

Integrative Assessment of Pb and Cd Pollution in Porong Estuaries Using Sediment Chemistry, Bioavailability, and Bioconcentration Factor

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ABSTRACT

The aims of the research were to perform an integrative assessment of high metal pollution in Porong Estuary by determining (i) the distribution of heavy metals fraction in sediment, (ii) the potential risk of sediment to the metal bioavailability, and (iii) the bioaccumulation factor of heavy metals in benthic. Fractionation of heavy metals in the sediments was carried out by the European Community Bureau of Reference (BCR) sequential extraction method. The potential risk of sediment was determined from RAC (risk assessment code) value. Bioconcentration factor was determined based on the ratio of the concentration of heavy metals in benthic to the concentration of bioavailable metals from sediments. Heavy metal concentrations were measured using AAS. The results showed that non-resistant Pb and Cd was higher than resistant fractions. As a non-resistant fraction, Pb was found mostly as second fraction, i.e., metal fraction adsorbed on the surface of the iron oxy/hydroxide sediment ($34.5 \pm 4.9\%$). Cd was more prevalent as fraction 3, i.e., an organic bound fraction ($29.0 \pm 1.8\%$). Furthermore, Porong Estuary sediments had a medium risk for contributing the bioavailable Cd in the water bodies based on the RAC ($15.6 \pm 1.8\%$). Based on the bioconcentration factor, accumulation of Cd and Pb was low ($48.00 \pm 7.62\%$ for BCF-Cd and $32.29 \pm 6.90\%$ for BCF-Pb). Based on the results above, it could be concluded that the Porong Estuary water bodies have not been polluted by Pb and Cd released from the aquatic sediment.

Keywords: Pb; Cd; BCR method; sediments; Porong Estuary

ABSTRAK

Tujuan dari penelitian ini adalah melakukan penilaian polusi logam berat di muara Sungai Porong secara integrative melalui penentuan: (i) distribusi fraksi logam berat dalam sedimen, (ii) potensi resiko sedimen terhadap ketersediaan hayati logam, (iii) faktor akumulasi logam berat dalam benthic. Fraksionasi logam berat dalam sedimen dilakukan dengan metode ekstraksi sekuensial dari European Community Bureau of Reference (BCR). Potensi risiko sedimen ditentukan dari nilai RAC (risk assessment code). Faktor biokonsentrasi ditentukan berdasarkan rasio konsentrasi logam berat dalam benthic terhadap konsentrasi logam berat hayati dari sedimen. Hasil penelitian menunjukkan bahwa Pb dan Cd non resistant lebih tinggi dari fraksi resisten. Sebagai fraksi non resisten, Pb sebagian besar ditemukan sebagai fraksi 2, yaitu fraksi logam yang teradsorpsi pada permukaan endapan besi oksida/hidroksida ($34,5 \pm 4,9\%$). Sementara, Cd lebih banyak ditemukan sebagai fraksi 3, yaitu fraksi terikat oleh bahan organik ($29,0 \pm 1,8\%$). Selanjutnya, sedimen muara Sungai Porong berpotensi memiliki risiko menengah untuk berkontribusi terhadap ketersediaan logam hayati Cd di badan air berdasarkan RAC ($15,6 \pm 1,8\%$). Berdasarkan faktor biokonsentrasi, akumulasi Cd dan Pb rendah (BCF-Cd adalah $48,00 \pm 7,62\%$, dan BCF-Pb adalah $32,29 \pm 6,90\%$). Berdasarkan hasil penelitian di atas, dapat disimpulkan bahwa badan air muara Sungai Porong belum tercemar oleh Pb dan Cd yang dilepaskan dari sedimen perairan.

Kata Kunci: Pb; Cd; metode BCR; sedimen; muara sungai Porong

INTRODUCTION

Contamination of heavy metals in the aquatic environment has been intensively investigated in recent years due to their toxicity, persistence, bioaccumulation, and a risk for human and ecosystem [1-2]. Heavy metals could come from industrial and urban effluents,

atmospheric and river inputs and leaching [3]. Assessments of pollutants in the aquatic environment based on the measurement of pollutant only in the water column are not accurately figuring the real condition of pollution due to water discharge fluctuations and low residence time of pollutants. In the aquatic environment, the sediments at the bottom of

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water column have the ability to accumulate heavy metals that are discharged into the seas and estuaries. Because of its role as contaminants reservoir, sediment is an important part of the aquatic ecosystem in maintaining the trophic status of any water body [4]. Assessment of heavy metals pollution in the aquatic sediment based on the total metals concentration is also not sufficient to understand the heavy metals behavior in the aquatic environment. Study of heavy metals geochemical fractions in the aquatic sediment gives more detail information regarding metals mobility [5-6] to predict the potential environment and ecotoxicological impacts. Bioavailable heavy metal fraction is one of the geochemical fractions of heavy metals in the sediment that take responsibility for increasing ecotoxicological problem in the aquatic environment [7-8].

