

Geochemical partitioning of Cu and Zn in Pelabuhanratu Bay sediment

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Abstract. Activities such as fishing ports and power plants on the coast of Pelabuhanratu Bay have recently developed and hence, their input of metal-containing waste may influence the seawater quality of the bay as the fishing grounds. This study aimed to determine the potential sources (i.e., anthropogenic and natural) and pollution status in sediments. Sediment samples were collected once at 10 stations in the bay using a Van Veen grab. The geochemical partitioning of non-residual and residual phases of metals was used to assess the anthropogenic and natural sources, respectively. The status of metal contamination was evaluated by determining the geo-accumulation index (I_{geo}), contamination factor (CF), and pollution load index (PLI). Generally, Cu was dominant in residual fractions ranging 62.79-81.24%, while Zn ranged 39.56-66.02%. This suggests that Cu and Zn in Pelabuhanratu Bay are naturally sourced. Furthermore, the average geo-accumulation index of Cu was categorized as unpolluted (-0.86), and Zn was lightly polluted (0.87). The CF of Cu indicates the uncontaminated category (0.85), whereas Zn indicates a moderate contamination category ($CF = 1.54$). The pollution level (PLI) in Pelabuhanratu Bay is generally lightly polluted (PLI 1,135).

1 Introduction

Studies related to metal contamination are important because of their potential toxicity in marine organisms and humans [1,2,3]. Metals are naturally derived from the weathering of rocks and subsequently enter marine systems through riverine transport [4, 5]. In general, trace metals can be derived from metal-containing waste released from industrial activities [6, 7], household waste, urbanization, and the application of fertilization in agriculture [8, 9]. Heavy metal concentrations in the water column gradually decreased as they moved away from offshore.

Most metals accumulate in the sediment in which the dissolved metals are precipitated through chemical reactions such as coagulation, aggregation, and scavenging with various materials in the water column [10, 11, 12]. An increase in the metal concentration in the

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sediment will continue to occur as improper wastewater containing heavy metals also occurs continuously.

Heavy metals are undegraded pollutants that can be transferred from stable to unstable (immobile) fractions in sediment bonds. The latter fraction can redissolve and enter the food chain system in seawater. Various studies have shown that heavy metals are weakly to strongly bound in sediment particles and are generally divided into residual/detrital and non-residual/non-detrital types [13]. The composition of heavy metals in various sediment component associations (residual/non-residual) can vary from one area to another [13].

Pelabuhanratu Bay on the southern coast of West Java, Indonesia, is a fishing ground, and its coastal area has recently been developed by a steam power plant using a coal source. It is clear that atmospheric fly ash is emitted from burning coal. As part of the aerosol component, ash is most likely deposited on the sea surface and is likely to dissolve in the water column. Information on the trace elements in this area is limited. The Pelabuhanratu district city of Sukabumi will continue to develop in the future; hence, this study provides baseline data. The level of metal pollution in the sediments was evaluated using three approaches: the geoaccumulation index (I_{geo}), contamination factor (CF) and pollution load index (PLI) [14–17]. These three indicators can be used to discriminate natural and anthropogenic metal sources [12]. In general, the principles of the three approaches are similar, and it looks at the level of metal pollution in the sediment by comparing the low variability in the environment.

2 Materials and method

2.1 Collection of sediment and sampling location

Surface sediment samples (~10–15 cm) from Pelabuhanratu Bay were collected once at 10 observation areas representing rivers, estuaries, and seas (**Fig. 1**) using a Van Veen grab. The subsampling of sediment was then carefully collected to avoid contact with metal-made grab sides, transferred into a polyethylene container, and placed in a cool box during transportation to the laboratory for analysis. The sampling tools and sample storage selections were based on ISO 5667-12 [18]. All the sediment samples were stored at 4°C until analysis. The sample analysis in the laboratory included sediment grain size, organic content, and heavy metals.

2.2 Sediment fractionation and organic compounds

The grain size and organic matter content of the sediment were used to determine possible correlations with metal concentrations. The grain size analysis of the sediment was fractionated using sieving and pipetting methods into 10 fractions using the Wentworth scale [19]. The first five fractions of the sieving method produced very coarse, coarse, medium, fine, and very fine sand. The remainder of this sample was analyzed using the pipetting method to provide five other fractions: coarse silt, medium silt, fine silt, coarse clay, and fine clay. The suspended particles were shaken 10 times and allowed to stand for ± 20 s. The cup was then placed in an oven and dried at 100°C. The cup was cooled in a desiccator and weighed.

