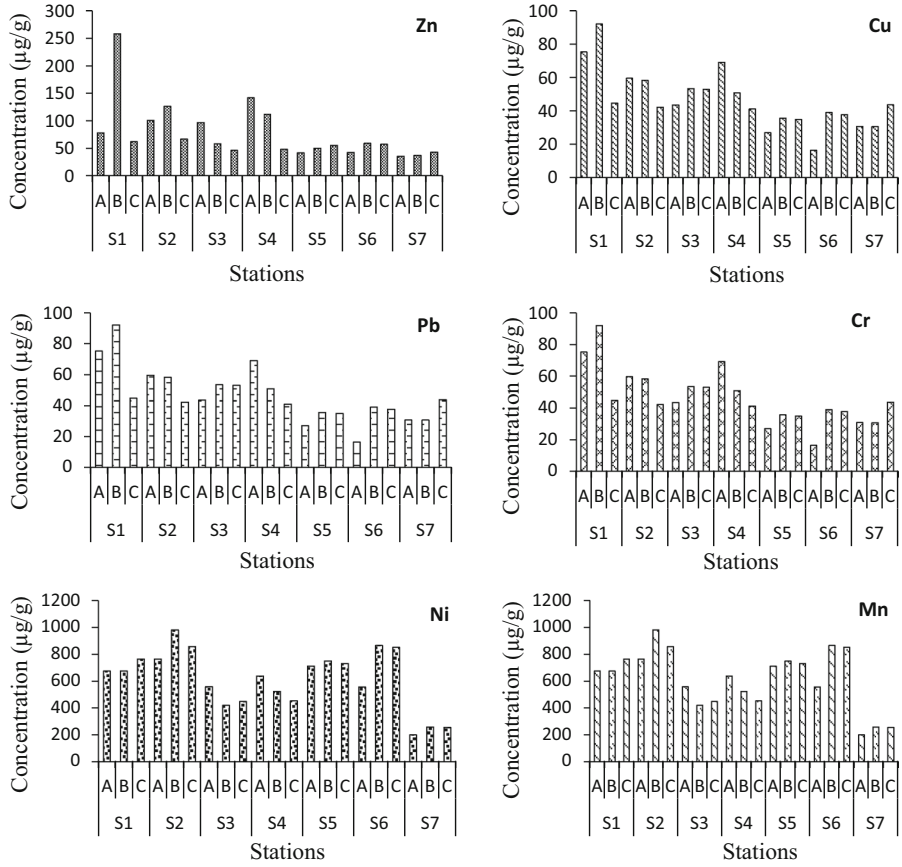

Fig. 2 Vertical distribution of heavy metals in sediment cores (A = 0–10 cm, B = 10–20 cm, C = 20–30 cm)

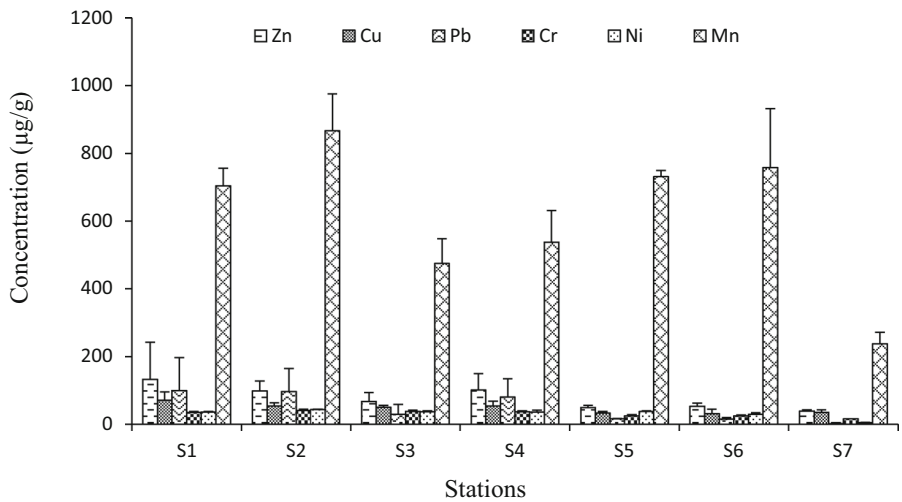

Fig. 3 Mean concentration of heavy metal in sediment cores of Sitakund, Chattagram, Bangladesh

concentrations (µg/g) of heavy metals in sediment cores sampled from seven stations were ranged as follows: Zn, 258–35.5 (mean = 76.9 ± 51.4); Cu, 92.1–16.4 (mean = 46.6 ± 17.4); Pd, 204–4.84 (mean = 48.1 ± 58.3); Cr, 42.7–14.6 (mean = 30.6 ± 9.16); Ni, 43.7–4.02 (mean = 31.7 ± 12.4); Mn, 980–198 (mean = 615 ± 217), respectively.

