

The Effect of Physico-Chemical Properties of Aquatic sediment to the Distribution of Geochemical Fractions of Heavy Metals in the Sediment

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Abstract— Heavy metals in the aquatic sediment could be fractionated into five geochemical fractions. Assessment of these fractions is valuable to determine the bioavailable metals provided by the aquatic sediment. Physico-chemical properties of sediment determine the distribution of the fractions. The aims of this research were to determine the physico-chemical properties of sediment sample and to determine its effect to the distribution of heavy metals fraction. Sediment samples were collected from the Porong River at two stations by using Eickman Grab sampler. The samples were stored in 4°C until analysis. Physico-chemical properties of sediment were investigated, including texture, pH, salinity, cationic exchange capacity (CEC), redox potential, and organic material concentration. The geochemical fractions of heavy metals (Pb, Cu, and Zn) were determined after sequential extraction using modified BCR method. As a result, texture of sediment correlated to the organic material concentration while the amount of organic material determines the third fraction of heavy metals, i.e. the oxidation fraction. CEC and pH, and salinity determined the amount of the first fraction, i.e. the exchangeable fraction. Redox potential of sediment affected the amount of the second fraction of heavy metals, i.e. the acid reducible fraction.

INTRODUCTION

The presence of heavy metals in an aquatic ecosystem has been increasing ecotoxicological problem when the metals enter the food chain. Even though some of the metals are essential and needed by organism to conduct metabolism process but high concentration of the metals lead metabolism disruption. In contrast, the non essential heavy metals, such as Pb, have high impact for organism even at low concentration.

The big sources of heavy metals in aquatic system is an anthropogenic sources from human activities, including agriculture, industries, and domestic. The metals may accumulate in the suspended particulate matter and settle at the bottom of aquatic sediment. Assessment of heavy metals contamination in an aquatic ecosystem based on total metal concentration could not provide sufficient information related to their behavior in environmental [1]. This is due to only a fraction of the metals which are immediately available for biological process. Assessment of heavy metals in the aquatic system should also consider their association to the solid phase [2]. Metal ions in aquatic sediments are fractionated between different phases, i.e. carbonate and sulfides, oxyhydroxides of iron, aluminum, and manganese, organic matter, and phyllosilicates minerals. The metals ions are retained in the solid phase of sediment through different mechanism, i.e. ion exchange, adsorption by forming inner/outer inner sphere surface complexation, precipitation and co-precipitation [3]. Physical or chemical condition both in water column and in the solid phase of aquatic sediment, such as pH, redox potential, temperature, organic matter decomposition, leaching and ion exchange process, influence the changing of metal association form in the sediment [4].

The exchangeable fraction of metals in sediment corresponds to the immediately available for biota uptake, thus causing contamination. It can be released from the aquatic sediment due to the changing of ionic strength of the medium. The metals fraction which is bound to carbonates will be released from the sediment when pH is lowered. Changing of redox potential in the environmental can cause mobilizing of the metal fraction bound to Fe-Mn oxy-hydroxyde and organic matter. The metal fraction associated with silicate of sediment may mobilize after weathering process, thus it causes long-term effect [5].

Metal fractions in sediment can be achieved by sequential extraction. The two most sequential extraction method are the Kersten/Forstner procedure [6] and the Tessier procedure [7]. A new extraction method has been introduced by European Community Bureau of Reference

(BCR). This three-step sequential extraction and a modification of the method have been used to extract various samples [8, 9]. The metal fractions extracted by this method including acid extractable/exchangeable fraction (first fraction), easily reducible metal fraction (second fraction), oxidizable metal fraction (third fraction), and residual fraction. The first fraction refers to the metal bound to carbonate and exchangeable metals fraction. The second fraction is the metal fraction which bound to amorphous Fe and Mn oxides and hydroxydes. Metals bound to organic matter and sulphides are extracted as the third fraction. Residual fraction refers to the metals associated with silicates of sediment [5, 9] investigating metal fractions in aquatic sediment, it can be assessed the degree of metal contamination and environmental impact on metal bioavailability, mobility, and its origin.