The organic material content is based on the percentage of combustion loss (% LOI) and is measured using the organic material lost during combustion [19, 20]. Sediment samples were heated at 105°C for 1 h and raised to 550°C, after which they were left for 5–6 h. The samples were allowed to cool in a desiccator between two stages of increasing temperature. The organic matter content was calculated based on the difference between the initial and final weights of the sediment multiplied by 100% [21].

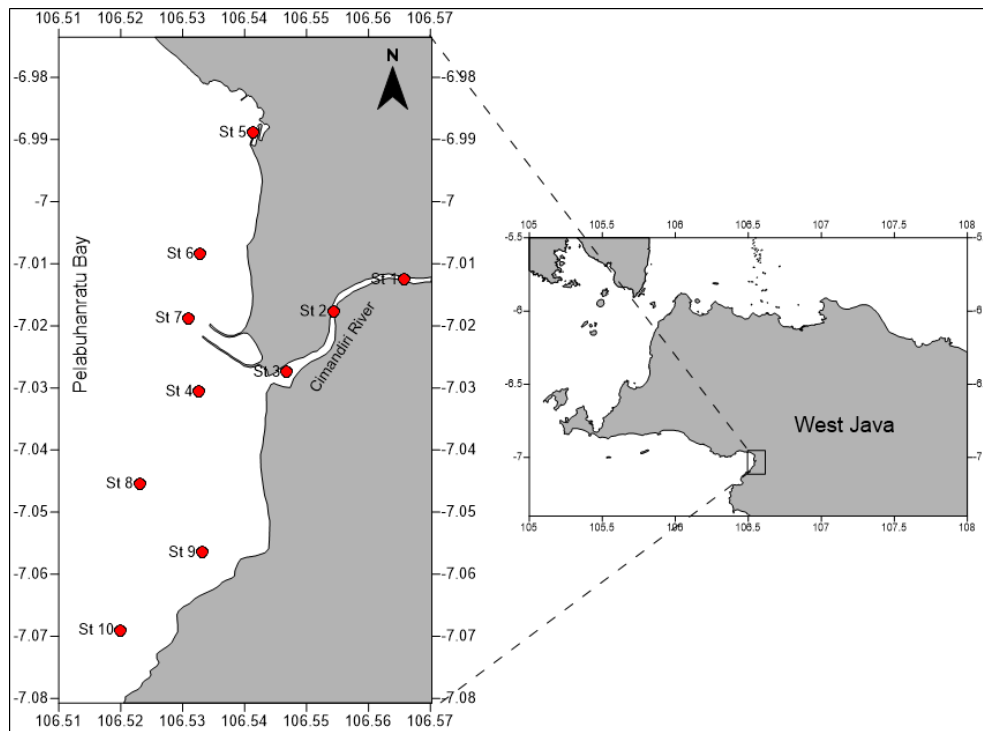


Fig. 1. Sampling stations for collecting sediment samples in the Pelabuhanratu Bay.

2.3 Heavy metals sequential extraction

Quantification of the geochemical partitioning of heavy metals in sediments is necessary to understand the nature of the metals in sediments. The nature and bonds of metals in sediment were analyzed using a geochemical partitioning method of the sequential extraction process (SEP), proposed by the European Community Bureau of Reference (BCR), or the BCR-SEP procedures used in many studies [22-26]. The geochemical partition method has been applied in many studies to provide information such as i) characteristics of pollution sources, ii) evaluation of bioavailability and metal mobilization, and iii) identification of metal binding to assess metal accumulation, pollution, and transport mechanisms [27, 28, 29].

The principle of sequential extraction schemes involves several extractions, which are sequentially applied to a solid sample aliquot. Extractants were applied in order of increasing reactivity so that the successive fractions obtained corresponded to trace elements associated with less mobile fractions in the sediment (**Table 1**). The sequential stages of metal use refer to the stages described in [30]. The residual fraction consists of metals associated with very strong bonds, and these metals cannot be separated in the presence of a series of solvents in the previous three stages. The metal concentrations were determined by atomic absorption spectrophotometry (AAS).

Table 1. Stages of sequential extraction procedure for heavy metals in sediment.