The heavy metals (Zn, Cu, Pb, Cr, Ni, Mn) concentration measured in current study was in agree with others (Hasan et al., 2013; Rahman et al., 2019) that carried out in the ship breaking areas of Bangladesh (Table 1). The concentration of examined heavy metals was less than the Kaohsiung Harbor, Taiwan (Chen et al., 2016). The maximum concentration of Cu, Zn and Pb was recorded in the present study than the Sangu River estuary (Hossain et al., 2019) and Karnaphuli River estuary of Bangladesh (Wang et al., 2016), Raoyanghe Wetland of China (Wang et al., 2019) and standard value (Turekian & Wedepohl, 1961). The higher metal content is attributable to the release of heavy metals as a result of anthropogenic activities (Islam et al., 2018; Wang et al., 2015) such as ship breaking activities (Hossain et al., 2016). Higher Zn concentrations were caused by the release of toxic wastes from shipbreaking operations (Aktaruzzaman et al., 2014), and a large volume of industrial wastes result in high Cu concentrations (Mohiuddin et al., 2012). The use of Pb as a pairing material between metallic parts and ship painting can account for the high Pb content (Obhođaš et al., 2006). Mn concentration (198–980 ug/g) in sediment cores samples was comparatively higher than the Feni river estuary (17.9–48.7 ug/g) which revealed discharge of Mn from ship breaking activities (Hasan et al., 2013).

Assessment of heavy metal contamination in sediment cores

The sediment cores contamination through heavy metals and the potential biological effects as enrichment factor (EF), contamination factor (CF), geo-accumulation index (Igeo), potential ecological risk factor (E_r^i) and risk index (RI) are broadly applied (Fu et al., 2014; Gao et al., 2016) which are summarized in Table 2.

Enrichment factor (EF)

The enrichment factor is a consistent measurement of geochemical aptitudes for comparing between areas (Bhuiyan et al., 2020; Mohammadi et al., 2018; Sinex & Helz, 1981). The EF values of six investigated trace metals at each station are presented in Table 2. In the ship breaking areas, EF value of Pb was highest ($10 \leq \text{EF} < 25$) at S1 in middle layer which indicates severe enrichment and also higher ($5 \leq \text{EF} < 10$) in surface layer of S1 to S4 and middle layer of S2, S4 that states moderately severe enrichment. Cu belonged

Table 1 Comparison of heavy metal concentration (μg/g) in sediment cores with different other studies

Regions	Zn	Cu	Pb	Cr	Ni	Mn	Reference
Ship breaking area, Chattagram, Bangladesh	35.5–258	16.4–92.1	4.84–204	14.8–42.7	4.02–43.7	198–980	Present study
Ship breaking area, Chattagram, Bangladesh	124–176	15.4–21.9	65.5–116	7.95–19.2	BDL		Rahman et al., (2019)
Ship-breaking area, Chattagram, Bangladesh	58–978	6–1635	17–22	311–1232	8–45	334–2524	Hasan et al., (2013)
Sangu River estuary, Bangladesh	22.8–161	15.4–39.8	12.0–33.4	9.52–27.2	15.6–79.7		Hossain et al., (2019)
Feni River estuary, Bangladesh			0.36–17.0	13.9–41.7	8.56–45.7	17.9–48.7	Islam et al., (2018)
Karnaphuli River estuary, Bangladesh	59.7–74.3	20.3–33.1	23.7–25.1	77.7–99.1	24.1–41.3		Wang et al., (2016)
Raoyanghe Wetland, China	5.84–93.8	2.00–42.9	9.56–30.3	10.0–75.8	2.00–39.3		Wang et al., (2019)
Kaohsiung Harbor, Taiwan	42–2990	12–2840	14–219	12–1303			Chen et al., (2016)
Hongfeng Reservoirs, Southeast China		14.4–93.6	1.20–89.2	34.1–141		130–3870	Wang et al., (2015)
Tirumalairajn River, India	23.4–56.3	13.7–28.2	1.73–6.74	0.96–4.01	0.52–2.01		
Standard value	95	45	20	90	68	850	Turekian & Wedepohl, (1961)

