Bioavailibility of Cd, Pb, Cu, and Zn in Sediment in Garapan, Cibungur, and Ciliman Rivermouth

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Abstract. Garapan, Cibungur, and Ciliman Rivermouths are known as places for fishing. Those areas are surrounded by human activities such as human settlement, agricultural and industrial activities. The aim of this study is to investigate the bioavailibility of Cd, Pb, Cu, and Zn in sediment for biota (clams) from related location. Bioavailibility was determined using sequential extraction technique consisted of residual and nonresidual fractions. Samples of sediments taken using Ekman grab, while clams *Anadara pilula* taken using "garo". Heavy metals content was analyzed using AAS. Regression linear was used to see relationship between bioavalibility and heavy metal content in clams. Result showed that heavy metal content Cd, Pb, Cu, and Zn in sediment were highest in Garapan so were the content of Pb, Cu, and Zn in *Anadara pilula*. Result also showed that Cd and Pb were mostly bound to nonresidual fraction 100% and 54,65 – 64,69% respectively, while Cu and Zn were mostly bound to residual fraction 54,63 – 54,79% and 67,28 – 79,37%, respectively, except in Garapan for Cu. Relationship between each fraction of heavy metal in sediment with heavy metal content in *Anadara pilula* showed ascending pattern except, for Cd.

Keywords: bioavailibility, heavy metals, sediment, *Anadara pilula*, rivermouth.

Introduction

Availability of metal can be influenced by associations/ relationships between one or more of the sediment fraction [1]. Total metal concentrations do not reflect the relationship between abiotic and biotic factors, so the understanding of bioavailable metal is very important [2]. This may explain the risk of heavy metal accumulation by organisms such as mollusks bivalves [3].

Geochemical characteristics of the sediments is an important factor in determining bioavailibity [4]. Studies on geochemical fractionation of heavy metals in sediments and its relationship with bioaccumulation by *Mytilus edulis* [5] and *Perna viridis* [6] have been done. [7] stated that sediment particles is a source of heavy metal uptake by *Perna viridis* caused by resuspension of sediment due to tidal currents. According to [8] contamination of sediments become secondary pollutant in water surface. Therefore, it is estimated that the heavy metals in the sediments could be a source of bioavailable to aquatic biota. The negative impact of heavy metal accumulation in the organism causes morphological changes at the same time physiological and biochemical functions in the body shells

Groups of *Anadara* like *Anadara indica*, *A. pilula*, and *A. inaequivalvis* were found in the Ciliman and Cibungur Rivermouth, Panimbang and Garapan Rivermouth, Tanjung Pasir. The clam is fisheries product and sold at market and fish auction.

Number of industrial, residential, and various other human activities in the coastal waters of Tanjung Pasir (near the estuary Cisadane) is higher than around Panimbang whose inhabitants have activity in agriculture and traditional fisheries. Based on the results of the water quality analysis in coastal waters and marine [9] there is an indication of heavy metal pollution cadmium above a predetermined threshold according to PP No. 82 Thn 2001. Given that condition, this study is aimed to determine the biological availability of heavy metals in sediment and its bioacumulation in clams.

Methodology

Time and Location

The study was conducted at three locations: Garapan, Cibungur, and Ciliman Rivermouth. The location was chosen in regard to the extent of human activities such as residential, industrial, and agriculture along the river. Tanjung Pasir is densely populated areas while in Panimbang, mangrove can still be found. Both areas are included in the clams catch. Sampling stations showed in Figure 1.