Hence, an integrative assessment of heavy metals pollution in an aquatic ecosystem should be performed by measuring heavy metals availability in the sediment, the potential risk of sediment for metals mobility, and bioconcentration of metals in such of benthos. The metal mobility, bioavailability, and its related ecotoxicity depend especially on its geochemical fractions in sediment [6]. Heavy metals are retained in the solid phase of sediment by a different mechanism, including ion exchange, outer- and inner-sphere surface complexation (adsorption), precipitation or coprecipitation [9]. Natural and anthropogenic environmental changes influence the changing of metals behavior as the association form, including pH, temperature, redox potential, organic matter decomposition, leaching and ion exchange processes, and microbial activity [10].

From a practical point of view, the geochemical fractions of metal can be extracted from sediment sample by sequential extraction. Three-step sequential extraction and its modification have been introduced by the European Community Bureau of Reference (BCR) [11]. The metals fractions based on the three-step BCR sequential extraction methods are the acid/exchangeable fraction (the first fraction), easily reduction fraction (the second fraction), an oxidizable fraction (the third fraction), and the resistant fraction. The first fraction metals consist of dissolved metal ions, metals bound to carbonate, and the exchangeable metals [12]. The exchangeable fraction of metals is the most available metals fraction for aquatic plant uptake. It can be released from sediment due to the changing of ionic strength in the medium. The metal which is bound to carbonate can be released due to lowering pH [13]. The second fraction is metals bound to amorphous Fe/Mn oxides/hydroxides. The third fraction is the metals bound to organic matter and sulfide [12]. The second and third fractions can be mobilized with the increasing of oxidation or reduction condition in the environments

[13]. The resistant fraction is metal associated to phyllosilicate. It can be mobilized after weathering processes so it will cause long-term effect [13]. The non-resistant fractions are accounted from the total amount of the first to the third metal fractions. Besides its impact on the aquatic living organism, the non-resistant fractions are most likely due to anthropogenic inputs instead of the natural origin [14].

Meanwhile, assessment of sediment reactivity can be predicted from Risk Assessment Code (RAC) [15]. RAC assesses the percentage of metal in dissolved, exchangeable, and carbonate fractions (the first fraction) which are called bioavailable metals. When the percentage is less than 1%, the sediment has no risk to the environment. The percentage of 1–10, 11–30 and 31–50% reflects low risk, medium risk, and high risk, respectively. The percentage above 50% means that sediment has a very high risk and tend to be dangerous to the environment in term of easily uptake or entering the metal in the food chain [16-17].

Bioavailable metals, which are released from sediment into water column, will be absorbed by benthos. Bioconcentration is the process of chemical substance absorption by the organism from the ambient environment only through its respiratory and dermal surfaces (chemical exposure in the diet is not included). The degree to which bioconcentration occurs is called bioconcentration factor (BCF) [18]. In correlation to bioavailable metals from sediment, the BCF can be calculated as the ratio of metal in the benthos to the concentration of bioavailable metal in the sediment.

Sidoarjo is one of big industries district in East Java, Indonesia. Many industries have been operated in the area, such as textile, leather, pulp and paper, chemicals, and electroplating industries. Activities of the industries produce waste containing heavy metals (Pb and Cd) that are discharged into the Porong River, flowing to the Porong Estuary. The main use of the Porong Estuary water is for commercial shrimp ponds that become a big commodity for the Sidoarjo Regency. Estuaries are regarded as a buffer between land and oceans due to high sorption capacity of sediments for heavy metals and other pollutants [19]. Estuaries tend to be depositional environments dominated by soft sediments which readily adsorb metals [20]. Pollution of heavy metals in Porong Estuary can be lowering the exported shrimp quality so will decrease the Sidoarjo Regional income from fisheries sector due to the rejection of export products. In addition, a load of sediment in the Porong Estuary has been increased due to Lapindo mud discharging since 2006. The mud was indicated consisting of heavy metals, such as Pb and Cd [21]. Therefore,

assessment of heavy metals pollution in the Porong Estuary is important. The aim of this research was to determine (i) the distribution of Pb and Cd in the sediments, (ii) the potential risk of sediment to the metal bioavailability, and (iii) the bioaccumulation factor in benthos found in the sediment of Porong Estuary.