Table 2 Summary of heavy metal pollution status in sediment cores of Sitakund, Chattagram, Bangladesh

Stations	Depth (cm)	Index	Zn	Cu	Pb	Cr	Ni	Mn
Ship breaking area (S1-S4)	Surface layer (0–10)	EF	1.43 ± 0.44	1.78 ± 0.32	6.45 ± 1.87	0.58 ± 0.10	0.86 ± 0.07	–
		CF	1.08 ± 0.25	1.37 ± 0.30	5.06 ± 1.72	0.85 ± 0.84	0.59 ± 0.04	0.78 ± 0.10
		Igeo	− 0.49 ± 0.36	− 0.16 ± 0.35	1.69 ± 0.52	− 1.77 ± 0.13	− 1.36 ± 0.11	− 0.96 ± 0.19
		E_r^i	1.08 ± 0.25	5.61 ± 1.90	25.3 ± 8.61	3.29 ± 4.84	2.94 ± 0.20	0.78 ± 0.10
		RI	26.0 ± 37.5 (Range: 3.10–101)					
	Middle layer (10–20)	EF	1.93 ± 1.05	1.98 ± 0.68	6.85 ± 4.60	0.63 ± 0.22	1.00 ± 0.34	–
		CF	1.46 ± 0.90	1.42 ± 0.43	5.57 ± 4.04	0.85 ± 0.86	0.55 ± 0.06	0.76 ± 0.29
		Igeo	− 0.24 ± 0.88	− 0.13 ± 0.39	1.39 ± 1.64	− 1.81 ± 0.11	− 1.46 ± 0.16	− 1.05 ± 0.53
		E_r^i	1.46 ± 0.90	7.08 ± 2.14	27.9 ± 20.2	1.69 ± 1.73	2.74 ± 0.31	0.76 ± 0.29
		RI	27.7 ± 41.9 (Range: 3.05–111)					
	Bottom layer (20–30)	EF	0.66 ± 0.40	1.48 ± 0.58	1.18 ± 0.69	0.55 ± 0.17	0.88 ± 0.05	–
		CF	0.57 ± 0.14	1.01 ± 0.12	0.79 ± 0.32	0.74 ± 0.73	0.53 ± 0.08	0.74 ± 0.25
		Igeo	− 1.38 ± 0.26	− 0.58 ± 0.16	− 1.02 ± 0.60	− 1.97 ± 0.06	− 1.50 ± 0.22	− 1.08 ± 0.49
		E_r^i	0.57 ± 0.14	5.03 ± 0.61	3.96 ± 1.61	1.76 ± 1.37	2.66 ± 0.40	0.74 ± 0.25
		RI	9.80 ± 7.13 (Range: 2.26–20.1)					
Non-ship breaking area (S5-S7)	Surface layer (0–10)	EF	0.93 ± 0.58	1.37 ± 1.33	0.51 ± 0.42	0.47 ± 0.21	0.69 ± 0.29	–
		CF	0.41 ± 0.04	0.55 ± 0.17	0.46 ± 0.23	0.21 ± 0.04	0.33 ± 0.26	0.58 ± 0.31
		Igeo	− 1.84 ± 0.14	− 1.50 ± 0.48	− 1.82 ± 0.75	− 2.86 ± 0.31	− 2.73 ± 1.72	− 1.57 ± 0.98
		E_r^i	0.41 ± 0.04	2.73 ± 0.83	2.28 ± 1.15	0.42 ± 0.09	1.63 ± 1.30	0.58 ± 0.31
		RI	4.03 ± 3.06 (Range: 1.24–6.85)					
	Middle layer (10–20)	EF	0.84 ± 0.40	1.32 ± 0.77	0.57 ± 0.49	0.40 ± 0.17	0.63 ± 0.31	–
		CF	0.51 ± 0.02	0.78 ± 0.10	0.80 ± 0.03	0.25 ± 0.06	0.37 ± 0.26	0.73 ± 0.38
		Igeo	− 1.57 ± 0.34	− 0.95 ± 0.18	− 0.91 ± 0.06	− 2.63 ± 0.39	− 2.48 ± 1.64	− 1.21 ± 0.95
		E_r^i	0.51 ± 0.12	3.90 ± 0.48	2.67 ± 2.31	0.50 ± 0.12	1.83 ± 1.30	0.73 ± 0.38
		RI	5.07 ± 4.15 (Range: 1.5–11.7)					
	Bottom layer (20–30)	EF	0.92 ± 0.05	1.64 ± 1.35	0.60 ± 0.52	0.43 ± 0.15	0.63 ± 0.21	–
		CF	0.54 ± 0.08	0.86 ± 0.10	0.89 ± 0.05	0.25 ± 0.07	0.34 ± 0.25	0.72 ± 0.37
		Igeo	− 1.48 ± 0.23	− 0.80 ± 0.16	− 0.73 ± 0.13	− 2.61 ± 0.46	− 2.60 ± 1.68	− 1.23 ± 0.95
		E_r^i	0.54 ± 0.08	4.32 ± 0.49	2.95 ± 2.56	0.49 ± 0.18	1.72 ± 1.21	0.72 ± 0.37
		RI	5.37 ± 4.67 (Range: 1.46–12.95)					