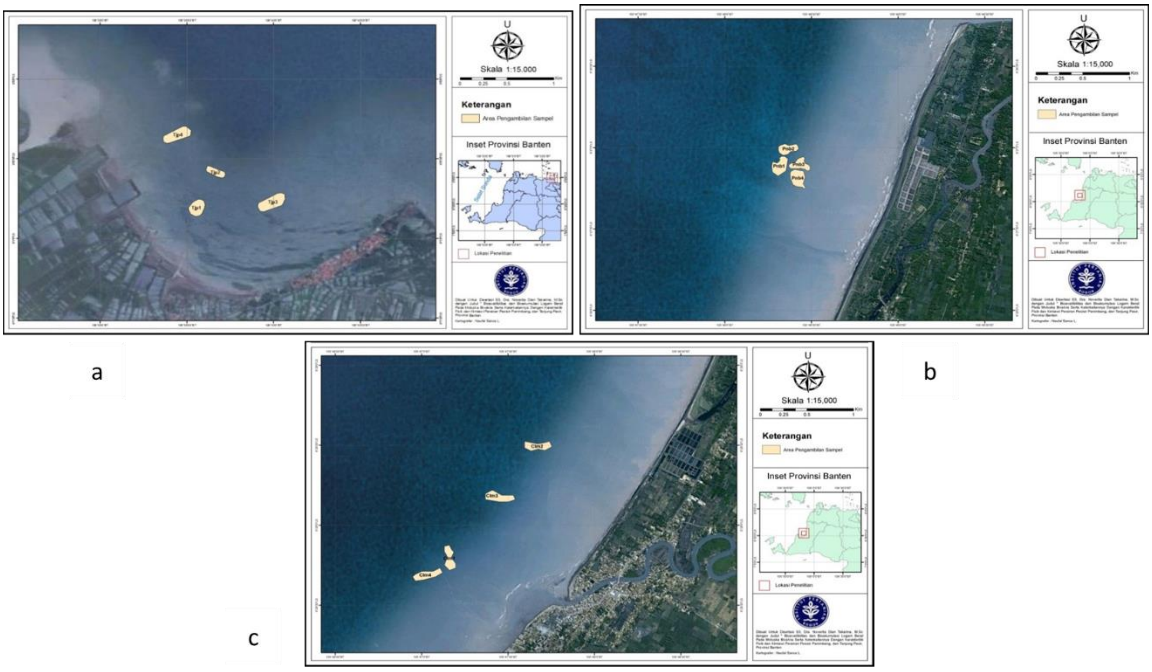

Figure 1. Sampling stations in Garapan (a), Cibungur (b), and Ciliman (c) Rivermouth

Sampling

Samples taken in this study were sediments and clams. Sediment samples were taken using Ekman Grab. Sediment samples were used, only a sample contained in a layer of 2-5 cm. Sampling of clam using *garo* towed by a boat. Sampling at each station repeated were three times. The sample is then inserted into the cooler box.

Analysis of Grain Size and Organic Carbon Content

Grain size analysis by wet sieving method. Analysis assisted by ASTME USA Standard Sieves. The results, divided into sand, silt, and clay as well as expressed in %. Organic carbon is measured by the conversion method of organic carbon into carbon dioxide [10]. Measurements carried out by TrusPec CNS Analyzer, LECO, USA. Organic carbon measured as %.

Measurement of heavy metal content

Samples of sediment and clam samples (meat) is dried before the analysis. Sediment samples were oven overnight at 80 °C, while clam samples for 3 hours at a temperature of 105 °C. The samples were then crushed with a mortar. Furthermore, for sediment samples extracted through sequential extraction [11,12], while clams were destructed using HNO3 and HClO4. Samples were analyzed using Shimadzu AAS 6300.

Regression Analysis

Fractionation of heavy metals in sediments associated with the heavy metal content in the clams was done using simple regression.

Result and Discussion

Sediment consists of several different geochemical fractions and act as a potential reservoir for metals that enter the coastal waters. Fraction is divided into exchangeable fraction (Fr 1), oxide Fe - Mn fraction (Fr 2), organic fraction (Fr 3) , and residual fraction (Fr 4) . In this study, these values were depicted in Table 2.

The value of the fraction is then grouped into non- residual and residual fractions. The non residual fraction is the sum of Fr 1, Fr 2 and Fr 3, and non- residual fractions is Fr 4. Nonresidual and residual fraction of the sediment in the study were shown in Table 3

Table 2. Gheochemical fractionation metal geochemistry of Cd, Pb, Cu, Zn at sampling location.

	Garapan				Cibungur				Ciliman			
	Fr 1	Fr 2	Fr 3	Fr 4	Fr 1	Fr 2	Fr 3	Fr 4	Fr 1	Fr 2	Fr 3	Fr 4
Cd	0.00	0.08	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.01	0.00	0.00
Pb	0.33	9.14	24.15	18.35	0.14	3.92	8.05	10.05	0.08	3.34	8.41	9.79
Cu	5.60	0.56	14.26	15.94	0.54	0.00	1.92	2.93	0.96	0.00	1.11	2.63
Zn	18.76	22.87	7.30	100	12.06	12.03	0.69	96.53	23.49	9.11	0.59	85.99

Table 3. Residual fraction residual and non residual Cd, Cu, Pb, Zn (μg/g) at the sampling location.

	Garapan		Cibungur		Ciliman	
	Non residual	Residual	Non residual	Residual	Non residual	Residual
Cd	0.08	0.00	0.04	0.00	0.01	0.00
Pb	33.62	18.35	12.11	10.05	12.93	9.79
Cu	20.42	15.94	2.46	2.93	2.07	2.63
Zn	48.92	100.44	24.78	96.53	33.34	85.99

Based on Table 3 it seems that the metals Cd and Pb bound to non residual fraction in estuaries Garapan, Cibungur and Ciliman were 100% and 54.65 - 64.69%, respectivelly. Cadmium was dominated by Fe oxide fraction - Mn, while Pb is dominated by organic fraction. Based on [13] cadmium was highly bound to easy reducible fraction (18.7 – 79.1 %). In sediment, cadmium were bound to easy reducible compare to residual one [3]. According to [14], cadmium will associate with organi, sulfit, and Fe-Mn oxide, since it attached to sediment. Lead is usually abundant in the earth's crust and is associated with suspended solids that accumulate in the sediment . According to [15] elements Fe -rich sediments hamper the availability of lead . This is also supported that the mobility of Pb is also lower than cadmium.