EXPERIMENTAL SECTION

Materials

All reagents were of analytical reagent grade unless otherwise stated. Deionized water (Milli-Q Millipore) was used for all dilutions. All standards, reagent solutions, and samples were kept in polyethylene containers. Cadmium (II) nitrate ($\text{Cd}(\text{NO}_3)_2$) (Merck) and Lead(II) nitrate ($\text{Pb}(\text{NO}_3)_2$) (Merck) were used to prepare standard solutions. The chemicals used for metals fractionation in sediment were nitric acid (HNO_3) 65% (v/v) (JT Baker), glacial acetic acid (CH_3COOH) (Merck), acetate ammonium ($\text{NH}_4\text{CH}_3\text{COO}$) (Merck), hydroxylammonium chloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) (Merck), hydrogen peroxide (H_2O_2) (Merck). Extraction of metals from benthos was conducted using aqua regia. Reagent solutions used for extraction of geochemical fractions of Pb and Cd in sediment were: (i) The solution I (acetic acid, 0.11 M): glacial acetic acid, 25 ± 0.2 mL, was added to about 500 mL of deionized water (in a fume cupboard) in a 1000 mL volumetric flask and made up to the mark with deionized water. Two hundred and fifty milliliters of this aliquot was diluted to 1.0 L to obtain acetic acid of 0.11 M; (ii) Solution II (hydroxylammonium chloride, 0.5 M at pH 1.5): 34.75 g of hydroxylammonium chloride was dissolved in deionized water. The solution was acidified with concentrated nitric acid to pH 1.5 and made up to 1000 mL with deionized water; (iii) Solution III (hydrogen peroxide 8.8 M): hydrogen peroxide supplied by the manufacturer was stabilized to pH 2.0–3.0; (iv) Solution IV (ammonium acetate, 1.0 M): 77.08 g of ammonium acetate was dissolved in 900 mL of deionized water. The solution pH was adjusted to 2.0 by using concentrated nitric acid and the volume of solution was finally marked up to 1000 mL.

Instrumentation

Volumetric glasses were used for preparing

extractant solutions and standard solutions. Instrumentations used were centrifuge (Hettich), digital pH meter (HANNA instrument), refractometer, Eickman grabs sampler, oven (Memmet), shaker, and AAS (AA 240 VARIAN).

Procedure

Sampling

For investigation of Pb and Cd distribution in sediment and absorbed in the organism, sediments and benthos (shrimps and muscles) samples were collected from four stations in the Porong Estuary, Sidoarjo, East Java, Indonesia in October 2016 (Table 1). Samples were collected using Eickman grab sampler. Large objects including stones, pieces of brick, concrete, and cinders were removed. The sediment samples were kept in the sealed dark plastics. Benthos samples (> 1 cm in diameter) were stored in the sealed plastic bag. All samples were labeled and kept cool in a cool box during delivering to the laboratory.

Sequential extraction

In the laboratory, sediment samples were dried at 40 °C to remove volatile compounds. The dried sediments were sieved through a 1 mm nylon mesh, coned, and quartered to about 20 g. One gram of sub-samples was collected for sequential extraction using a three-stage modified procedure recommended by BCR plus the residual fraction (Table 2) [12]. All extractions were carried out for 16 h at room temperature using a mechanical shaker. The extract was separated from the solid residue by centrifugation for 20 min at 3000 rpm. The concentration of metal fraction in supernatant then was measured using AAS. The residue was washed with 20 mL of deionized water, shaken for 15 min, centrifuged for 20 min at 3000 rpm. Subsequently, the supernatant was decanted, and the solid phase was used for the next step of extraction.