Fraction	Solution for Extraction	Processing
F1, Acid Soluble	40 mL CH ₃ COOH 0.11 mol	1 g of sample, was shook with auto-shaker for 16 h at 320 rpm and the extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min

F2, Reducible	40 mL HONH ₂ .HCL 0.5 mol (pH 1.5)	The F1 residue, was shook for 16 h and was separated by centrifugation at 3000 rpm for 20 min
F3, Oxidizable	10 mL H ₂ O 8.8 M (pH 2-3, twice), 50 ml NH ₄ OAc 1.0 M (pH 2)	The F2 residue, was heated to 85 ± 2 °C for 1 h until the volume was reduced to 2–3 mL (twice). Agitation for 16 h at 320 rpm and the extract was separated by centrifugation as above
F4, Residue	10 ml aqua regia, 0.5 M HNO ₃ to adjusted 50 mL of final volume	The F3 residue, aqua regia was added drop by drop to reduce foaming. Agitation for 16 h and heated for 2 h. The digests were filtered through the fine filter paper and were adjusted until 50 mL of final volume

2.4 Quality control and quality assurance

All analyses used established protocols in the laboratory, including sample collection in the field. Acid-precleaned polyethylene bottles were used to collect sediment samples [31]. Caution must be exercised during scooping samples from the grab into the bottles to ensure that no portion of the scooped sample is in contact with the metal-sampler walls and to avoid contaminants from the environment of the boat. All bottles containing the sediment samples were placed in a sealed transparent plastic bag and stored in an ice box during transportation to the laboratory. To control and check for metal impurities and background contamination, no metal or glassware was used during preparation of the samples, and all reagents, including distilled water, were tested. The coefficient variation of the AAS reading ranged from < 10%, and the recovery rates were 96-98%.

2.5 Assessment of metal contamination

The geoaccumulation index (I_{geo}) was used to evaluate metal accumulation in the sediment [14-17]. The geo-accumulation index developed by [32] for assessing the accumulation of pollution in sediments is shown as follow (Eq.1).

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5 B_n} \right] \dots\dots\dots (1)$$

where C_n is the measured concentration of metal n and B_n is the geochemical background metal n in the average crust (55 ppm and 70 ppm of Cu and Zn) [33]. A factor of 1.5 is used to include possible variation of background values due to lithogenic effects.

The contamination factor (CF) describes the pollution level of sediment with a given heavy metal and is calculated as the ratio between the concentration of each measured heavy metal (C_n) and its background value (C_{bn}) (Eq.2) [14-17].

$$CF = \frac{C_n}{C_{bn}} \dots\dots\dots (2)$$

The level of pollution in the sediment was also determined using the pollution load index (PLI) [14-17] (Eq. 3), where PLI is the pollution load index, $CF_{Me1,2,3,\dots,n}$ represents the contamination factor of each metal $Me1, 2, 3, \dots, n$ and n is the number of metals.

$$PLI = [CF_{Me1} \times CF_{Me2} \times CF_{Me3} \dots CF_{Men}]^{1/n} \dots\dots\dots (3)$$

Tabel 2. Catagories of pollution level in sediment.

Geo-accumulation Index (I_{geo})*	Contamination Factor (CF)**	Pollution Load Index (PLI)* (PLI)
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0, unpolluted	<1, low contamination	< 1, Unpolluted
>0 -1, unpolluted to moderately polluted	1- <3, Moderate contamination	> 1, Polluted
>1 -2, Moderately polluted	3- <6, Considerable contamination	
>2 -3, Moderately to strongly polluted	>6, Very High contamination	
>3 -4, Strongly polluted tinggi		
>4 -5, Strongly to extremely polluted		
>5, Extremely polluted		

*[32, 34]; **[35]; ***[36]

3 Results and discussion

3.1 General characterization of the sediments

The grain size of the sediment from the stations varied from very coarse to fine clays. However, it might be said that very fine sand was predominant in the foreshore stations and medium to very fine sand was predominant in the estuarine stations (Fig. 2). This was probably related to the hydrodynamic processes at these two sites. Stronger currents can deposit coarser materials (gravel and sand) [37, 38]. It is necessary to note that Stations 1-3 are areas of traditional sand mining transported from upstream. This area is considerably turbid, and the suspended mud continuously flows towards the bay. Because the bay is influenced by the breaker of waves, some material is pushed back to the river mouth, leading to a small shoal formation. This bottom morphology, together with the strong energy of the bay, causes unavailable mud-observed estuaries and small portions of silt and clay in the foreshore areas (i.e. Stations 5-10).