In Cibungur and Ciliman rivermouth, Cu bound to the residual fraction of 54.63 - 54.79%, but in Garapan bound to nonresidual fraction. Metal Zn bound to residual fractions in the three locations: 67.28 - 79.37%. Based on [16], in some rivermouth at Jakarta Bay, copper was bound to residual fraction as much as 50-65 %. According to [8], zinc tend to have high affinity to resiudal fraction. With those condition, zinc may not available for organism.

In terms of location, content of heavy metals in the estuary Garapan greater than Ciliman and Cibungur estuary. This is supported by the organic carbon content higher in the estuary of Garapan compared to other locations. Even so, the grain size is dominated by silt at the three locations. This might be related to industry that lies in Garapan was more than in Cibungur and Ciliman.

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The content of heavy metals in *Anadara pilula* shown in Table 4.

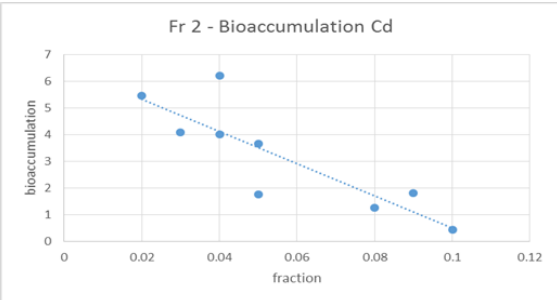
Table 4. The content of heavy metals in *Anadara pilula* at study site

	Garapan	Cibungur	Ciliman
Cd	1.32	4.83	4.47
Pb	7.00	4.44	2.30
Cu	5.32	3.58	3.28
Zn	130.70	61.59	59.70

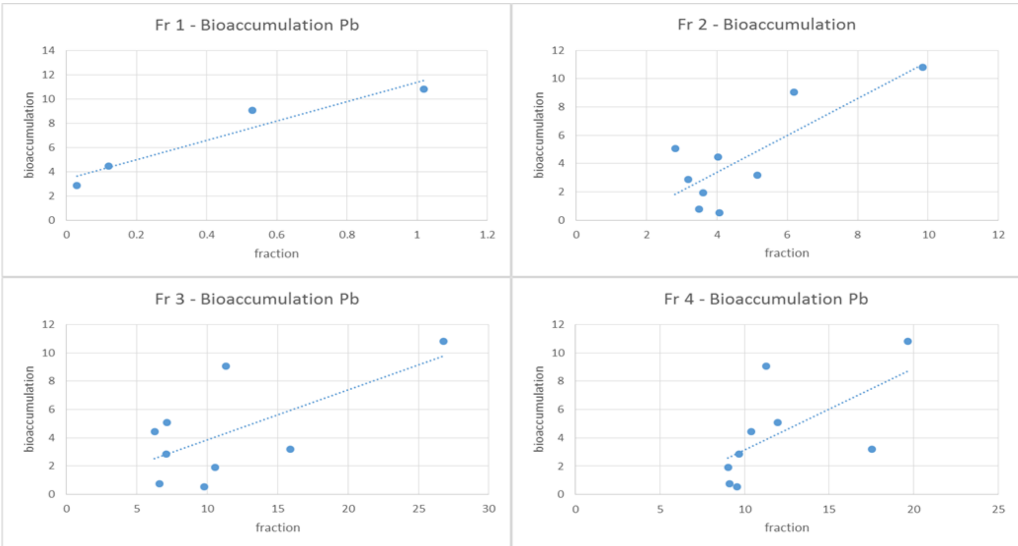
Results showed that, the content of heavy metals Pb, Cu, Zn in *Anadara pilula* have the same pattern. The highest content of heavy metals found in Garapan estuary. In contrast to metals Cd, the highest content of Cd was in the Cibungur estuary. The metal accumulation of Zn higher compared to other metals. Based on established standards [17] the metal content of Cd and Pb in *A. pilula* found in Cibungur and Ciliman and exceeds the threshold. Standards for Cd and Pb 3 μg/g and 4 μg/g respectivelly, a content of Cu and Zn were still below standard. The threshold for Cu and Zn were each 50 μg/g and 300 μg/g, respectivelly.

The relationship of geochemichal fractination of heavy metals in sediment and heavy metals in *A. pinula* were depicted on linear regression.