Table 1. Geographical of sampling site locations

Sampling locations	Latitude	Longitude
1	7°33,894' S	112°52,311' E
2	7°34,822' S	112°53,000' E
3	7°32,439' S	112°50,506' E
4	7°32,700' S	112°43,347' E

Table 2. BCR three-stage sequential extraction scheme (adapted from sequential)

Step/Fraction	Extractants	Target phase(s)
1	HOAc (0.11 M)	Soil solution, carbonates, exchangeable metals
2	$\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.1 M)	Oxides Fe/Mn metals
3	H_2O_2 (8.8 M) then NH_4OAc (1.0 M) at pH 2	Organic and sulfide bound metals
Residual	Aqua regia	Resistant metals

Step 1 (acid extractable/exchangeable fraction). One g of sub-samples was added with 40 mL acetic acid 0.11 M and shaken for 16 h. The extract was separated from the solid residue by centrifugation. The supernatant was decanted followed by metal concentration measurement using AAS. The solid phase was rinsed and dried up.

Step 2 (easily reduction fraction). The residue from step 1 was weighed then added with 40 mL of freshly prepared hydroxylammonium chloride (solution II). The mixture was shaken for 16 h. The extract was separated from the solid phase by centrifugation. The concentration of second fraction was then determined using AAS. The solid phase was rinsed up with deionized water and dried up.

Step 3 (oxidizable fraction). The residue of step 2 was weighed and treated with solution III, twice. First, the residue from step 2 was added with 10 mL of hydrogen peroxide (solution III). The digestion was conducted firstly for 1 h at room temperature and followed by digestion at 85 °C for another 1 h in a water bath until the volume reduced to about 2-3 mL. An additional 10 mL of hydrogen peroxide was added, and the digestion was continued with cover at 85 °C for 1 h. Heating was continued until the volume was 2–3 mL. Then, 50 mL of ammonium acetate 1.0 M (solution IV) was added to the cold mixture and shaken for 16 h at room temperature. Afterward, the resulting mixture was centrifuged, and the supernatant was decanted for the measurement of fraction 3 concentration. The solid residue was rinsed for the final step of sequential extraction.

Step 4 (residual fraction). The residue from step 3 was digested using aqua regia for 16 h. The mixture was centrifuged. The supernatant was decanted and the resistant concentration then was measured using AAS.

Risk Assessment Code (RAC)

The potential risk of sediment in the Porong Estuary for the bioavailable metals was assessed by determining the RAC value. RAC was calculated as the ratio of bioavailable metals fraction (the first fraction) to the total fractions of metals in sediment (Eq. 1).

$$RAC = \frac{\text{Concentration of the first fraction}}{\text{total fraction concentration}} \quad (1)$$

Physical and chemical properties of sediment

Distribution of geochemical fractions of heavy metals in sediment is affected by physical and chemical properties of sediment. It included distribution of particle size, pH, salinity, potential redox, and organic matter level. Correlation between sediment properties and the metal fractions was tested statistically using the Pearson correlation test.

Bioconcentration Factor (BCF) of Pb and Cd in benthos

Shrimp (*Litopenaeus vannamei*) and muscle are potential fisheries commodity from Sidoarjo Regency. It has been already exported to many overseas countries. The products should not consist of heavy metals, especially the non-essential metals such as Pb and Cd. The presence of these metals in shrimp and muscle causes the rejection of the commodity. Hence the ability of shrimp and muscle in absorbing the bioavailable metals should be studied. The BCF value for Pb and Cd in shrimp and muscle was determined after the determination of Pb and Cd concentration in the solution of digested shrimp and muscle. Benthos was air dried and grounded. One gram of benthos paste was added with 100 mL aqua regia and digested on a hot plate. The digestion was conducted until the volume of the liquid phase was one-third of the initial volume. The mixture then was filtered. The filtrate was diluted up to 100 mL with deionized water. Metals concentration in the filtrate phase was determined by AAS. BCF was calculated using Eq. 2.

$$BCF = \frac{\text{Metal concentration in organism extract}}{\text{Bioavailable metal concentration}} \quad (2)$$

RESULT AND DISCUSSION

Distribution of Pb and Cd Fractions in Porong Estuary Sediment

Distribution of Pb and Cd fractions in Porong Estuary sediment for each location was presented in Fig. 1. It can be seen from the figure that at all sampling locations, a non-resistant fraction of Cd and Pb was dominant than the resistant fraction. The concentration of non-resistant Cd was higher than the one of Pb (Cd: 0.231–0.259 mg/kg; Pb: 6.583–8.173 mg/kg). Non-resistant Cd contribution was $68.7 \pm 4.1\%$ of the total concentration from four sampling locations while Pb contributed $62.4 \pm 2.6\%$ of total concentration. It indicates that Cd effluent from anthropogenic sources was higher than Pb. However, Pb was more remained stable as a resistant fraction in the sediment than Cd. In another word, Cd was more mobile than Pb to be available for benthos uptake.