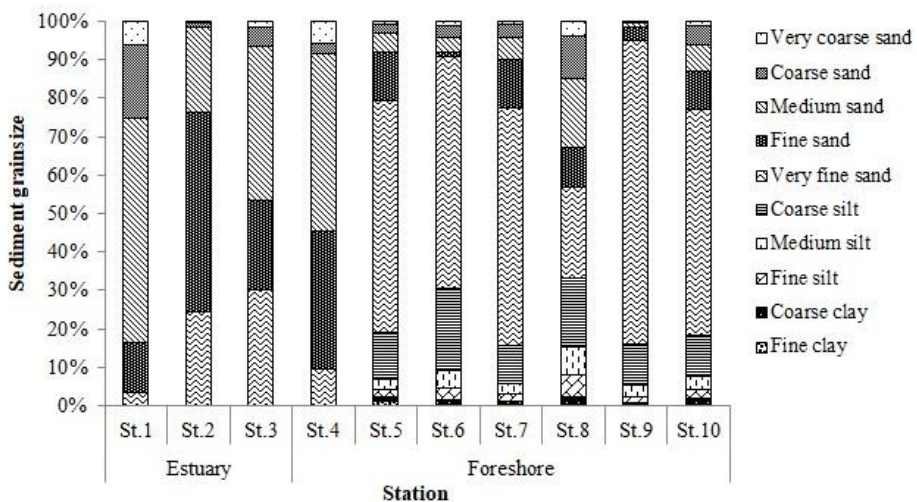


Fig. 2. Grain Size (%) of the Sediment collected from sampling stations of Pelabuhanratu Bay.

The grain size composition is important, leading to potential interactions with the binding of organic materials and heavy metals [39]. Silt and clay easily absorb organic materials and heavy metals compared with the sand fraction [40, 41]. The organic matter content in

Pelabuhanratu Bay varied between 1.43%-5.47% (**Fig. 3**). The estuary stations (Station 1-4) contained less organic material (1.43%-2.22%) than those in the foreshore (Station 5-10) ranging from 3.46% to 5.47%. This appears to be related to grain size, that is, there is no mud or clay in the estuary but on the shore (**Fig. 2**).

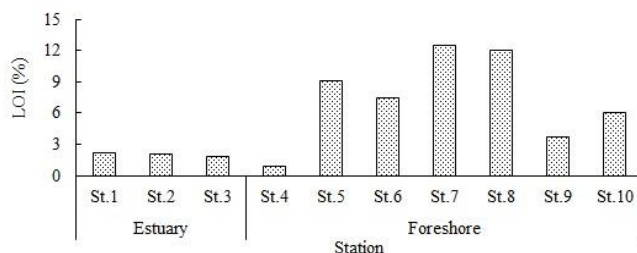


Fig. 3. Organic content (%) in the sediment collected from sampling stations of Pelabuhanratu Bay.

3.2 Concentration total of metals

The total metal concentrations of Cu and Zn varied from 20 to 60 mg/kg and 70.92 to 154.10 mg/kg, respectively (**Fig. 4**). It is clear that the concentrations of Zn are higher than those of Cu, and this difference in the concentrations of these metals is common in nature. For instance, in the pristine river sediment, concentrations of Cu and Zn varies from 7.1-27.1 mg/kg and 36-146 mg/kg, respectively [42]. Furthermore, concentration of these metals in upper continental crust is 14.3 mg Cu/kg and 52 mg Zn/kg [24]. However, the concentrations of these metals were mostly lower than those of standard quality according to the Australian and New Zealand Environment and Conservation Council and Hong Kong Interim Sediment Quality Guidelines, that is, 65 mg Cu/kg and 200 mg Zn/kg [43, 44].