Since 2006, the Lapindo mud has been discharged into the Porong River, Sidoarjo. Heavy metals in the mud may contaminate the river water which is used as water source for fish pond surrounding the estuary of the river. So far, assessment of heavy metal contamination was carried out by determining the total metal concentration in the mud [10]. There is no report regarding with the mobility, reactivity, and the impact of environmental to the release of heavy metals from the Lapindo mud which settled at the bottom of the Porong River so contribute to the contamination. The aims of this research were to determine the physical and chemical characteristics of the Porong River sediment affected by the Lapindo mud and to determine the environmental parameters to the heavy metals fractions in the Porong River sediment.

METHODS

a. Sample collection and Pretreatment

Sediment samples were collected from two locations at estuary area of the Porong River. The first sample was collected from 7°34'26.76" S; 112°52'53.76" E while the second sample was collected from 7°33'31.35" S; 112°51'05.56" E (Fig.1). At each location, the sediment samples were collected from three sites and then were mixed. Sediment samples were collected using Eickman Grab sampler. The samples were placed in the dark sealed plastic bag and stored at 4°C. Sediment was air dried for overnight, grounded, and sieved between 100 and 120 meshes. The sediment powder was stored in the glass bottle at 4°C.



Figure 1. Sampling location in the estuary of Porong River. Location 1 was closed to the East Sea while location 2 was at the river mouth.

b. Reagents

All reagents were of analytical reagent grade unless otherwise stated. De-mineralized water was used for all dilutions. Acetic acid (glacial, 100% Merck), hydroxylammonium chloride (Merck), hydrogen peroxide (30%, Merck), ammonium acetate (Merck), HCl (36%, Merck), HNO₃ (65%, Merck). Standard metals solution (for Pb, Cu, and Zn) were prepared by diluting appropriate metal salts.

c. Apparatus

Standards and reagents solution were prepared using calibrated glassware. Metals concentration in the sediment extract was determined using an Flame Atomic Absorption Spectroscopy (Shimadzu) with mixture of oxidant and acetylene as flame source. The operating parameters for working metals were set as recommended by the manufacturer.

d. Heavy Metals Fractionation using Modified BCR Sequential Extraction method

Sequential fractionation of heavy metals in the sediment samples were carried out using BCR method by modification. This method has three stage plus the residual fraction (Table 1).

Table 1. BCR extraction scheme (adapted and modified from [9]).

Extraction steps	Reagents	Metals fraction
1	HOAc (0.1 mol/L)	Soil solution, Carbonates, Exchangeable
2	NH ₂ OH.HCl (0.1 mol/L)	Oxides Fe/Mn
3	H ₂ O ₂ (8.8 mol/L) then NH ₄ OAc (1.0 mol/L) at pH 2	Organic matter and sulphides
Residual	HCl:HNO ₃ 1:3	Remaining, non-silicate bound metal

All extractions were carried out for 16 h (overnight) at room temperature followed by centrifugation for 20 minutes at 3000 rpm. The supernatant liquid was collected, transferred into volumetric flask. The metal concentration in the supernatant then was measured. Before performing next step of extraction, the residue was washed using demineralized water and shaken for 15 minutes and followed by centrifugation for 20 minutes at 3000 rpm. Subsequently, the supernatant was decanted.

RESULTS AND DISCUSSION

Sediment samples were collected using purposive sampling method. The sediments were collected from the reclamation area of Lapindo mud in the mouth of the Porong River. Characteristic of estuary ecosystem, where freshwater meets saline water, determines the solubility of heavy metals in water column and sediment pore water. The physical and chemical characteristic of the

Porong river sediment affected by the Lapindo mud from two locations were not differ (Table.2).

Table 2. Physical and chemical properties Porong River sediment

Parameters	Station 1	Station 2
pH	7.0	6.8
Salinity (mS/cm)	2.43	1.71
Redox potential (mV)	6.6	4.5
Organic matter (%)	6.49	0.46
Cationic exchange capacity (me/100 g)	32.57	11.42
Clay (%)	33	27
Silt (%)	66	69
Sand (%)	1	4

than the one of the sediment in station 1 (river mouth). However, the physical properties, *i.e.* was closely same. With the clay, sand, and silt composition, the texture for both sediments was silty clay loam. The difference of chemical characteristic of the sediment affected metals fractions in the sediment (Fig. 2 and 3).