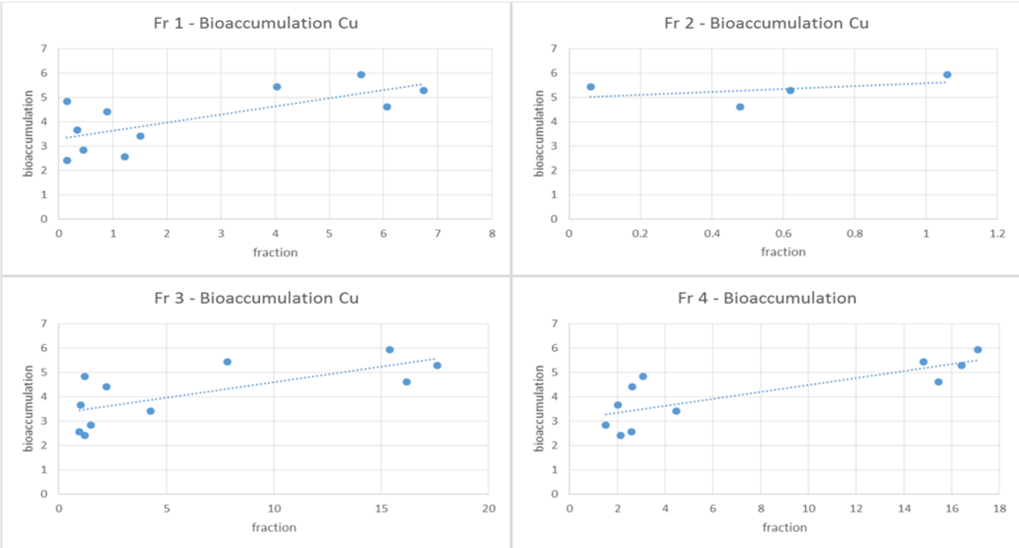
Fractionation – Bioaccumulation of Cadmium



Fractionation – Bioaccumulation of Lead



Fractionation – Bioaccumulation of Copper



Fractionation – Bioaccumulation of Zinc

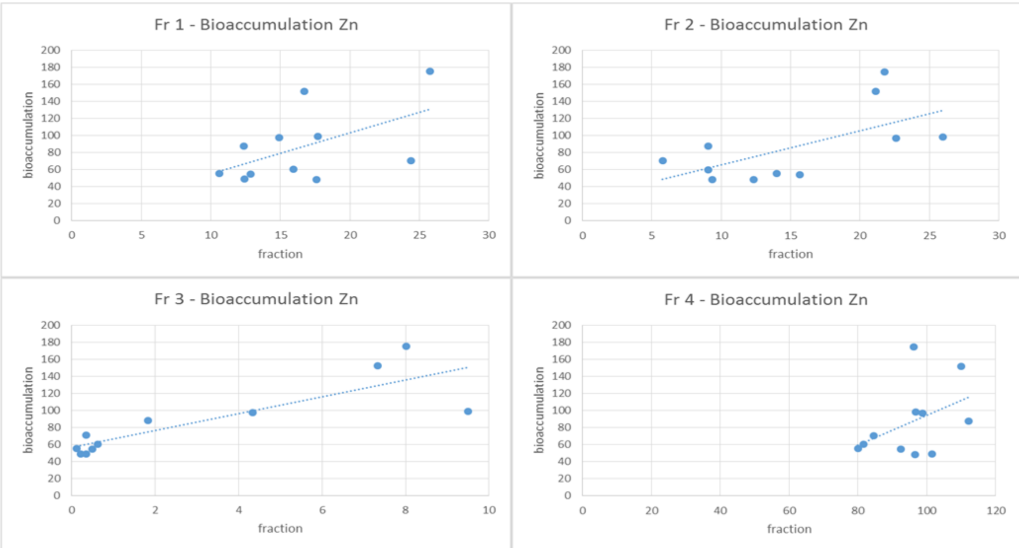


Figure 2. Relationship between geochemical fractionation of Cd, Pb, Cu, Zn and its bioaccumulation in *A. pilula*.

According to figure above mostly fraction show ascending pattern except, Fr 2 Cd and its bioaccumulation in *A. pilula*. It can be said that mostly fraction in sediment influence the metal accumulation. Based on [18], there is positive correlation between fractionation of Cu and its bioaccumulation in *A. indica*, between Fr 2, Fr 3, Fr 4 of Pb and its accumulation in *A. indica*, and between Fr 2 and Fr 3 with its accumulation in *A. indica*. [6] also found strong positive correlation between Pb concentration in soft tissue of *Perna viridis* with resistant and total fraction Pb in sediment.

Conclusion

Cd and Pb were mostly bound to non residual fraction, while Cu and Zn were mostly bound to residual fraction. Content of Zn were highest in sediment and *Anadara pilula*. There is proportional relationship between geochemical fractionation of Pb, Cu, and Zn with its bioaccumulation in *A. pilula*.

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