to moderate enrichment ($2 \leq EF < 5$) in surface and middle layer of S1, middle and bottom layer of S3 and all layers of S4. Zn belonged to moderate enrichment ($2 \leq EF < 5$) in middle layer of S1, surface and middle layer of S4. On the contrary, the EF value of all studied metals in all layers of sediment cores indicated no enrichment in non-ship breaking area except for Cu, which belonged to moderate enrichment ($2 \leq EF < 5$) in all layers of S7 located in opposite side of ship breaking areas. Ghosh et al. (2016) reported a higher enrichment factor (EF) value of Cu and Zn. The enrichment factor value of Cu, Pb and Zn ($EF > 1$) in the depth of 0–10 cm and 10–20 at four stations (S1–S4) indicated that these heavy metals were primarily derived from ship breaking activities (Chen et al., 2007, 2013).

Contamination Factor (CF)

The measured contamination factor of heavy six heavy metals is presented in Table 2. The contamination factors of heavy metals belonged to moderate contamination ($1 \leq CF < 3$) for Zn in surface and middle layer of S2, S4, in middle layer of S1and surface layer of S3; for Cu in all layers of S3, surface and middle layer of S1, S2, S4; for Cr in all layers of S2 and for Pb in bottom layer of S4, respectively. The Pb belonged to considerable contamination ($3 \leq CF < 6$) in surface layer of S1 and middle layer of S4 as well as very high contamination ($6 \leq CF$) in middle layer of S1, surface layer of S4, surface and middle layer of S2, respectively. On the contrary, the CF values of all investigated metals stated low contamination ($CF < 1$) in non-ship breaking areas (S5–S7).

Geo-accumulation index (Igeo)

The computed geo-accumulation index (Igeo) of heavy metals in sediment cores is shown in Table 2. In the 0–10 cm (surface layer) of sediment cores, Cu belonged to uncontaminated to moderately contaminated ($0 < Igeo \leq 1$) at S1, S4; Pb belonged to moderately contaminated ($1 < Igeo \leq 2$) at S1, S3, as well as moderately to strongly contaminated ($2 < Igeo \leq 3$) at S2, S4, respectively. In the middle layer of sediment cores (10–20 cm), Zn and Cu belonged to uncontaminated to moderately contaminated ($0 < Igeo \leq 1$) at S1; Pb belonged to moderately contaminated ($1 < Igeo \leq 2$) at S4 and moderately to strongly contaminated ($2 < Igeo \leq 3$) at S1, S2. The rest heavy metals (Cr, Ni, Mn) in sediment cores were belonged to class 0, particularly unpolluted ($Igeo < 0$). On the contrary, the Igeo values in all layers of non-ship breaking areas (S5–S7) were belonged to class 0, particularly unpolluted ($Igeo < 0$). Aktaruzzaman et al. (2014) reported Pb as class 2, moderately polluted; Mn as class 0, unpolluted; Cr, Cu, and Zn as class 1, unpolluted to moderately pollute for all stations.