Non-resistant fraction could be divided into first, second, and third fractions. It can be seen from Fig. 2 that Pb was found dominant as the second fraction, i.e., the acid reducible fraction. The contribution of Pb as the second fraction was $34.5 \pm 4.9\%$. As the second fraction, Pb was adsorbed on the oxides of Fe/Mn by any or a combination of the following mechanism:

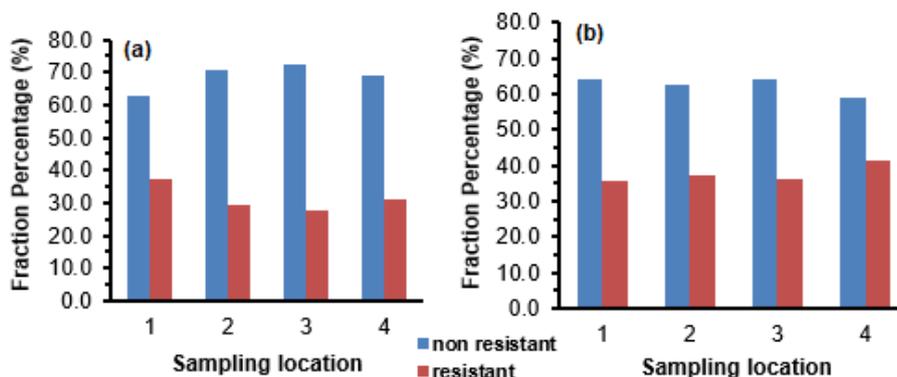


Fig 1. Non-resistant and resistant fractions of Cd (a) and Pb (b) in Porong Estuary sediment

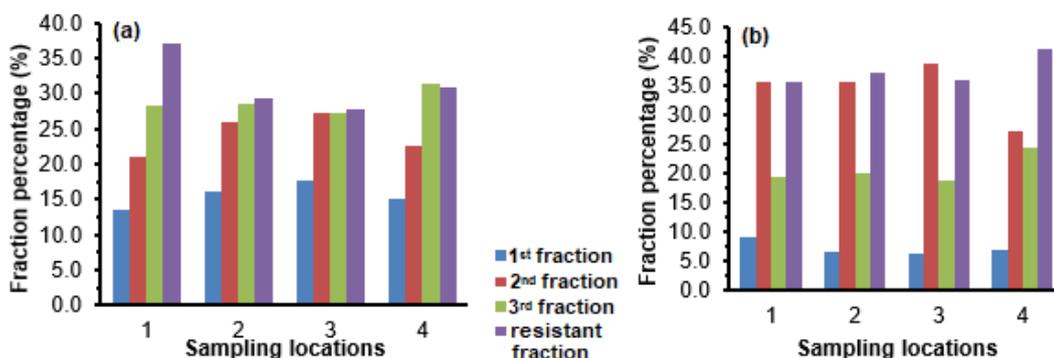


Fig 2. Percent distribution of Cd (a) and Pb (b) fractions in Porong Estuary sediment

Table 3. Physical and chemical properties of water and sediment in the Porong Estuary

Sampling location	pH*	Salinity* ‰	Redox** potential (mV)	Organic matter** (%)	Cationic exchange capacity** (meq/100g)	Sand** (%)	Silt** (%)	Clay** (%)
1	8.0	3.3	5.6	15.4	23.9	1.3	70.3	28.3
2	8.1	3.0	5.6	16.0	14.5	5.7	64.7	29.3

*pH and salinity of the water

**Properties of sediment

coprecipitation, adsorption, surface complex formation, ion exchange, penetration of the lattice. In the soil and sediment, the proportion of Fe/Mn oxides is large [22], so the oxides are known well as a sink for heavy metals in the surface environment [23]. As presented in Table 3, redox potential in location 1 and 2 was the same of 5.6 mV. In another word, the sediment of Porong Estuary at location 1 and 2 was under oxic condition. It could be due to seawater intrusion which has a high concentration of dissolved oxygen as a consequence of the tidal process.