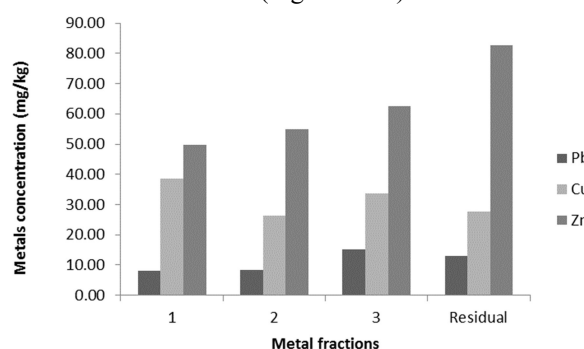


Figure 2. Metal fractions concentration in the sediment at the first station.

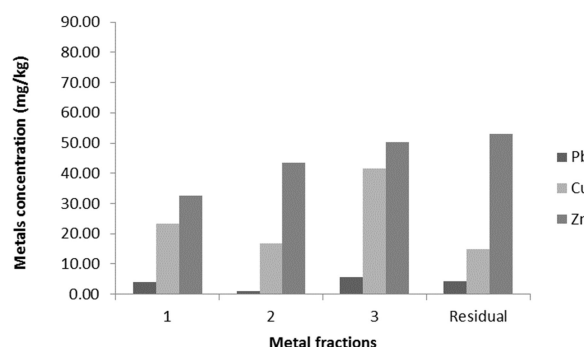


Figure 3. Metal fractions concentration in the sediment at the second location.

It can be seen from Fig. 2 and 3 that overall the concentration of heavy metals in station 2 was lower than its concentration from station 1. It can be correlated to the high value of pH, salinity, redox potential, organic matter, and CEC in the first station. However, profile of the metals was the same. In both stations, Zn was more dominant than Cu and Pb. High concentration of Zn could be due to its natural origin. The presence of Cu and Pb in both locations could be due to anthropogenic sources from domestic or industries sewage which are spread over the river bank.

The chemical properties of sediment determine the distribution percentage of metal fractions (Fig. 4 and 5). It can be seen from Fig. 4 that the exchangeable fraction (first fraction) was dominated by Cu, followed by Zn and Pb. In contrast, the exchangeable fraction of Pb was the highest one at the second station (Fig. 5). The exchangeable metals fraction includes weakly adsorbed metals on the solid surface by electrostatic interaction so

it can be released by ion-exchange processes. This fraction also refers to the fraction of metals which can be coprecipitated with carbonates in sediment [5]. Lowering pH of sediment causes remobilization of this metal fraction from sediment into water column. This fraction can be referred as immediately available metal or bioavailable metal. High concentration of this fraction causes high risk of toxicity.