Potential ecological risk factor (E_r^i) and risk index (RI)

The measured potential ecological risk factor (E_r^i) and risk index to assume the ecological risk asserted by the studied heavy metals are summarized in Table 2. For ship breaking areas (S1–S4), in the all layers of sediments (0–30 cm) the E_r^i values of examined heavy metals (Cr, Cu, Ni, Mn, Zn) were less than 40 for all stations which indicated low ecological risk ($E_r^i < 40$) by heavy metals. Pb posed considerable risk ($40 \leq < 80$) in the middle layer (10–20 cm) at S1. Highest ecological risk by Pb was also reported by Rahman et al., (2019) which is attributed by usage of Pb as a junctioning material of two metallic parts and painting of ships (Obhođaš et al., 2006; Rahman et al., 2019). For non-ship breaking areas (S5–S7), the E_r^i values of all investigated heavy metals (Cr, Cu, Ni, Mn, Pb, Zn) in all layers were less than 40 for all stations indicated low ecological risk ($E_r^i < 40$) by heavy metals. The potential ecological risk index values revealed low ecological risk ($RI < 150$) in both ship breaking area (S1–S4) and non-ship breaking area (S5–S7) in all layers (0–30 cm) of sediment cores for all studied heavy metals (Cr, Cu, Ni, Mn, Pb, Zn). Low ecological risk condition of sediment in the ship breaking area of Bangladesh also reported by others (Aktaruzzaman et al., 2014; Rahman et al., 2019) and west coast of Peninsular Malaysia, an international shipping waterways (Looi et al., 2019). Particular attention should be drawn on the heavy metal contamination in the ship breaking area of Bangladesh even though the sampling stations posed low ecological risk as uncontrolled release of heavy metals within aquatic environment is detrimental to aquatic livings.

Pearson's correlation coefficient

Pearson's correlation matrix was employed to identify the source of heavy metals (Suresh et al., 2011), and correlation among the heavy metals indicates a single controlling factor (Kükrer et al., 2014). Observed correlations between the investigated heavy metals in sediment cores of study areas are summarized in Table 3. Pearson's correlation revealed significant relationship between heavy metals of sediment cores in five cases were as follows: surface layer (Cr–Zn, Mn–Cr); surface and middle layer (Cu–Zn, Pb–Zn, Pb–Cu, Cr–Cu); surface and bottom layer (Ni–Zn, Ni–Pb); bottom layer (Mn–Zn, Mn–Pb) and all layers (Cr–Pb, Ni–Cr, Mn–Ni). Strong positive correlations were observed between Cu–Zn (0.77), Pb–Zn (0.93), Pb–Cu (0.87), Cr–Zn (0.88), Cr–Cu (0.75), Cr–Pb (0.88), Ni–Cr (0.78), Mn–Ni (0.91) in surface layer; Cu–Zn (0.96), Pb–Zn (0.96), Pb–Cu (0.91), Ni–Cr (0.80) in middle layer and Ni–Zn (0.75), Ni–Cr (0.89), Mn–Zn (0.93), Mn–Ni (0.78) in bottom layer of sediment cores. The strong correlations between pairs of heavy metals denote similar contamination level and common anthropogenic sources in the sediment cores (Li et al., 2009; Malvandi, 2017).

Table 3 Correlation coefficient of the heavy metal in sediment cores of ship breaking area

	Zn	Cu	Pb	Cr	Ni	Mn
Surface layer (0–10 cm)						
Zn	1.00					
Cu	0.77**	1.00				
Pb	0.93**	0.87**	1.00			
Cr	0.88**	0.75**	0.88**	1.00		
Ni	0.68*	0.53	0.68*	0.78**	1.00	
Mn	0.44	0.42	0.56	0.60*	0.91**	1.00
Middle layer (10–20 cm)						
Zn	1.00					
Cu	0.96**	1.00				
Pb	0.96**	0.91**	1.00			
Cr	0.58	0.71*	0.69*	1.00		
Ni	0.35	0.43	0.44	0.80**	1.00	
Mn	0.27	0.22	0.40	0.42	0.73*	1.00
Bottom layer (20–30 cm)						
Zn	1.00					
Cu	− 0.33	1.00				
Pb	0.49	− 0.49	1.00			
Cr	0.50	0.26	0.63*	1.00		
Ni	0.75**	− 0.03	0.69*	0.89**	1.00	
Mn	0.93**	− 0.46	0.60*	0.44	0.78**	1.00