Theoretically, Pb in Porong Estuary could be remobilized into water column under anoxic condition. However, as shown in Table 4, the second fraction of Pb had low correlation to redox potential (correlation value was 0.134, $\alpha = 0.05$, 2-tailed). It means Pb in the Porong Estuary could be remobilized not only at reducing environment. In comparison between two chemical properties of sediment, i.e. redox potential and organic

matter concentration to the second fraction of Pb and Cd, it seems that organic matter level have higher correlation to the second fraction of Pb (0.576 at $\alpha = 0.05$, 2-tailed) than to the second fraction of Cd (0.405 at $\alpha = 0.05$, 2-tailed). It could be due to the hydroxylammonium chloride used as a reagent to extract the second fraction in sediment. One of the problems when using hydroxylammonium chloride in the nitric acid medium as a reagent for leaching the easily reducible fraction is the releasing of a substantial amount of trace element bound to organic matter [24].

Meanwhile, Cd was dominant as an organic oxidizable fraction (the third fraction) (Fig. 2). Its contribution was $29.0 \pm 1.8\%$ of total concentration. As the third fraction, Cd could be associated with bioaccumulation process [23] or complexation with various forms of organic materials such as a living organism, detritus or coating on mineral particles [25]. This metal fraction could remain in the sediment for longer

Table 4. Pearson correlation test

	pH	Salinity	Redox potential	Organic matter level	CEC	Sand	Silt	Clay
pH								
Salinity	-0.171							
Redox potential	-0.217	-0.297						
Organic matter level	0.210	-0.621	0.770					
CEC	-0.762	0.108	0.051	-0.311				
Sand	0.718	-0.273	0.023	0.333	-0.962**			
Silt	-0.859*	0.381	0.058	-0.243	0.809*	-0.891*		
Clay	0.695	-0.352	-0.026	0.067	-0.279	0.405	-0.769	
Cd fraction 1	0.009	0.739*	-0.028	-0.249	-0.437	0.329	-0.032	-0.332
Pb fraction 1	-0.415	0.874*	-0.274	-0.727	0.546	-0.645	0.596	-0.268
Cd second fraction	0.434	-0.620	-0.069	0.405*	-0.729	0.792	-0.638	0.119
Pb second fraction	0.362	-0.930**	0.134	0.576*	-0.425	0.560	-0.579	0.333
Cd fraction 3	0.072	0.781*	-0.757	-0.732*	0.090	-0.288	0.287	-0.243
Pb fraction 3	0.035	0.234	-0.047	0.030	-0.651	0.594	-0.187	-0.445
Cd resistant	0.293	0.437	-0.345	-0.282	0.250	-0.418	0.176	0.192
Pb resistant	0.372	-0.354	0.710	0.836*	-0.662	0.688	-0.513	0.152

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

Table 5. Potential risk of Pb and Cd in the Porong Estuary sediment

Fraction/locations	Cd concentration (mg/kg)				Pb concentration (mg/kg)			
	1	2	3	4	1	2	3	4
1 st fraction	0.050	0.057	0.056	0.056	1.050	0.696	0.660	0.970
2 nd fraction	0.078	0.092	0.087	0.085	4.051	3.771	4.164	3.813
3 rd fraction	0.105	0.101	0.087	0.118	2.210	2.116	2.018	3.390
Residual	0.138	0.104	0.088	0.116	4.044	3.933	3.861	5.736
Total	0.371	0.355	0.319	0.375	11.354	10.516	10.703	13.908
RAC (%)	13.4	16.2	17.7	15.0	9.25	6.62	6.17	6.97

periods. It will be released into the water column by decomposition process, or degradation of organic matter under oxidizing condition. However, it was not clear whether the third fraction of Cd in this research was able to be released following the degradation of organic matter under oxidizing condition. It could be seen from Table 4 that the third fraction of Cd showed a negative correlation to organic matter concentration in sediment (correlation value was -0.732, $\alpha = 0.05$, 2-tailed).

As seen in Fig. 2, the first fraction of Pb and Cd has the lowest contribution. The contribution of the fractions were $15.6 \pm 1.8\%$ and $7.3 \pm 1.4\%$ of the total concentration of Cd and Pb, respectively. The first fraction of heavy metals correlate to the dissolved fraction, the exchangeable fraction, and carbonate bound metal fraction. The dissolved fraction consists of free metal ions and ions complexed with soluble organic matter and other constituents. The exchangeable metals fraction includes the weakly adsorbed metals retained on the solid surface by weak electrostatic interactions. Meanwhile, carbonate becomes an important adsorbent when organic matter and Fe/Mn oxides less abundant in the aquatic system [23].