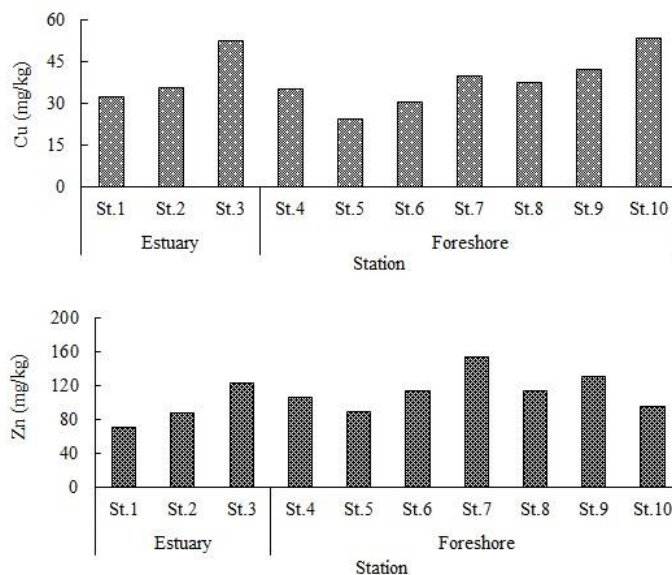


Fig. 4. Concentration total (mg/kg) of Cu and Zn in the sediment collected from sampling stations of Pelabuhanratu Bay.

3.3 Geochemical partitioning

Information on total heavy metal concentrations in sediments is less able to describe their mobility and toxicity. Geochemical partitioning of heavy metals in sediment is needed to analyze the level of metal association in the environment, so that the extent to which metals can affect the marine environment can be determined. Heavy metals in the residual/resistant phase are metals contained in the crystal structure of minerals or heavy metals originating from natural sources, such as the decomposition of silicate crystals in rocks. The metals in this fraction are strongly bound to sedimentary minerals and are generally not available for absorption by biota (nonbioavailable) [45]. In contrast, the acid-soluble, reduced, and oxidized fractions, which are metals that can be absorbed and accumulated by organisms, are known as non-residue/resistant. The metals in this fraction generally originated from anthropogenic activities.

In general, metals in the Pelabuhanratu Bay sediments are dominated by residual fractions ranging 62.79-81.24% for Cu metal and 39.56-66.01% for Zn (**Fig. 5**). The high concentration in the residue fraction indicates that the heavy metals Cu and Zn in the waters of Pelabuhanratu Bay were predominantly natural sources. In addition, the anthropogenic source can be indicated by the other fractions (i.e., acid soluble-, reducible-, oxidizable-associated metals). These non-residual/non-resistant fractions are environmentally introduced metals that react with various materials during transportation in rivers before reaching coastal deposition. The reaction can be subject to environmental changes, such as pH, salinity, and dissolved oxygen. The relatively different compositions (i.e., non-residual/residual ratio) could also be influenced by the level of the sources. In other words, the higher non-residual fractions of Zn compared to Cu in the bay indicated an increase in anthropogenic Zn sources (**Fig. 5**).

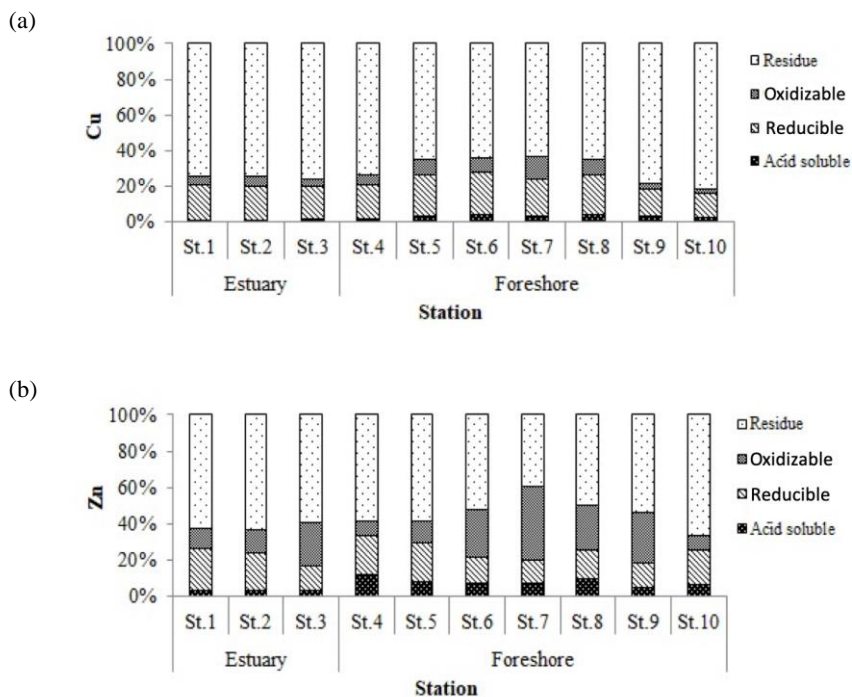


Fig. 5. Geochemical partition (%) of (a) Cu and (b) Zn in the sediment collected from sampling stations of Pelabuhanratu Bay.