*Significant at $p < 0.05$, **Significant at $p < 0.01$

Cluster analysis

Cluster analysis is applied to determine the relationship and possible sources (natural and anthropogenic) of heavy metals (Li et al., 2009). For this, a typical dendogram is created based on Ward's method with Euclidean distance at (Dlink/Dmax) < 300 which includes three clusters (Fig. 4a). Significant correlations were observed between Zn-Pb and Cr-Ni. The occurrence of Cr and Ni is connected with Cu. The first cluster group (cluster 1) contained Mn only, which may be due to its highest concentration in the sediment cores in comparison with other heavy metals and also revealed its different origin (Nawrot et al., 2019). A significant relationship of heavy metals in clusters 2 and cluster 3 suggested that they may have same anthropogenic source, mainly discharge of these metals from ship breaking industries.

Cluster analysis is also applied to express the similarity and dissimilarity of sampling sites (Simeonov et al., 2000). Sites with similarities are included one group of cluster while sites have dissimilarities are displayed by another group of cluster depending on concentration (Chung et al., 2011). The sites in a particular cluster stated similar properties as well as anthropogenic and natural sources; thus, each of the clusters varied with the significance level (Varol & Şen, 2012). For measuring similarity and dissimilarity, a cluster analysis of hierarchical agglomerative is generated from the standardized data set hinge upon Ward's method with Euclidean distance at (Dlink/Dmax) < 250. Five major clusters were formed by combination of both stations and layers of sediment cores (Fig. 4b). The cluster 1 contained 6 stations, cluster 2 contained 3 stations and others (cluster 3, cluster 4, cluster 5) each contained 4 stations, respectively.

Principal component analysis (PCA)

Principal component analysis can effectively determine the source, come from soil parent materials and/or human activities, of heavy metals (Wang et al.,

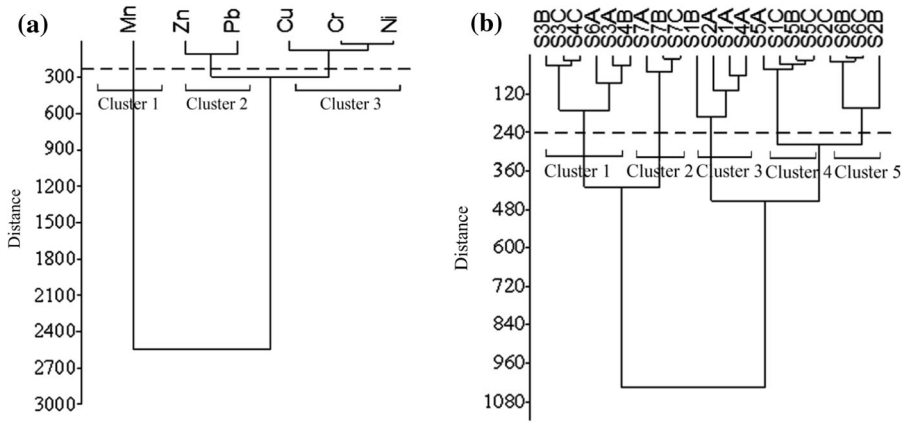

Fig. 4 Cluster analysis **a** metals and **b** stations of sediment cores

2019). Heavy metals with maximum loads on the identical principal component (PC) may homologous, and loading value in PC1 indicates anthropogenic origin while PC2 indicates natural origin of heavy metals (Mohiuddin et al., 2012). PCA results including the eigenvalue, variance and cumulative variance for every factor are abridged in Table 4. In total, two significant PCs were extracted with an eigenvalue of greater than 1 explaining 87.30% of total data variation. PC1 explained 65.20% of the total variance with the high loading of Zn, Cu, Pb and Cr (R = 0.43, 0.42, 0.45, 0.44) which exhibited an eigenvalue of 3.92 (Fig. 5). PC2 explained 22.10% of total variance with an eigenvalue of 1.32 with the high loading of Ni and Mn (R = 0.52, 0.59). The higher load values of Zn, Cu, Pb and Cr indicated their anthropogenic origin and higher load values of Ni and Mn indicated their natural origin in sediment cores.