The lowering pH of the system will release the first metal fraction so it will be readily available for benthic consumption. In addition, salinity affected the mobility of

Cd and Pb. At location 1 and 2, the water salinity was similar, with the average of 3.15 ‰. Pearson correlation test proved that there was a correlation between the first fraction of Pb and Cd and salinity (related to the ionic strength). Correlation of the first fraction of Pb to salinity (0.874, $\alpha = 0.05$, 2-tailed) was higher than the correlation of the first fraction of Cd to salinity (0.739, $\alpha = 0.05$, 2-tailed) (Table 4). Even though the correlation of Cd to salinity was lower than the correlation of Pb to salinity, Cd is more sensitive to the salinity alteration [26]. Increasing salinity is inherent with the increasing of concentration of Cl⁻ ion to form a stable compound such as CdCl⁺ and CdCl [27]. The stability and solubility of these complexes were higher than the affinity of the affinity of Cd for the solid soil phase, causing higher mobility of Cd [28].

Risk Potential of the Porong Estuary Sediment for Heavy Metals

The ability of sediment in providing the bioavailable metals could be a risk factor for ecotoxicology. Assessment of sediment potency for the availability of bioavailable metals can be performed by calculating the RAC value. RAC refers to the percentage

Table 6. The bioconcentration factor of Pb and Cd in shrimp from Porong Estuary

Sampling location	Benthic	BCF	
		Cd	Pb
1	Shrimp*	45.05	25.78
2	Muscle**	43.93	34.56
3	Shrimp*	59.40	40.98
4	Shrimp*	43.63	27.85

*Sergestidae families

**Corbulidae families

Benthic observed had diameter >1 cm

of the first sediment fraction in the BCR method (% fraction 1). The value indicates the metals that easily leachable and freely exchangeable. It can be seen from Table 5, the concentration of the first fraction of Pb in the Porong Estuary sediment (0.844 ± 0.195 mg/kg) was higher than Cd (0.055 ± 0.003 mg/kg), but Porong Estuary sediment becomes a risk for the availability of Cd based on the RAC value. The RAC values for bioavailable Cd and Pb were $15.6 \pm 1.8\%$ and $7.3 \pm 1.4\%$, respectively. It refers to the easy mobility of the first fraction of Cd from sediment to the water column. Based on the RAC, the sediment of Porong Estuary had a medium risk for the bioavailability of Cd (11–30%) and low risk for the bioavailability of Pb (1–10%).

Bioconcentration Factor of Pb and Cd

Another assessment of heavy metals pollution could be conducted by determining the bioconcentration factor (BCF) value. This value represents the ability of benthos in the absorption of heavy metals through respiration and skin absorption only. In this study, BCF is the ratio of metals concentration extracted from benthos to the first fraction metals in sediment. It can be seen from Table 6, that BCF of Cd was higher than BCF of Pb. It means that benthos in Porong Estuary had a higher capacity to absorb Cd which related to the abundant of the first fraction of Cd. Accumulation (bioconcentration) can be categorized as high (BCF > 1000), medium ($100 < \text{BCF} < 1000$), low (BCF < 100) [29]. In average, the accumulation of Cd and Pb was categorized as low. The value of BCF depends on the properties of metals, benthic species, exposure time, and physical-chemical properties of the environment [30]. The high BCF in shrimp could be due to its protein characteristic which has the ability to bind Cd. It will become a problem for shrimp export commodity because of the high absorption capacity of shrimp to Cd. It also can be concluded from Table 6 that BCF of Pb and Cd in shrimp at location 3 was the highest among the investigated locations. It explains that location 3 could receive high anthropogenic effluent consisted of Cd which is accumulated in the sediment.

CONCLUSION

Based on the results, Pb would longer remain in the sediment as the second fraction while Cd was dominant as the third fraction in the Porong Estuary. The sediment provided higher bioavailable of Cd rather than Pb. Sediment of the Porong Estuary had medium risk for the bioavailability of Cd and low risk for Pb based on the RAC values. Bioaccumulation of Pb and Cd released from the Porong Estuary sediment (BCF) in shrimp and muscle was categorized low. BCF of Cd was higher than of Pb. Shrimp showed higher absorption capacity to Cd than to Pb due to the characteristic of shrimp protein. Overall, it can be concluded that Porong Estuary water bodies has not been polluted by Cd and Pb released from the aquatic sediment based on the sediment chemistry, RAC value, and BCF value.

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