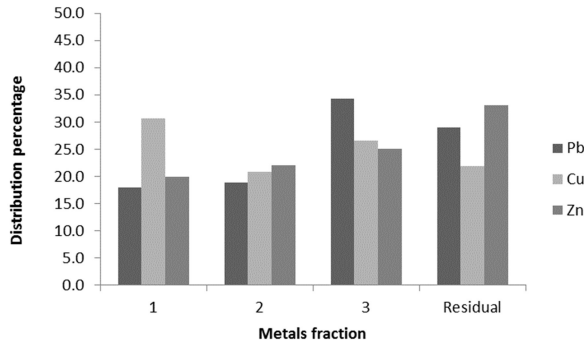


Figure 4. Distribution of metal fraction at station 1

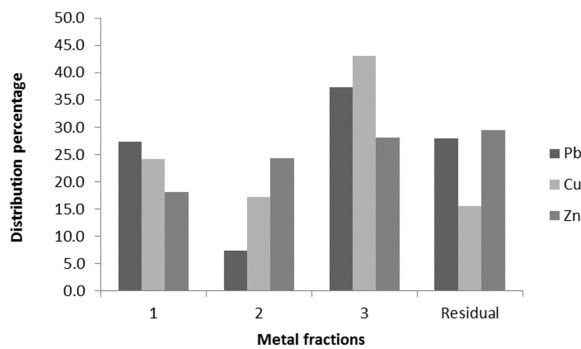


Figure 5. distribution of metal fraction at station 2

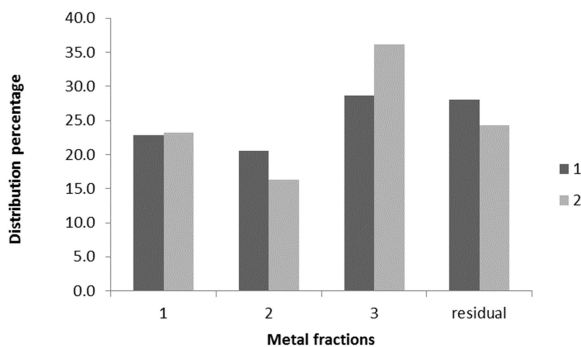


Figure 6. The average metal fractions at station 1 and station 2.

pH at station 2 was more acid than the one at station 1. Metals in this location should be more dissolved into sediment pore water and then diffused into water column. However, percentage of the first fraction in the station 1 was higher due to higher salinity and CEC. In average, percentage of the first fraction at station 1 was relatively the same as of at the second station (Fig. 5).

The second fraction of metals are called reducible fraction. It indicates metal which is attached to hydroxide-oxides of manganese and iron by any or combination of the following mechanism: coprecipitation, adsorption, surface complex formation, ion exchange, and penetration of the lattice. As shown in Fig. 4 and 5, Zn was dominant as acid reducible fraction in both stations. In average from three heavy metals, the percentage of acid reducible fraction at station 1 was higher than the one at station 2. It could be related to the higher redox potential at station 1.

Association of heavy metals with various form of organic material, such as living organism, detritus, or coating on mineral particles, through complexation or bioaccumulation process [11] is classified as oxidisable

metals fraction (the third fraction). Selectivity of organic substances for divalent ions is higher than to monovalent ion [12]. The order of binding strength for metal ions onto organic matter is $Hg > Cu > Pb > Zn > Ni > Co$. Heavy metals which are associated with organic materials could possibly be released by decomposition process under oxidizing conditions. In unpolluted sediment, the release of this metal fraction may be negligible due to stable association of metal with high molecular weight humic substances so it will be released slowly. The highest percentage of oxidisable metal fraction at station 1 was Pb while at station 2, it was Cu (Fig. 3 and 4). At unpolluted neutral sediment, affinity of Cu to the organic matter was high. High percentage of Pb in saline sediment at station 1 could be due to high concentration of organic matter and pH in the location. In average, the oxidisable metal fraction at the second station was higher than the fraction at the first station. It could be assumed that sediment at station 2 was polluted so easy to release organic matter associated metals.

Residual fraction is correspond to the metal fraction which is strongly attached in the sediment mineral. Strong acid condition is needed to release the metals. Higher concentration of metal in this fraction means that high natural origin of the metal. As shown in Fig. 3, 4, and 5, Zn residual fraction at both stations was the highest. In addition, the percentage of residual fraction at station 1 was higher than the fraction percentage at station 2. Naturally, mineral at station 1 contribute more Zn than mineral at station 2.

CONCLUSION

Distribution of heavy metals fractions in the aquatic sediment was determined by physical chemical properties of the sediment and the metals itself. pH, CEC, and salinity determined the percentage of exchangeable metal fraction. Redox potential determined the percentage of acid reducible fraction. Oxidation condition determined the oxidisable metal fraction. The order of heavy metals fractions was oxidisable fraction > residual fraction > exchangeable fraction > acid reducible fraction. Even though oxidisable fraction was high, it was relatively stable in the aquatic sediment so not directly give impact to ecotoxicity. Cu could be immediately released and available for biota at station 1 while Pb is easily released from sediment at station 2. It means, aquatic ecosystem in the Porong River mouth could be contaminated by Pb.

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