Table 4 Principal component analysis of collected sediment cores of ship breaking area

	PC 1	PC 2
Zn	0.43*	− 0.36
Cu	0.42*	− 0.37
Pb	0.45*	− 0.29
Cr	0.44*	0.15
Ni	0.39	0.52*
Mn	0.30	0.59*
Eigenvalue	3.91	1.32
% variance	65.2	22.1
% cumulative	65.2	87.3

*Significant at 5% level

Conclusions

This is the first study on vertical distribution and contamination assessment in sediment cores of ship breaking area, Chattagram, Bangladesh. The results evidenced the magnitude of sediment cores pollution through eight investigated heavy metals pursued the lessening order of Mn > Zn > Pb > Cu > Ni > Cr. The concentration of Zn, Cu, Pb exceeded the standard values, and Cr and Ni were below the standard values. The study revealed maximum concentration of examined heavy metals in the middle layer of sediment cores than the surface and bottom layer. Different contamination indices, i.e., enrichment factor (EF), stated moderate to severe enrichment, contamination factor (CF) disclosed moderate to high contamination and geo-accumulation index (Igeo) indicated moderate to strong contamination of ship breaking areas through Zn, Cu, Pb derived from human activities. On the other hand, potential ecological risk factor (E_r^i) and risk index (RI) expressed low ecological risk ($E_r^i < 40$ and RI < 150) by studied heavy metals excepting Pb. According to CM, CA and PCA, heavy metals (Cr, Cu, Pb, Zn) have common anthropogenic sources and major contributors for heavy metal contamination.

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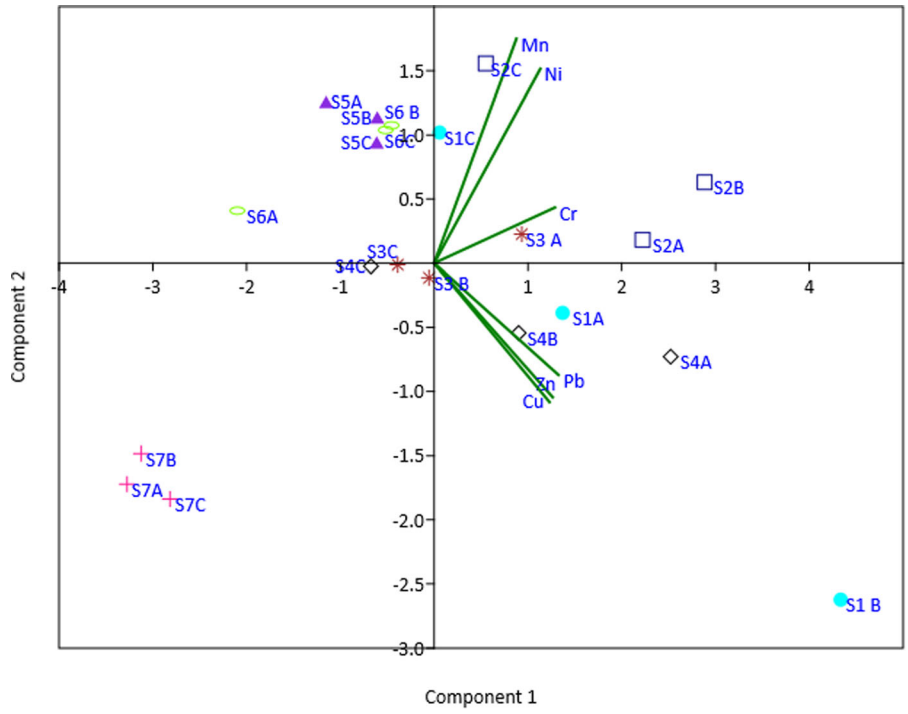

Fig. 5 Principal component analysis of heavy metals along stations with three layers of sediment cores

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Code availability Not applicable for this study.

Declarations

Conflict of interest The authors have no competing of interest to declare with any others.

Consent to participate Not Applicable.

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