3.4 Assessment of metal contamination

I_{geo} provides information regarding a quantitative measure of the level of metal accumulation in sediments [46] ranging from unpolluted to extremely polluted [38]. The results of the analysis showed that the I_{geo} of Cu metal was categorized as unpolluted, and that of Zn ranged from unpolluted to moderate levels (**Table 3**, **Table 4**). This value indicates that the non-natural source of Zn was apparently elevated. Pelabuhanratu Bay has recently been developed, including fishing port activities and the operation of coal-fired steam power plants. [47] reported that Zn had the highest concentration in coal ash compared to Cu, Pb, Cd, and Cr. Furthermore, the contamination factor (CF) was close to that I_{geo} . Cu metal, with an average CF of 0.695, indicates a low contamination category compared to Zn, which is in the moderate contamination category (average CF 1.492).

Table 3. Assessment of I_{geo} , CF and PLI for Cu and Zn in Sediment of Pelabuhanratu Bay.

Station		I_{geo}		CF		PLI
		Cu	Zn	Cu	Zn	
Estuary	St.1	-1.363	-0.566	0.583	1.013	0.769
	St.2	-1.216	-0.272	0.646	1.242	0.896
	St.3	-0.658	0.228	0.951	1.757	1.293
Foreshore	St.4	-1.246	0.017	0.632	1.518	0.980
	St.5	-1.757	-0.231	0.444	1.278	0.753
	St.6	-1.435	0.112	0.555	1.621	0.948
	St.7	-1.055	0.142	0.722	1.655	1.093
	St.8	-1.139	0.108	0.681	1.617	1.050
	St.9	-0.980	0.306	0.761	1.855	1.188
	St.10	-0.627	-0.141	0.971	1.360	1.150

Table 4. Categories of level contamination for cu and zn in sediment of Pelabuhanratu Bay.

Station		I_{geo}		CF		PLI
		Cu	Zn	Cu	Zn	
Estuary	St.1	Unpolluted	Unpolluted	Low	Moderate	Unpolluted
	St.2	Unpolluted	Unpolluted	Low	Moderate	Unpolluted
	St.3	Unpolluted	Unpolluted to mod. Polluted	Low	Moderate	Polluted
Foreshore	St.4	Unpolluted	Unpolluted to mod. Polluted	Low	Moderate	Unpolluted
	St.5	Unpolluted	Unpolluted	Low	Moderate	Unpolluted
	St.6	Unpolluted	Unpolluted to mod. Polluted	Low	Moderate	Unpolluted
	St.7	Unpolluted	Unpolluted to mod. Polluted	Low	Moderate	Polluted
	St.8	Unpolluted	Unpolluted to mod. Polluted	Low	Moderate	Polluted
	St.9	Unpolluted	Unpolluted to mod. Polluted	Low	Moderate	Polluted
	St.10	Unpolluted	Unpolluted	Low	Moderate	Polluted

The pollution load index (PLI) was used to quickly assess the overall pollution status in the bay and can be used for comparison with the status of other locations. Evaluation of the two metals in Pelabuhanratu Bay showed PLI values of 0.753 – 1.293, and most of the areas were > 1 , suggesting that the areas had been contaminated. However, this evaluation was

based only on two metals; hence, it needs to be further assessed with more metal information. The variation in *PLI* shown by each station is due to differences in the sensitivity of the index to metal pollutants in the sediment.

4 Conclusions

Although the Cu and Zn concentrations in the sediment varied and were relatively high, they remained below those in the sediment quality guidelines. The sources of Cu and Zn were predominantly natural. The concentrations may have increased with the development of coastal areas for various activities. Based on individual evaluations, moderate contamination occurred with regard to Zn. These metals in the sediment of Pelabuhanratu Bay can be categorized under pristine conditions, which could be an important baseline for pollution monitoring in the bay in the future. However, further evaluation with metal analysis is required to confirm the status of contamination in the bay.

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